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Dielectric response of polymer relaxors

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Dielectric response of vinylidene fluoride type ferroelectric polymers is dominated by that of segmental motions in the amorphous phase in temperature range 200–300 K and contributions related to the local mode and ferroelectric–paraelectric transition in the crystalline phase of the polymer at higher temperatures. Diffuse and frequency-dependent dielectric anomaly observed in fast electron irradiated polyvinylidene fluoride-trifluoroethylene P(VDF/TrFE) has been related to relaxor-like behavior induced in the semicrystalline ferroelectric copolymers. As random field and the response of polar nanosize clusters determine the relaxor behavior the effects of disorder and fast electron irradiation (below and above T_C) on the three contributions to the dielectric response of PVDF, P(VDF/TrFE)(75/25) and P(VDF/TrFE)(50/50) are shown. The processes involved in radiation-induced functionalization of PVDF-type polymers are discussed on the basis of results of ESR, IR and Raman spectroscopy studies.

1. Introduction

Ferroelectrics, exhibiting also pyroelectric and piezoelectric properties are attractive for applications since both the sensing and actuating functions can be realized in the same element. After the discovery of ferroelectricity in polyvinylidene fluoride (PVDF) type polymers in 1980 [1–3] the materials have received particular attention for many reasons. One of the most important features is that the polymers can be easily produced in the form of large thin flexible sheets and in a variety of shapes. Moreover, low dielectric permittivity ε and elastic stiffness of PVDF-type polymer films at room temperature, resulting in high voltage sensitivity, as well as their low acoustic impedance, fitting well to that of water and tissue, make them attractive for application in electromechanical transducers using the piezoelectric constants d_{31} and d_{33} [4, 5]. As the permittivity and dielectric losses are involved in figures of merit of pyroelectric sensors, PVDF-type polymers with high pyroelectric activity and low ε and tan δ values are used in pyroelectric applications [4–6].

The vacuum dipole moment of vinylidene fluoride unit $\mu(\text{VDF}) = 7.07 \cdot 10^{-30}$ Cm originates from the distribution of positively charged hydrogen atoms and negatively charged fluorine atoms and lies in the plane of C–C bond. In the $[–CH_2–CF_2–]_n$ polymer the dipoles are attached to the main chain and can adopt various orientations resulting in several molecular conformations of the chain. The chains can be packed in various manner forming polymorphous modifications of PVDF [7, 8]. Both the conformations of the polymer chains and their packing in the unit cell are determined by the processing conditions. Nonpolar polymorph II with antiparallel packing of trans-gauche-trans-gauche′ (TGTG′) chain conformation is obtained on cooling molten PVDF to room temperature. Chains with planar-zigzag all-trans conformations packed in a parallel manner form ferroelectric PVDF I modification with dipole moments perpendicular to the chain axis. The ferroelectric PVDF polymorph can be obtained from melt-crystallized polymer by mechanical orientation or poling in high electric field. Polar modification PVDF III, consisting of a parallel packing of TTTGTTTG′ conformation is obtained by annealing the polymorph II at ∼430 K. It should be noted that PVDF is a semicrystalline polymer with the degree of crystallinity of ∼50%.

The long-range interactions of dipoles in PVDF I crystalline modification are rather strong since the ferroelectric ordering persists, depending on processing conditions, to the temperatures just below the melting point or the polymer melts before it undergoes a transition to the paraelectric phase [9–12]. The long-range forces can be weakened by incorporation into the PVDF chain units with dipole moment different from that of vinylidene fluoride. Trifluoroethylene (TrFE) was found to

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be the most interesting unit to functionalise the properties of PVDF [8, 9]. The dipole moment of trifluoroethylene unit $\mu(\mathrm{TrFE}) = 5.74 \cdot 10^{-30}$ Cm is lower by $\sim 20\%$ than that of vinylidene fluoride and goes out of the plane of the –C–C– bond defined as the (x, y) plane: $\mu_x(\mathrm{TrFE}) = 0.37 \cdot 10^{-30}$ Cm, $\mu_y(\mathrm{TrFE}) = 3.77 \cdot 10^{-30}$ Cm, $\mu_z(\mathrm{TrFE}) = 4.30 \cdot 10^{-30}$ Cm, as shown in Fig. 1 [13]. Vinylidene fluoride and trifluoroethylene copolymerise in a random copolymer at any VDF/TrFE ratio and the Curie point of the copolymers is shifted linearly towards lower temperatures with increasing contents of TrFE [14].

The chemical heterogeneity in the polymer chain is increased in terpolymers of VDF with TrFE and chlorotrifluoroethylene (CTrFE) or chlorofluoroethylene (CFE) units. The dipole moment of chlorotrifluoroethylene $\mu(\mathrm{CTrFE}) = 2.14 \cdot 10^{-30}$ Cm with projections $\mu_x(\mathrm{CTrFE}) = 1.58 \cdot 10^{-30}$ Cm, $\mu_y(\mathrm{CTrFE}) = 1.40 \cdot 10^{-30}$ Cm and $\mu_z(\mathrm{CTrFE}) = 0.03 \cdot 10^{-30}$ Cm in rectangular coordinates with C–C bond in the (x, y) plane [13] differs considerably from the dipole moments of VDF and TrFE (Fig. 1). Statistical disorder in terpolymers based on the zigzag PVDF chain was found to exhibit diffuse and dispersive dielectric anomaly described by Vogel–Fulcher law, characteristic of ferroelectric relaxors [15–17]. Similar relaxor-like behaviour was observed earlier in P(VDF/TrFE) copolymers irradiated with fast electrons [18–21] and the authors claimed on a giant electrostrictive response and high elastic energy density in the materials. Moreover, Zhang and his co-workers pointed at an ability to tailor the properties of polymer relaxors to the requirements of transducer and actuator technology due to their strain anisotropy [20, 21]. The volume strain and either the longitudinal or transverse strain, parallel or perpendicular to the direction of electric field applied, may be used in various applications. Also the reliability of the devices can be improved due to the high strain anisotropy that can be achieved in polymer relaxors and can reduce the unwanted mechanical coupling between different directions.

