

# Relaxor ferroelectric behavior of $\gamma$ -irradiated poly(vinylidene fluoride-trifluoroethylene) copolymers

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We have conducted a systematic investigation on  $\gamma$ -irradiated poly(vinylidene fluoride-trifluoroethylene) equimolar samples. The appearance of relaxor features is clearly demonstrated for this copolymer, for gamma-irradiation doses comparable to those of electron irradiated samples. This material constitutes a new class of relaxor ferroelectrics, since its structure has no direct relationship with perovskite or tungsten-bronze structures and it is also the first non-displacive relaxor ferroelectric. Dielectric, calorimetric, structural, and spectroscopic data allowed us to draw a picture of the chemical and morphological modifications that cause the appearance of the relaxor behavior of the material. In particular, the loss of stability of the ferroelectric domains is attributed to the freezing of the amorphous phase, which forbids the establishment of long-range ferroelectric order.

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## I. INTRODUCTION

Relaxor ferroelectrics are disordered materials which present a smeared phase transition and a frequency dispersion of the temperature where the dielectric constant attains its maximum. In general, they are displacive inorganic materials, belonging either to the perovskite or to the tungsten-bronze structures.<sup>1</sup> Since their discovery circa 50 years ago,<sup>2</sup> these materials have attracted much attention because of their high electrostrictive response—which gives them technological applications as sensors and actuators<sup>3–6</sup>—and the absence of a satisfactory description of their macroscopic behavior. It is well known that quenched chemical defects are always at the origin of the relaxor features of these disordered ferroelectrics. An old idea that is also well accepted is that these systems present polar nanoregions which could have quenched random critical temperatures (or fields).<sup>7,8</sup> In the last ten years, two models appeared that explained the physical behavior of most relaxor ferroelectrics: one that considered that they are caused by frustrated interactions between randomly distributed dipole moments<sup>9–13</sup> and other which was based upon the idea of quenched random fields.<sup>14–17</sup> The most recent advances in experiments and theory show that these models are not completely exclusive and that frustrated interaction would be the dominant effect in dipolar glasses like KTL and DRADP, while random fields would predominate in cubic (PMN-type) and uniaxial (SBN-type) relaxors.<sup>18–21</sup>

Relaxor effects have been recently found in two kinds of organic materials: high-energy electron irradiated vinylidene fluoride-trifluoroethylene copolymers,<sup>22,23</sup> henceforth P(VDF-TrFE), and a tetrathiafulvalene-para-chloranil complex.<sup>24</sup> Both are one-dimensional ferroelectrics and the relaxor features were intentionally provoked by irradiation or chemical modification, respectively. Similar examples of externally driven normal-to-relaxor ferroelectric crossovers in inorganic materials were also recently demonstrated by elec-

tric field,<sup>25</sup> pressure,<sup>26</sup> or chemical impurities.<sup>27,28</sup> The common feature between these quite different systems was always linked to the appearance of nano-scale random electric dipoles. In this paper, we shall consider the relaxor behavior of P(VDF-TrFE) copolymers.

P(VDF-TrFE) copolymers are semi-crystalline materials that can show ferroelectricity at room temperature either, by direct crystallization from the melt, for TrFE contents ranging from 18 to 63 mol %, or by stretching the solid films by 3–4 times their original length, for lower TrFE contents.<sup>29–33</sup> The polar phase belongs to the orthorhombic  $Cm2m$  space group. In this structure, the polymer chains adopt a nearly planar zigzag conformation, the so-called all-trans conformation, along the crystallographic  $c$  axis. The resultant chain dipole is consequently perpendicular to this direction and the chains are packed with all dipoles pointing along the crystallographic  $b$  axis. The basal plane is a distorted hexagon, the distortion being caused by the presence of the ordered dipoles. The copolymers with 18–50-mol % TrFE present a diffuse phase transition into a high temperature paraelectric phase.<sup>34,35</sup> This transition has a first-order thermodynamic character, being of an order-disorder type and it leads to a parent hexagonal phase, whose structure possess the 6/mmm point-group.<sup>30–33</sup> Thus, during the phase transition (PT), the loss of the ordered conformation by the appearance of disordered chain segments (*gauche*) destroys the elastic deformation of the quasi-hexagonal phase.