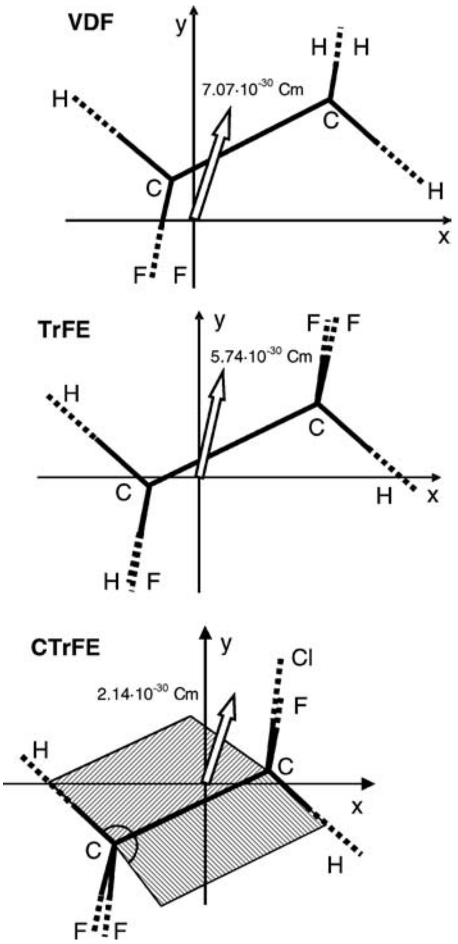


Figure 1 Schematic of spatial dipole moment arrangement of vinylidene fluoride (VDF), trifluoroethylene (TrFE) and chlorotrifluoroethylene (CTrFE) units [13].

As the properties of electron irradiated P(VDF/TrFE) were interesting for applications in modern transducers and actuators, radiation-induced functionalization of the copolymers has been studied repeatedly [22–31] it should be observed however, that the physical origin of relaxor behaviour in PVDF-type polymers has not been demonstrated clearly. Recently, Chen stressed that the dielectric response of electron irradiated P(VDF/TrFE)(50/50) copolymer and terpolymer of P(VDF/TrFE/CTFE)(65/35/9) is dominated by the response of non-crystalline regions and termed the behaviour as ‘‘dielectric relaxor’’ [32]. We proposed to consider PVDF to be similar to the PSN and PST-type relaxors with a coexistence of both the short-range polar order in the amorphous phase and long-range polar order in the crystalline phase of the polymer [30]. Here we would like to present in detail changes in the dielectric response of PVDF as well as P(VDF/TrFE)(75/25) and (50/50) copolymers caused by fast electron irradiation and discuss processes involved in radiation-induced functionalization.

2. Experimental procedures

As we would like to discuss the effect of fast electron irradiation on PVDF-type polymers with different ferroelectric ordering (different temperatures of ferroelectric-paraelectric transitions) we studied dielectric response of PVDF, P(VDF/TrFE)(75/25) and P(VDF/TrFE)(50/50) films. PVDF and P(VDF/TrFE)(50/50) films were 10–80 μm thick and radially oriented by hot-pressing at $p = 600$ MPa and $T = 450$ K. The P(VDF/TrFE)(75/25) copolymer samples with thickness of 25 μm were biaxially oriented and corona-charged.

The samples were irradiated with electrons of energy $E^* = 0.5$–1.5 MeV in a Van de Graaff accelerator with doses $D^* = 0.5$–4.3 MGy both below and above the Curie point. The current density of the electrons amounted to 0.1 μA/cm^2. Calculated energy losses of 0.5 MeV electrons yield the extrapolated range of ~0.8 mm, thus the incident electrons of $E^* = 0.5$–1.5 MeV passed through the samples studied [31, 33]. The samples were transferred from the high vacuum of the accelerator into the air and the radiation damage to the polymers was studied.

Electron spin resonance (ESR) technique with CW X-Band Radiopan SE/X-2547 spectrometer was used to study free radicals and their decay at room temperature. The ESR spectra were recorded from a few days up to 2 months after termination of irradiation. Number of spins in the samples was determined by ESR with respect to the Ultramarine Blue Standard sample having $6 \cdot 10^{15}$ spins of the $S_3{}^{\bullet -}$ radicals.

After the decay of free radicals we studied the concentration of isolated and conjugated C=C bonds in the samples by IR spectroscopy on Perkin-Elmer FT-IR 1725X spectrometer. IR and Raman spectroscopy was used also to characterize the conformational order/disorder in the samples. NIR Raman spectra were obtained with Bruker IFS66 FRA 106 spectrometer in back scattering geometry at room temperature. The samples were excited by Nd:YAG laser radiation of 1064 nm wavelength and 200 mW power.

Dielectric response of the films was measured in the frequency range 100 Hz–1 MHz by using computer controlled HP-4284A LCR Meter later than 2 months after termination of irradiation. The samples with gold sputtered electrodes were placed in an Oxford Instruments Cryostat CF 1240 where the temperature was changed from 100 to 450 K at a rate of 1 K/min.

3. Results

3.1. Radiation damage

Modification of the dielectric properties of P(VDF/TrFE) by fast electron irradiation was observed for the first time by Odajima *et al.* who reported a broadening of the dielectric anomaly, a downward shift of the Curie point and a decrease of the thermal hysteresis at the ferroelectric-paraelectric transition in irradiated copolymers [34]. Daudin, Legrand *et al.* [35–40] studied systematically the effect of electron irradiation on the properties of (70/30) and (60/40)P(VDF/TrFE) copolymers. The authors confirmed radiation-induced changes observed by Odajima *et al.* and found a small upward shift of the glass transition caused by electron irradiation. Moreover, their UV and XPS spectroscopy studies revealed double C=C bonds in irradiated samples and a decrease in the degree of crystallinity was observed by XRD [38]. They discussed also various contributions responsible for the downward shift of the Curie temperature and considered the defect-induced decrease of the dipolar energy to be most important [39]. The decrease in the polarization as well as the decrease in the crystallinity of irradiated P(VDF/TrFE) copolymers were also reported by Bharti *et al.* [26].