Although the ferroelectric PT of P(VDF-TrFE) copolymers is always smeared, in general, this transition does not show glassy behavior. In fact, relaxor behavior has been clearly demonstrated only for high-energy electron irradiated samples.<sup>22,23,36,37</sup> An acknowledged consequence is that this system presents the largest known electrostrictive response (strain level of 4%) of all electro-active materials.<sup>23,38,39</sup> Although the appearance of cross-linking bonds on the electron irradiated polymer has been demonstrated,<sup>36,40,41</sup> the mechanisms responsible for the induction of the relaxor and electrostrictive features have not yet been established. Some

uncertainty even remains concerning the relationship between crystallinity decrease and the appearance of cross-linking and about the nature of defects in the crystalline region.

The effects of  $\gamma$  irradiation on the ferroelectric properties of P(VDF-TrFE) copolymers were previously studied by Odajima *et al.*<sup>42</sup>. A similarity has been shown between the dielectric behaviors of electron- and gamma-irradiated samples, i.e., the smearing of the phase transition and the loss of stability of the ferroelectric phase.<sup>42–44</sup> Nevertheless, the delivered doses to the  $\gamma$ -irradiated samples were insufficient to provoke the appearance of the relaxor effect. In this work, we conducted systematic investigations of a  $\gamma$ -irradiated P(VDF-TrFE) equimolar copolymer, for gamma-irradiation doses comparable to those of electron ones. The appearance of relaxor features is clearly demonstrated. Dielectric, calorimetric, structural and spectroscopic measurements were used to investigate the chemical and morphological modifications responsible for the relaxor behavior of the material.

## II. EXPERIMENTAL PROCEDURES

PVDF and equimolar P(VDF-TrFE) films with 80- $\mu$ m thickness were prepared from commercial resins (ATOCHEM) melted at 200 °C, pressed (300 bar) and quenched to room temperature. Some of the obtained samples were irradiated with 500 kGy (50 Mrad) of a <sup>60</sup>Co source (1.25 MeV, dose rate 0.1 Mrad/h) under ambient atmosphere, at room temperature, at EMBRARAD/IPEN-CNEN, Brazil, and their behaviors compared with those of nonirradiated samples.

Structural characterization was made by x-ray diffraction (RIGAKU), with a 2° 2 $\theta$ /min scan rate, using CuK $\alpha$  radiation (30 mA, 40 kV). Thermal analyses were performed by differential scanning calorimetry (DSC, Mettler TA10-DSC30 system), with heating/cooling rates of 20 °C/min and by dielectric spectroscopy (DETA, Impedance Analyzer HP 4192A) at 1 °C/min, for frequencies ranging from 300 Hz to 10 MHz and temperatures from -40 to 115 °C. Typical sample weight and area were 10 mg (DSC) and 45 mm<sup>2</sup> (DETA). Fourier transform infrared (FTIR) spectroscopy was used to verify structural and chemical modifications of the samples. The spectra were recorded between 1500 and 4000 cm<sup>-1</sup> with a BOMEM-DA8 spectrometer, equipped with a Globar source, a KBr beamsplitter and a HgCdTe detector. The spectral resolution was better than 2 cm<sup>-1</sup>.

## III. RESULTS AND DISCUSSIONS

Melt-crystallized PVDF and copolymers present randomly oriented crystallites embedded in an amorphous matrix.<sup>45</sup> The crystallite dimensions are in the nano-scale region, i.e., 5 nm along the *c*-axis (chain direction) and 10 nm perpendicular to it. It is also accepted that the crystalline-amorphous interface, called an anchored or strained amorphous phase, is partially oriented.<sup>46</sup> The degree of crystallinity ( $\chi$ ), a measure of the crystalline fraction in the material, is generally higher than 50%. At room temperature, PVDF ho-

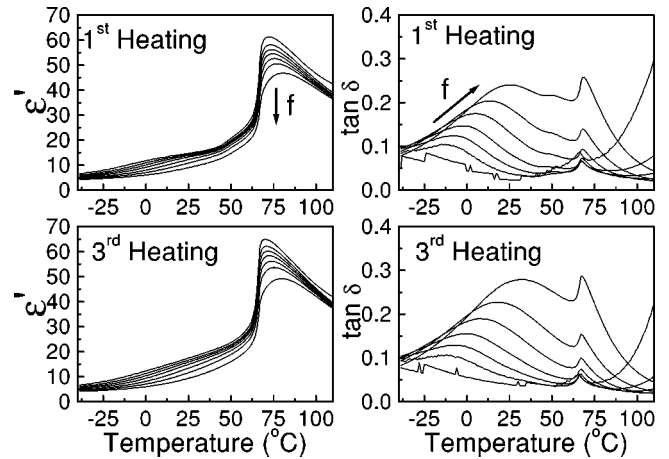


FIG. 1. Dielectric responses of the non-irradiated copolymer samples for the first and third thermal heatings, for the increasing frequencies: 500 Hz, 3 kHz, 10 kHz, 30 kHz, 100 kHz, 300 kHz, and 1 MHz. The arrows indicate increasing frequencies.

mopolymer belongs to the centrosymmetric monoclinic  $P2_1cm$  space group,<sup>45</sup> while its copolymer with 50-mol% TrFE belongs to the polar  $Cm2m$  space group, as already pointed out.

PVDF and its copolymer with 50 mol% TrFE were irradiated within the same experimental conditions, i.e., 500 kGy of 1.25 MeV  $\gamma$  rays. The homopolymer showed a high stability under irradiation, while the copolymer showed microscopic and macroscopic changes and relaxor behavior. We can initially wonder why the copolymer is susceptible to irradiation and the homopolymer is not. Besides the structural difference, the main difference between these polymers is of chemical nature: the presence of CHF segments in the copolymers. In this paper, we first show and then discuss the results of our investigations.

The dielectric response of as-crystallized P(VDF-TrFE) copolymer samples is shown in Fig. 1, for the first and third heating runs, for several frequencies ranging between 500 Hz and 1 MHz. Thermal cycling is necessary to stabilize the sample properties (crystallinity, defect relaxation). We notice the diffuse character of the ferroelectric PT (broad  $\epsilon'$  peaks with a maximum at 66 °C) without frequency dispersion. The curves for dielectric loss tangent ( $\tan \delta$ ) show three features: a low-temperature broad peak with a relaxation character, a thinner peak around 66 °C without any frequency dependence, and the tail of a high absorption at high temperatures. The first peak is linked to the micro-Brownian motion of the main polymer chain into the amorphous phase, the so-called  $\alpha$  relaxation which freezes at -22 °C (the quasi-static glass transition temperature of this polymer).<sup>47</sup> The second peak is the signature of the ferroelectric PT and is linked to dielectric losses into the crystalline region due to dipole fluctuations in the critical region and the tail is due to increasing losses near the melting point. Although the PT is of a first-order thermodynamic character, we did not discern any thermal hysteresis within the experimental accuracy of about 1 °C.

Let us discuss now the results of the dielectric investigations of the irradiated copolymer samples, presented in Fig.