It has been pointed out by many authors that the radiation-chemistry of fluoropolymers differs somewhat from that of their hydrocarbon analogues [41]. This is attributed to the fact that though the fluorine atom provides the strongest bond with carbon atom (dissociation energy of C–F bond amounts to 530.5 kJ/mol whereas that of the C–H bond is equal to 429.7 kJ/mol) irradiation breaks both C–H and C–F bonds leading to formation of in-chain radicals and elimination of hydrogen fluoride. Of course the C–C bonds are also susceptible to radiation-induced scissions producing end-chain radicals. Let us discuss the effect of electron irradiation on PVDF-type polymers in the high vacuum of Van de Graaff accelerator. The cleavage of C–H and C–F bonds by fast electrons can produce two kinds of in-chain and two kinds of end-chain radicals in PVDF:

$$\begin{aligned}&(\mathrm{I})\text{–CF–C}^{\bullet}\text{H–CF}_2\text{–}+(\mathrm{II})\text{–CH}_2\text{–C}^{\bullet}\text{F–CH}_2\text{–}\\&\quad+(\mathrm{III})\text{–CH}_2\text{–C}^{\bullet}\text{F}_2+(\mathrm{IV})\text{–CF}_2\text{–C}^{\bullet}\text{H}_2.\end{aligned}$$

In random copolymers P(VDF/TrFE)(75/25) and P(VDF/TrFE)(50/50) one can expect additional three kinds of in-chain and two kinds of end-chain radicals:

$$\begin{aligned}&(\mathrm{I})\text{–CF}_2\text{–C}^{\bullet}\text{H–CF}_2\text{–}+(\mathrm{II})\text{–CH}_2\text{–C}^{\bullet}\text{F–CH}_2\text{–}\\&\quad+(\mathrm{III})\text{–CH}_2\text{–C}^{\bullet}\text{F}_2+(\mathrm{IV})\text{–CF}_2\text{–C}^{\bullet}\text{H}_2\\&\quad+(\mathrm{V})\text{–CH}_2\text{–C}^{\cdot}\text{F–CFH–}\\&\quad+(\mathrm{VI})\text{–CH}_2\text{–C}^{\bullet}\text{F–CHF}+(\mathrm{VII})\text{CF}_2\text{–C}^{\bullet}\text{F–CF}_2\text{–}\\&\quad+(\mathrm{VIII})\text{–CF}_2\text{–C}^{\bullet}\text{FH}+(\mathrm{IX})\text{–CHF–C}^{\bullet}\text{F}_2.\end{aligned}$$

When the irradiated samples are transferred from the high vacuum into the air some alkyl radicals become oxygenated forming alkoxy or alkyl peroxy radicals [42]. Electron spin resonance studies yield information on the kinds of free radicals introduced by fast electrons and on the free radical decay. It should be noted however, that the detailed analysis of the ESR spectra of electron irradiated PVDF-type polymers is difficult since the kinetics of the radical formation and decay is unknown [41]. The chain-end radicals can undergo radical recombination reactions with other radicals which may lead to branching structures whereas desorption of HF is responsible for the formation of double C=C bonds [41].

Fig. 2 shows room temperature ESR spectra of PVDF and P(VDF/TrFE)(75/25) and (50/50) copolymers irradiated at $T^* = 300$ K with the dose $D^* = 1.25$ MGy of 1 MeV incident electrons recorded at different times after termination of irradiation. The multicomponent spectrum of PVDF with the separation of outermost peaks of

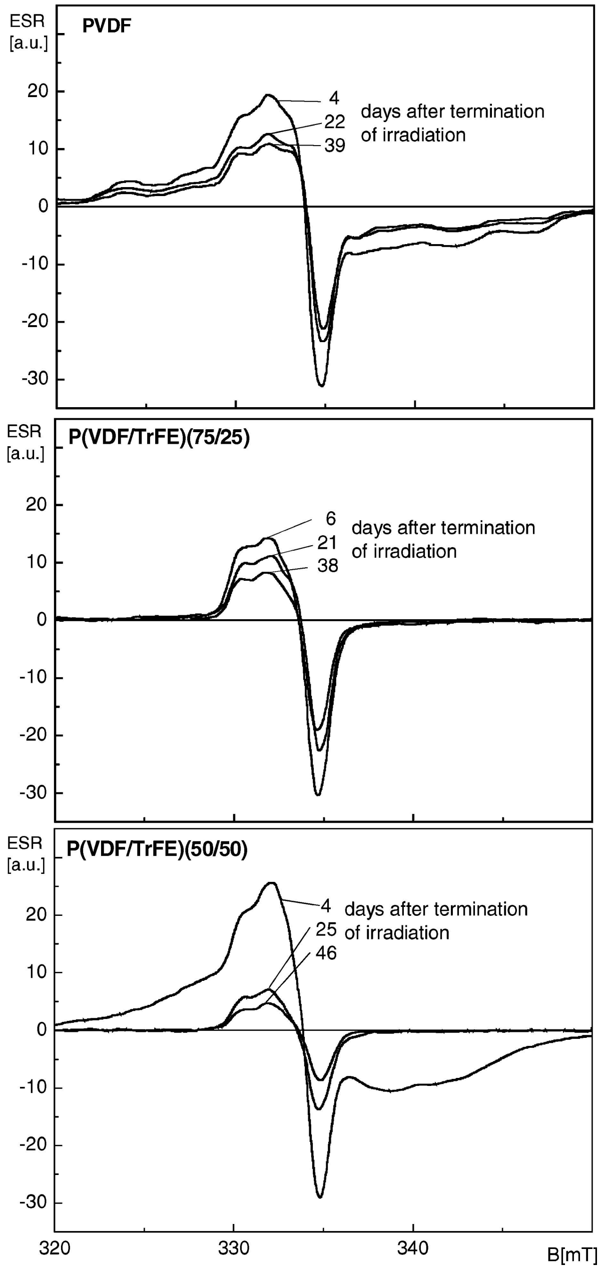


Figure 2 Room temperature ESR spectra of PVDF, P(VDF/TrFE)(75/25) and P(VDF/TrFE)(50/50) irradiated at 300 K with a dose of 1.25 MGy of 1 MeV electrons recorded at different time after termination of irradiation.