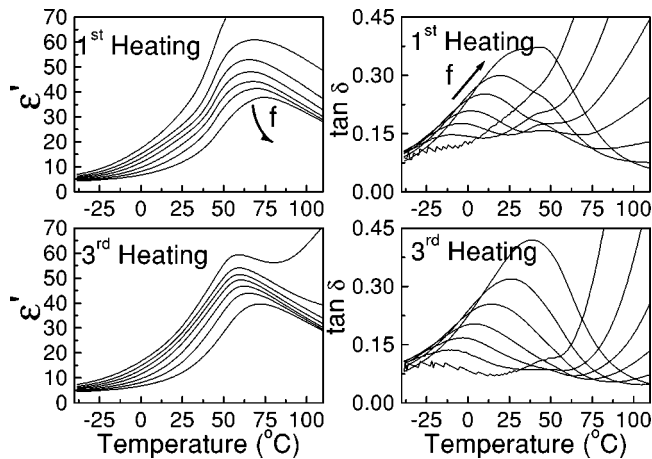


FIG. 2. Dielectric responses of the irradiated copolymer samples for the first and third thermal heatings, for the increasing frequencies: 500 Hz, 3 kHz, 10 kHz, 30 kHz, 100 kHz, 300 kHz, and 1 MHz. The arrows indicate increasing frequencies.

2, for the first and third heating runs. We observe the appearance of a relaxation character of the dielectric constant peak around the ferroelectric PT, which is enhanced after the first heating, suggesting the creation of a relaxor phase. It is worth noting that the dielectric anomaly became also much broader after irradiation (the PT became more diffuse). In the dielectric loss curves, we observe the existence of a smaller frequency-independent peak around 48 °C, in the first heating curves, as a shoulder on the large relaxation absorption. This feature corresponds to the narrow peak that appeared at the critical temperature (66 °C) in the nonirradiated sample. Its presence on the first heating  $\tan \delta$  curve indicates that the irradiated sample still contains a fraction of a normal-ferroelectric phase beside the relaxor one. Nevertheless, after heating the sample up to 100 °C (total transformation into the paraelectric phase), only the relaxor phase subsists, as shown by the enhancing of the relaxation character of  $\epsilon'$  and  $\tan \delta$ . For PVDF, the only observable variation in the dielectric properties with irradiation was an increase of the dielectric loss at higher temperatures, which occurs also for the copolymer. This behavior can be explained by the increase of the ionic conduction in the dielectrics, since it is more important for lower frequencies, and can be attributed to the appearance of ionic species created by irradiation.

In order to demonstrate the relaxor behavior of the irradiated copolymer in Fig. 3 we plot the measurement frequencies versus the reciprocal apparent critical temperatures, taken from the dielectric constant maxima, for the third heating run of the irradiated copolymer. We note that this system obeys quite well the Vogel-Fulcher law, a characteristic of both glassy systems<sup>48</sup> and relaxor systems with activated critical dynamics.<sup>14</sup>

The above results show that gamma-irradiation is effective to change the macroscopic dielectric response of the ferroelectric polymer, by inducing a relaxorlike behavior. Then, we can wonder what are the microscopic changes that lead to this behavior? Let us present the results of our structural, thermal and spectroscopic investigations to discuss this question.

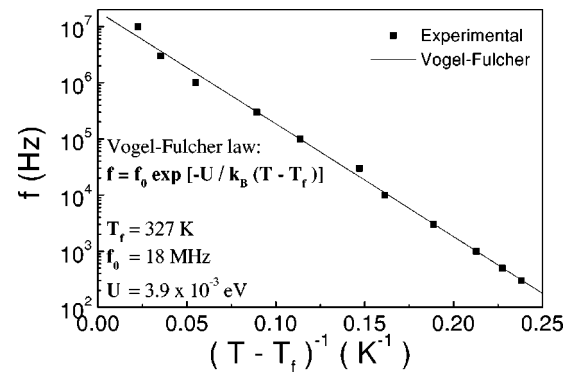


FIG. 3. The Vogel-Fulcher behavior of the apparent critical temperature for the irradiated copolymer, obtained from the dielectric constant peaks in the third heating run.

Figure 4 displays x-ray diffractograms of the P(VDF-TrFE) copolymer, before (a) and after (b) irradiation. The inset shows a zoom in the region of higher angles. These diffractograms show the typical profiles for the quasi-hexagonal  $Cm2m$  structure, also called the  $\beta$  phase.<sup>45</sup> The main peaks at 19.16, 19.60, and around 40  $2\theta$ -degrees correspond, respectively, to the (200), (110), and (201) Bragg peaks. We observe that, apparently, the 500-kGy  $\gamma$  irradiation dose does not change the crystallographic structure of the polymer. In fact, although the main peaks at lower angles present a little evolution, the (201) peak remains at the same position, which indicates that the interchain distance, linked to the  $c$  axis, remains close to 2.56 Å, a characteristic of the  $\beta$  phase of these polymers.

In order to explore the changes due to the irradiation in the strongest Bragg peaks, in Fig. 5 we present the fittings of these peaks around 19° by pseudo-Voigt functions, before and after irradiation. The vertical dashed line shows that the dot-dashed curve, corresponding to the (200) peak, remains approximately at the same position. Otherwise, the dashed curve, corresponding to the (110) peak, present an important downshift. By estimating the cell parameters from the (200), (110), and (201) peak positions, we got  $a=9.25$  Å,  $b=5.19$  Å, and  $c=2.58$  Å, before irradiation and  $a=9.26$  Å,  $b=5.48$  Å, and  $c=2.57$  Å, after irradiation. We

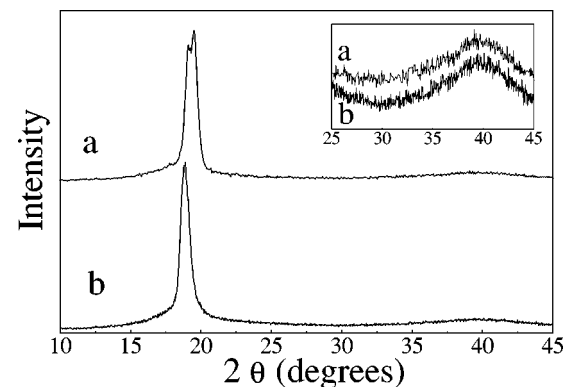


FIG. 4. X-ray diffractograms for the P(VDF-TrFE) copolymer, before (a) and after (b) irradiation. The inset shows a zoom in the region of the (201) Bragg reflection.

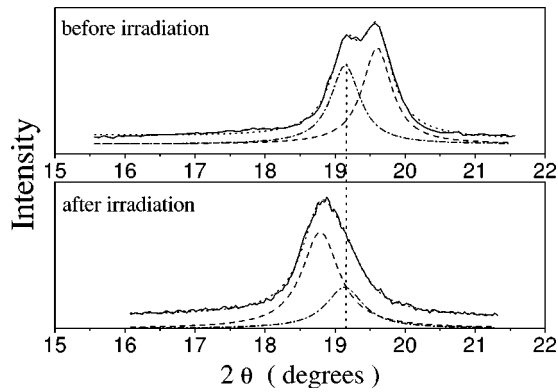


FIG. 5. Detail and fittings of the main x-ray Bragg peaks of the copolymers, before and after irradiation. Dashed and dot-dashed lines represent respectively the (110) and (200) Bragg peaks. The vertical dashed line shows that the position of the latest peak does not change with irradiation.

note that the structure remained quasi-hexagonal ( $a \sim \sqrt{3}b$ ), but that the cell volume increased by 5%. The volume increase is close to that undergone by this polymer in its ferroelectric-to-paraelectric phase transition, but the changes in cell parameters are very different. In fact, the hexagonal paraelectric phase has a contracted interchain distance ( $c \sim 2.2\text{--}2.3 \text{ \AA}$ ) (Refs. 30 and 32) and intrachain distances comparable to the  $b$  axis of the irradiated sample, though with  $a = \sqrt{3}b$ . Note that, as a consequence of the irradiation, the (ferro) elastic deformation, which is proportional to ( $a - \sqrt{3}b$ ), transforms from positive to negative. Thus, the main observable effect of irradiation on the crystalline cells is the 5% unit cell increase in the  $b$  direction. Concerning the irradiated PVDF homopolymer, we did not observe any change in its diffractograms with irradiation.