about 23 mT consists of overlapping lines of the hyperfine structure, which have been assigned to the chain-end –CF_2–$C^{\bullet}H_2$ and in-chain –CF_2–$C^{\bullet}H$–CF_2– alkyl radicals A large asymmetric peak in the centre of the spectrum is due to peroxy radicals either in-chain or end-chain [44]. The same kind of radicals was identified in the ESR spectra of irradiated P(VDF/TrFE)(50/50) copolymer, whereas in the case of P(VDF/TrFE)(75/25) copolymer the peroxy radicals are formed mainly as a result of rapid transformation of alkyl radicals to the peroxy ones in the presence of the air. The principal g-tensor values of this oxygenated radicals were estimated as $g_{||} = 2.0327$, $g_{\perp} = 2.0081$ and $\langle g \rangle = 2.0163$, and are characteristic of peroxy radicals produced from the alkyl radicals –CF_2–$C^{\bullet}F$–CF_2– [42]. Though the integral intensity of the ESR spectra of irradiated PVDF decreases with time the signals originating of both primary and oxygenated radicals are observed in the spectra after 2 months of storage at room temperature. The concentration of free radicals in the copolymers decays within ~2 months to a constant value that depends on the dose and temperature of irradiation and on the TrFE content [28, 31]. An example of room temperature decay of the free radical density in P(VDF/TrFE)(50/50) samples irradiated at $T^* = 300$ K with the same dose of electrons of incident energy $E^* = 1$ MeV and $E^* = 1.5$ MeV is shown in Fig. 3. It can be seen that the final concentration of free radicals is independent of the energy E^* of the incident electrons. The kinetics of free radical creation and decay is however, dependent on the temperature T^* of irradiation and in general is unknown for PVDF-type polymers [41]. We found that samples irradiated at high temperatures show low-intensity radical signal (Fig. 4) with $g = 2.0175$ and with peak–peak line width of 1.4 mT. The signal is two orders of magnitude lower than that of samples irradiated at 300 K and is attributed to polyenyl radicals CH_2–$(CF{=}CH)_n$–$C^{\bullet}F$–CH_2–CFH [44]. The unpaired electron in the radicals is delocalised over conjugated C=C bonds and we assessed the maximum number of C=C linkage from our IR studies to amount to $n = 5$.

The decay of free radicals and desorption of HF results in formation of isolated and conjugated C=C bonds, which can be revealed by IR spectroscopy. Examples of IR spectra of P(VDF/TrFE)(50/50) copolymer irradiated with various doses of 1 MeV electrons are shown in Fig. 5. The band at 1754 cm^{-1} is attributed to vibrations of isolated C=C bonds and the bands of conjugated C=C bonds appear at smaller wavenumbers [45].

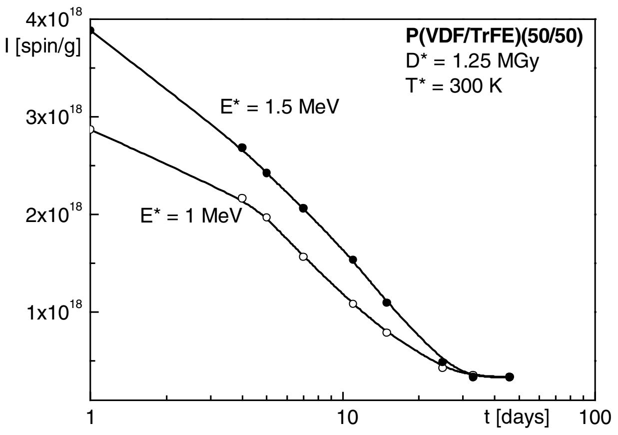


Figure 3 Room temperature decay of the density of free radicals in P(VDF/TrFE)(50/50) copolymer irradiated at $T^* = 300$ K with the dose $D^* = 1.25$ MGy of 1 and 1.5 MeV electrons.

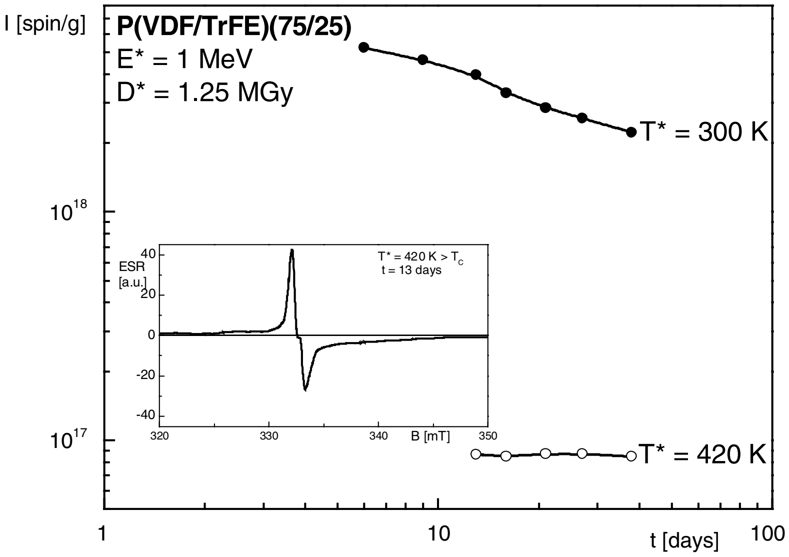


Figure 4 Room temperature decay of the density of free radicals in P(VDF/TrFE)(75/25) copolymer irradiated with the dose $D^* = 1.25$ MGy of 1 MeV electrons at 300 and 420 K; (Inset) ESR spectrum of the copolymer irradiated at $T^* = 420$ K recorded 13 days after termination of irradiation.

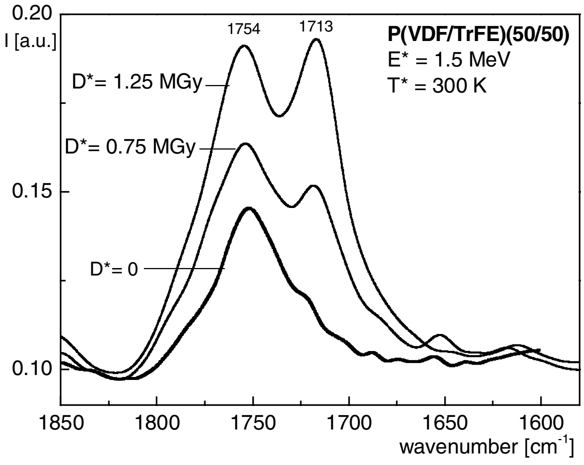


Figure 5 IR spectra of P(VDF/TrFE)(50/50) non-irradiated and irradiated at $T^* = 300$ K with various doses of 1.5 MeV electrons.