The x-ray results showed that the crystalline structure of the irradiated copolymer samples could be either the ferroelectric  $\beta$  phase or a very similar structure. The cell volume increase is surely linked to the presence of defects affecting the crystallites. But, what is the nature of such defects? Calorimetric techniques are well adapted to investigate whether these defects are of physical or chemical origin. Thus we have performed several cycles of DSC runs on our samples, and the results for the copolymers are presented in Fig. 6, for the nonirradiated (a) and irradiated (b) samples. The two endothermic peaks for increasing temperatures on the heating runs correspond, respectively, to the first-order ferroelectric PT and to the melting of crystallites. The cooling cycles present exothermic peaks for recrystallization and paraelectric-to-ferroelectric PT, for decreasing temperatures. In the two first cycles, the samples were heated only up to  $95^\circ\text{C}$ ; the samples were melted only during and after the third cycle. The temperatures and latent heats of PT and melting are given in Table I, showing a high stability after the first cycle.

The irradiated copolymer sample also presents an endothermic anomaly in the region of the ferroelectric PT [Fig. 6(b)]. Nevertheless, the transition temperature decreased about  $16^\circ\text{C}$  and the transition latent heat became much lower after irradiation (also see Table I), denoting the loss of sta-

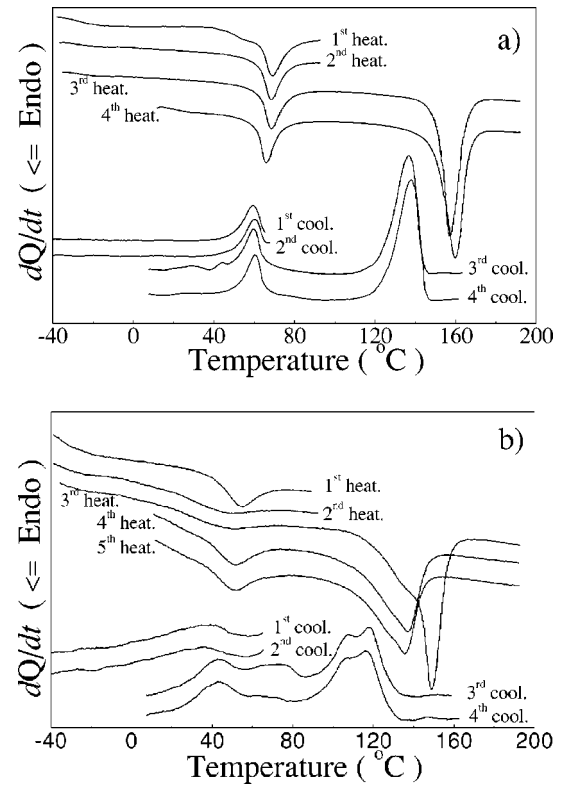


FIG. 6. DSC curves for the copolymer, before (a) and after (b) irradiation, for the various thermal runs indicated in the figure.

bility of the ferroelectric phase. We also note that the thermal anomalies became more complex after irradiation (double and triple peaks), which is a clear indication of the presence of defects into the polymer structure.

The calorimetric results show that the irradiation-induced defects do not disappear after melting the sample and that the loss of stability of the paraelectric crystalline phase is still higher for the melted recrystallized sample (downshift of the melting point). We interpret these results as follows: most of the induced irradiation defects are chemical bonds (they do not disappear after melting), mainly in the amorphous phase.

TABLE I. Endothermic peak temperatures and enthalpies at the structural phase transition (PT) and crystalline melting, obtained from the indicated DSC heating runs.

# Heating	$T_{PT}(^\circ\text{C})$	$\Delta H_{PT}(\text{J/g})$	$T_{\text{melt}}(^\circ\text{C})$	$\Delta H_{\text{melt}}(\text{J/g})$
Before irradiation:				
1st	69.0	8.5	—	—
2nd	68.5	6.7	—	—
3rd	68.5	6.3	157.0	25.2
4th	66.0	6.8	159.5	26.2
After irradiation:				
1st	54.5	3.8	—	—
2nd	52.0	1.4	—	—
3rd	52.0	1.6	149.0	20.6
4th	52.0	2.4	137.0	12.2
5th	52.0	2.5	136.0	11.9



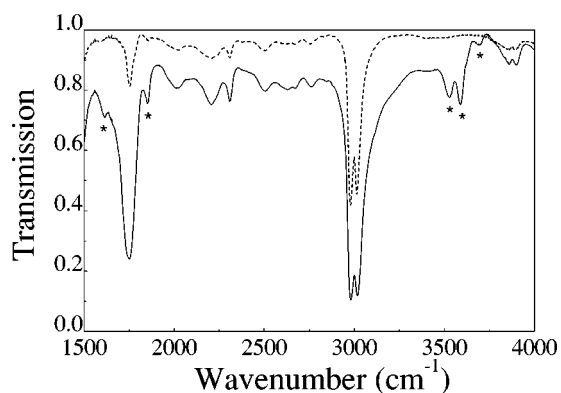


FIG. 7. Transmission FTIR spectra of the copolymer sample, before (dashed) and after (continuous line) irradiation. New bands induced by irradiation are indicated by asterisks.

In the crystalline region, the ordered chain packing prevents higher degrees of irradiation damages. In the melted recrystallized sample, the defects were segregated outside the crystallites, but they should be so numerous that they provoke a drastic decrease of the sample crystallinity (which is roughly proportional to the melting enthalpy).

As was also observed by other authors in electron or gamma-irradiated P(VDF-TrFE) copolymers, we verify that, after irradiation, the 50-mol % TrFE copolymer became insoluble in dimethylacetamide, which is compatible with the appearance of cross-linking chain bonds.<sup>36,40,41,49</sup> These bonds should be associated with defluorination of the CHF sequence, since calorimetric measurements of irradiated PVDF homopolymer show only a 4 °C melting temperature downshift, with no change in the melting enthalpy. Thus we conclude that the calorimetric behavior of the irradiated samples is compatible with the appearance of cross-linking bonds in the amorphous phase of the material. Within this picture, we can understand the relationship between crystallinity, a characteristic of linear polymers, and cross-linking, a characteristic of network polymers. In the present case, these two properties are present, but in different parts of the sample.

The structural and morphological modifications of P(VDF-TrFE) copolymer induced by the  $\gamma$  irradiation, i.e., the unit cell expansion along the  $b$  axis and the creation of cross-linking bonds in the amorphous phase, should both be responsible for the macroscopic relaxor-like dielectric behavior of the material. We can use FTIR spectra to investigate the changes in the chain conformation and the formation of new chemical bonds due to the irradiation. Thus in Fig. 7 we present the transmission FTIR spectra of the copolymer sample, before (dashed) and after (continuous line) irradiation. The strongest bands at 2978 and 3014 cm<sup>-1</sup> correspond, respectively, to the symmetrical and anti-symmetrical stretching CH<sub>2</sub> vibrations in the polar all-trans phase.<sup>50</sup> Their intensification after irradiation can signify the enhancing of this dipolar vibration. A shoulder in the higher frequency side of the 3014-cm<sup>-1</sup> band can indicate the increase of *gauche* segments, but there is no additional evidence that they are located in the crystalline region of the material. The strong band near 1750 cm<sup>-1</sup> is not predicted for this mate-

rial, and is probably due to C=O stretching vibration.<sup>42,50</sup> After ambient atmosphere irradiation this band becomes very intense. Beside this chain oxidation, we also observe the appearance or intensification of five bands, marked by asterisks, respectively at 1614, 1855, 3528, 3592, and 3698 cm<sup>-1</sup>. We believe that these bands correspond to bending and stretching vibrations of NH and OH bonds, participating of the cross-linking bonds in the amorphous phase.