Tashiro has shown that vibrational spectra are useful in characterization of conformational disorder in P(VDF/TrFE) copolymers [8]. We have used vibrational spectroscopy to show that fast electron irradiation of the copolymers results in a reduction of the coherence of long-range ferroelectric all-trans conformation and an increase of the concentration of TTTGTTTG′ and TGTG′ conformations [28, 29, 31]. The effect is illustrated in Fig. 6 where radiation-induced decrease of the intensity of all-trans band at ~850 cm^{-1} is visible in IR and Raman spectra, whereas the band intensity at ~810 in Raman spectrum, characteristic of TTTGTTTG′ conformation, increases.

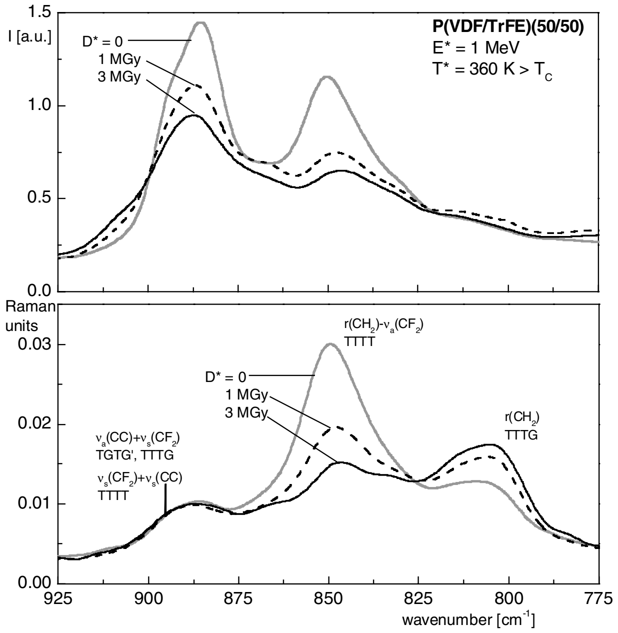
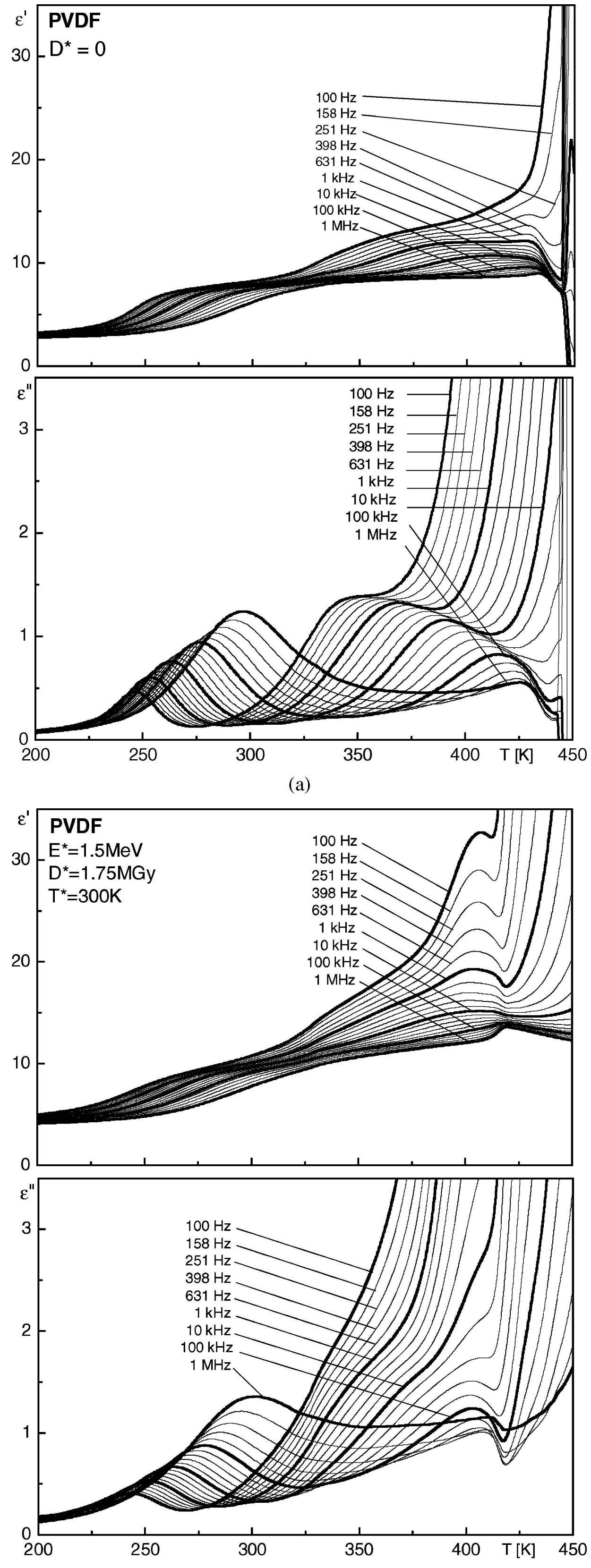


Figure 6 Room temperature IR and Raman spectra of P(VDF/TrFE)(50/50) non-irradiated and irradiated at $T^* = 360$ K with various doses of 1 MeV electrons.

3.2. Dielectric response

The scission of the PVDF-type chains by double C=C bonds, defects and conformational disorder introduced by fast electron irradiation affect the physical properties of the polymers. The radiation-induced modification in dielectric dispersion and absorption is clearly visible in the case of PVDF, where the Curie temperature is far above the glass transition (Fig. 7). The dielectric response in low-temperature range is characteristic of segmental



(a)

(b)

Figure 7 Dielectric response of PVDF films, non-irradiated (a) and after irradiation with the dose $D^* = 1.75$ MGy of 1.5 MeV electrons at $T^* = 300$ K (b).