At this point we can wonder how the appearance of cross-linking bonds in the amorphous phase could be related to the relaxor effect, which is a characteristic behavior of nanocrystalline materials? The morphological organization of the ferroelectric polymers could have the answer. In fact, the very small crystallites (typical dimensions  $\sim 10$  nm) are organized in groups of lamella, with a partially oriented amorphous intralamella phase.<sup>29,45</sup> The density of this intralamella amorphous phase is higher than that of the interlamella one. In normal ferroelectrics the domain size should be larger than a critical value; otherwise, the domain would not be stable and would collapse.<sup>51</sup> In PMN, it has been shown that the critical correlation length is of the order of 20 nm.<sup>9</sup> If the correlation length becomes higher than this value, below the freezing temperature, the polydispersive dynamics disappear (non-ergodic behavior) and the system behaves like a normal ferroelectric. On the other hand, on heating the sample the correlation length decreases continuously down to 5 nm, leading to the relaxor (ergodic) behavior.<sup>9</sup> Thus we believe that the amorphous phase in ferroelectric polymers plays an important role in the formation of stable ferroelectric domains, which should contain several crystallites and part of the amorphous phase. One or more lamella could participate of each domain. In nonirradiated samples, the chains in the amorphous phase are relatively free to rotate helping, neighbor crystallites to obtain parallel polarizations. After irradiation, the movements of those chains are somewhat frozen by the cross-linked bonds. Thus the interaction between adjacent crystallites is reduced and smaller polar clusters would be formed. Although P(VDF-TrFE) polymers are order-disorder ferroelectrics, these polar clusters could have similar behavior to that observed in inorganic relaxors, i.e., they would be dominated by correlated dynamical fluctuations into the relaxor phase, which freeze into ferroelectric nanodomains at low temperatures.

A last remark concerns the qualitative differences on using electron or gamma irradiation to induce the observed relaxor features in these polymeric materials. In fact, assuming that the same absorbed dose is delivered to the sample, some differences exist mainly related to the dose rate and to the oxidative degradation of the material, at or near the surface. For electron and gamma sources of same strength, the dose rate is much higher for electrons than that for the gamma source, because the electron beam is generally collimated and focused in a smaller region. This has the advantage of a lower exposition time, but some disadvantages when the recovery time is not respected (some systems can present saturation effects). Besides, the interaction of electrons with other electrons is much stronger than with photons. On the other hand, since the gamma rays have a deeper penetration length and reach the targets as plane waves, the

energy transfer to the sample is more homogeneous than for electrons. Finally, it can be said that all polymeric materials undergo less embrittlement under electron-beam than under gamma-ray irradiation as a result of reduced oxidative chain scission.<sup>52-56</sup> Although some work has been already done in irradiated P(VDF-TrFE) copolymers,<sup>40-44,49</sup> a systematic study of the differences under these different types of irradiation remains a task for the future.

#### IV. CONCLUSIONS

It has been shown that high doses of  $\gamma$  irradiation are as effective as equivalent electron-irradiation doses to induce the formation of a relaxor phase in ferroelectric polymers. These materials constitute a new class of order-disorder relaxor ferroelectrics. Another particularity is that their parent phase is of a hexagonal symmetry, with no relationship to the perovskite or tungsten-bronze structures, which hold for all known inorganic relaxors.

The  $\gamma$  rays produce a decrease of the copolymer crystallinity, the appearance of new chemical bonds, an increase of the  $b$  lattice parameter, and the loss of the stability of the normal ferroelectric phase. Although the mechanism for the relaxor formation is not yet completely understood, we propose that cross-linking bonds created in the amorphous phase of the polymer prevent the formation of stable ferroelectric domains: the correlation length would become smaller than the critical domain size, leading to the appearance of dynamically unstable polar clusters, which drive the macroscopic dielectric response of the system.

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