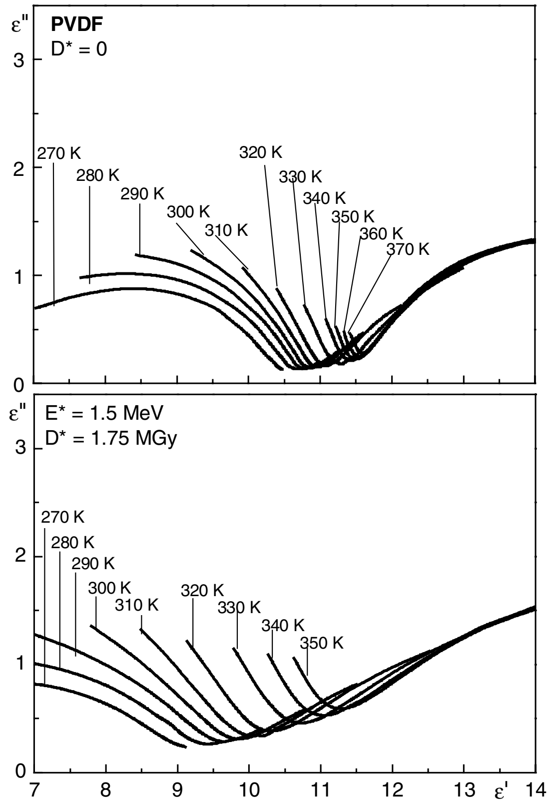


Figure 8 Cole-Cole plots of PVDF films, non-irradiated and after irradiation with the dose $D^* = 1.75$ MGy of 1.5 MeV electrons at $T^* = 300$ K.

motions of the polymer, i.e., freezing of dipolar motions in the amorphous phase of the semicrystalline polymer. The process is strongly temperature dependent and the frequency and temperature dependence of the imaginary part of the permittivity $\varepsilon''(f, T)$ yield the temperature variation of the relaxation times τ (T). The temperature dependence of the relaxation time can be described by Vogel–Fulcher relation:

$$\tau = \tau_{\mathrm{VF}} \exp[B/(T - T_{\mathrm{VF}})],$$

where T_{VF} is a characteristic temperature at which all relaxation times diverge and the relaxation time distribution becomes infinitely broad. At higher temperature dielectric response is dominated by a local mode in the crystalline phase of the polymer. The response due to wide-angle oscillations of dipoles attached to the main chain, followed by their rotation with chain cooperation is described by Arrhenius law [11]:

$$\tau = \tau_{\mathrm{A}} \exp[\Delta H/kT].$$

Torsional and rotational motions of dipoles attached to the main chain leading to changes from all-trans to TGTG′ are responsible for the dielectric anomaly, characteristic of the ferroelectric-paraelectric transition observed just before dynamical melting of the polymer, where a minimum in the permittivity appears. As is seen in Fig. 7b, fast electron irradiation results in a downward shift of the Curie point and in a considerable broadening and decreasing of the anomaly at T_C. Changes appear also in the response characteristic of the local mode and segmental mode of the polymer: the response of the local mode becomes smeared out and the dispersion increases. It is clearly visible in Fig. 8, where radiation-induced changes in the Cole–Cole plot are shown.

The comparison of $\varepsilon'(f, T)$ dependences of electron-irradiated PVDF and non-irradiated P(VDF/TrFE)(75/25) (Figs 7 and 9) indicates that the effect of introduction of units with dipole moment lower than that of the VDF into the PVDF chain is similar to that of electron irradiation. Radiation-induced modification of the dielectric response of the P(VDF/TrFE)(75/25) copolymer, shown also in Fig. 9, consists in further decrease and broadening of the permittivity maximum and lowering of the Curie temperature. Dielectric relaxation of P(VDF/TrFE)(75/25)

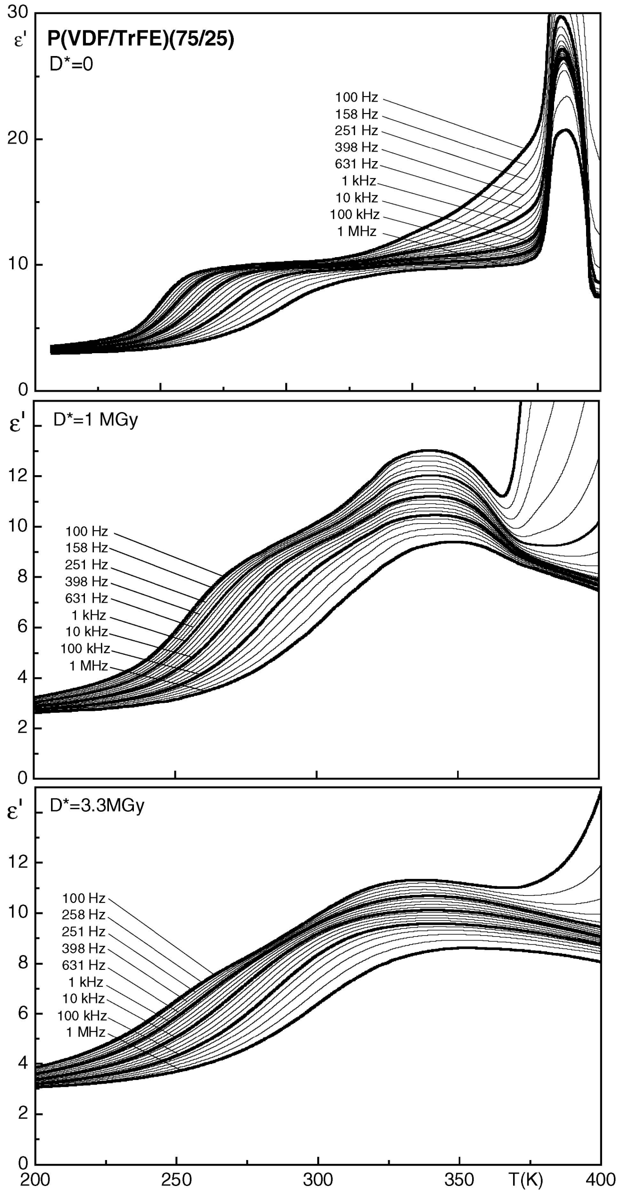


Figure 9 $\varepsilon'(T, f)$ dependences of non-irradiated P(VDF/TrFE)(75/25) film and the copolymer films irradiated at 420 K with various doses D^* of 1 MeV electrons.

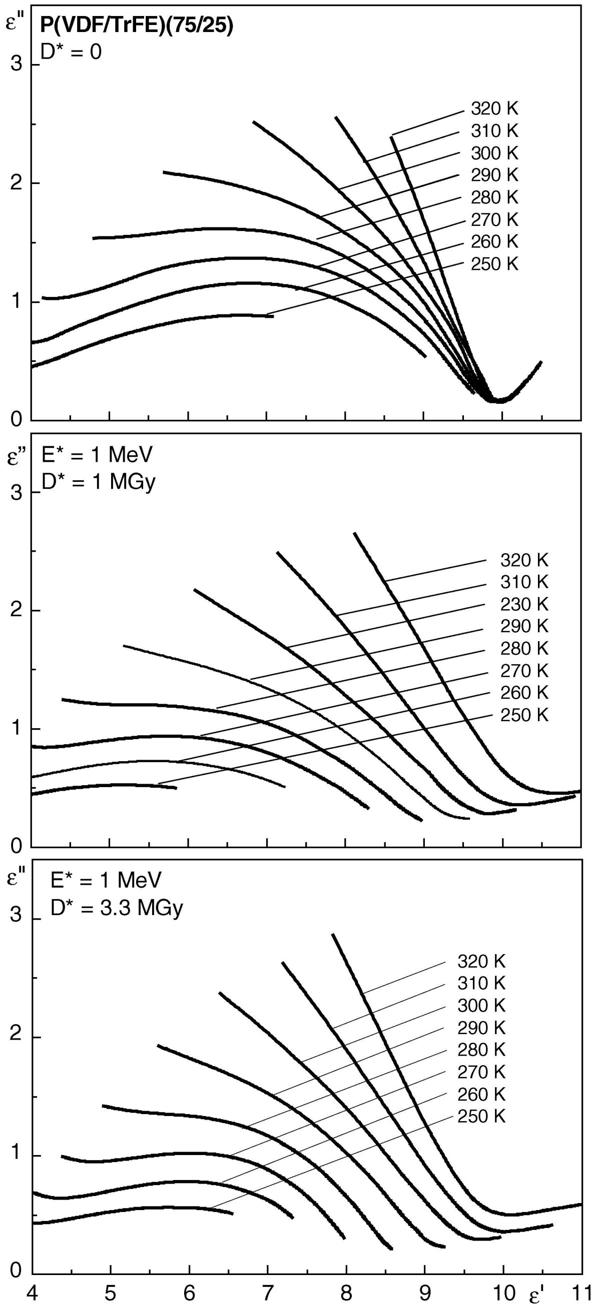


Figure 10 Cole-Cole plots for non-irradiated P(VDF/TrFE)(75/25) film and the copolymer films irradiated at 420 K with various doses D^* of 1 MeV electrons.

copolymer samples are well described by the Cole-Cole relation in the low temperature range, as shown in Fig. 10.

Dielectric anomaly related to the ferroelectric-paraelectric transition appears in radially-oriented P(VDF/TrFE)(50/50) film at ∼342 K, i.e., close to the glass transition anomaly, thus electron irradiation, even with low doses, results in a diffuse and dispersive dielectric response, characteristic of ferroelectric relaxors (Fig. 11). Radiation-induced changes in temperature dependence of the real and imaginary part of the permittivity of P(VDF/TrFE) copolymers are clearly visible in Fig. 12. Dielectric anomalies related to the glass transition and the ferroelectric–paraelectric transition merge in a broad maximum for P(VDF/TrFE)(50/50) irradiated with 1 MeV electrons using the dose as small as 0.75 MGy, whereas a single broad permittivity maximum appears in P(VDF/TrFE)(75/25) after irradiation with the dose of 3.3 MGy. Our results indicate that much lower doses of irradiation are needed to achieve relaxor-like dielectric response with high permittivity values for copolymers with higher intrinsic statistical disorder (for the (50/50) copolymer the dose $D^* \approx 0.75$ MGy, whereas for (75/25) the dose $D^* \approx 3$ MGy).

Changes in temperature variation of the relaxation times τ obtained from $\varepsilon''(f, T)$ dependences measured for P(VDF/TrFE)(75/25) irradiated with 1 MeV electrons are shown in Fig. 13. The solid lines represent the fits to the Vogel–Fulcher equation and the fitting parameters, B and T_{VF}, are plotted in Fig. 14 versus the dose of irradiation. The figure contains also the parameters obtained for PVDF and P(VDF/TrFE)(75/25) copolymer irradiated with 1.5 MeV electrons. The activation energy B of micro-

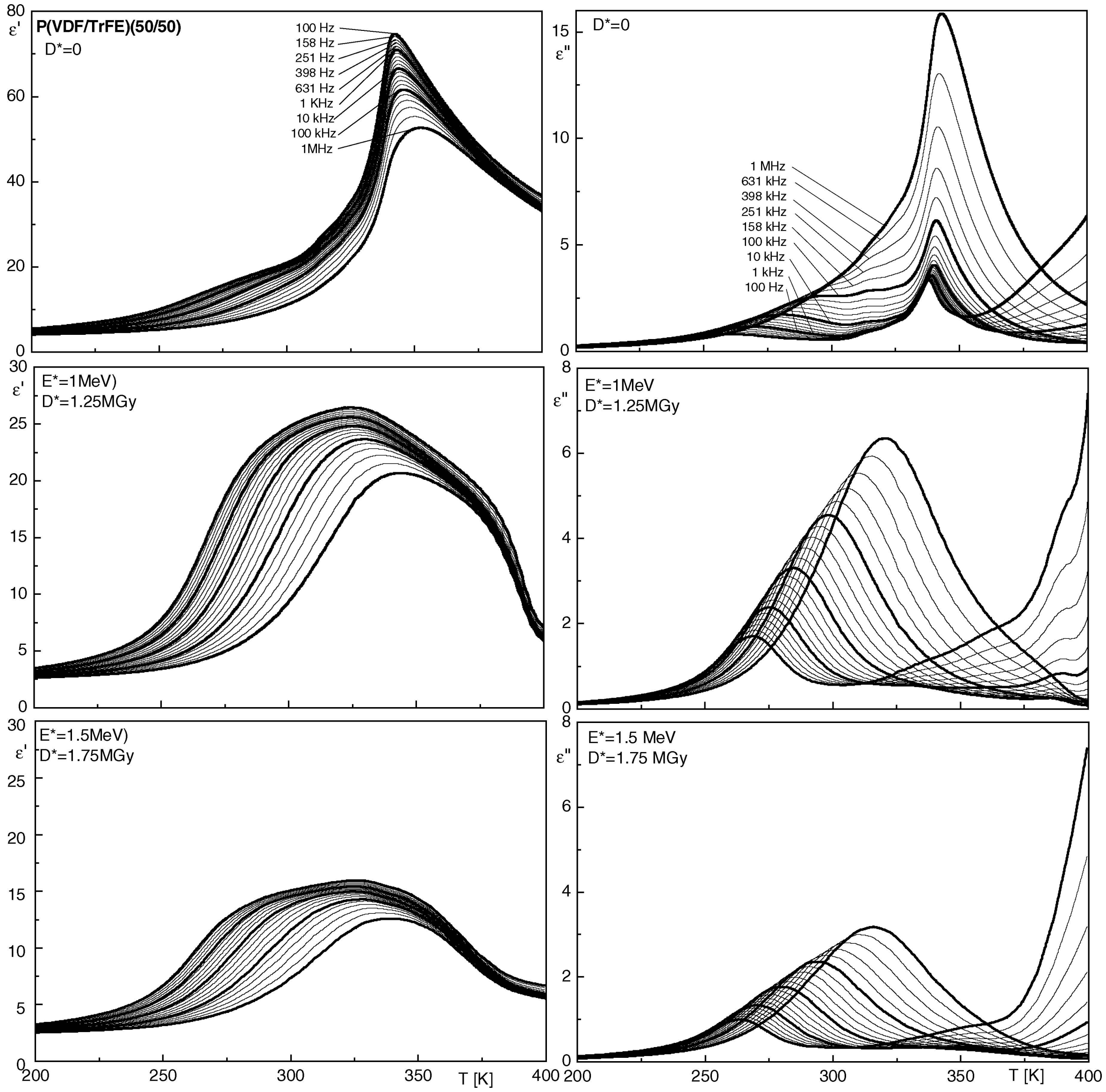


Figure 11 Dielectric response of P(VDF/TrFE)(50/50) copolymer, non-irradiated and after fast electron irradiation at $T^* = 300$ K.

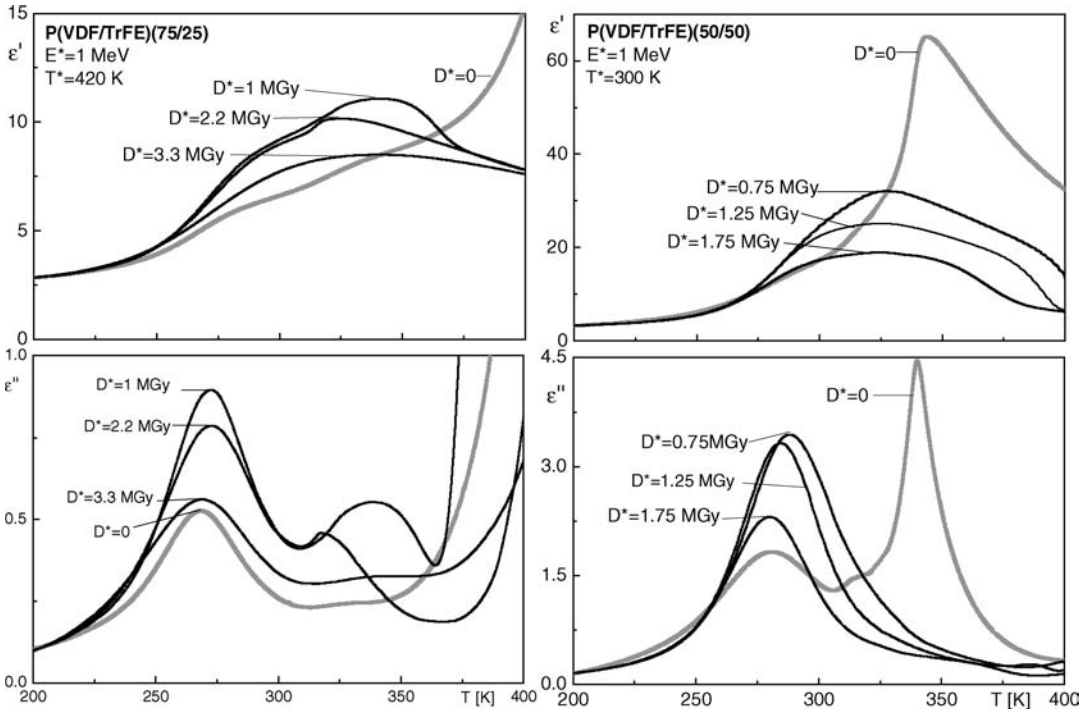


Figure 12 Temperature dependence of the real and imaginary part of dielectric permittivity measured at the frequency of 10 kHz for P(VDF/TrFE) copolymers irradiated with various doses D^* of 1 MeV electrons at various temperatures T^*.

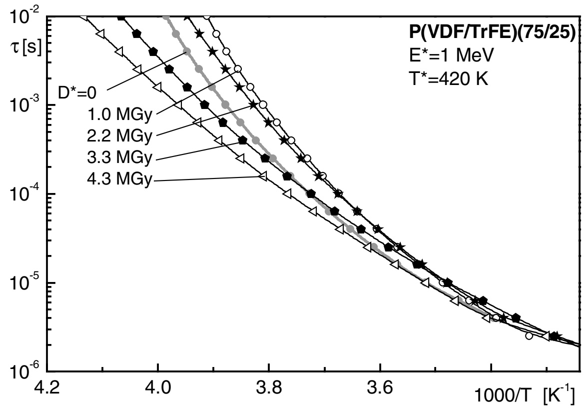


Figure 13 Dielectric relaxation times τ vs. the inverse temperature for P(VDF/TrFE)(75/25) irradiated at $T^* = 420$ K with various doses D^* of 1 MeV electrons.

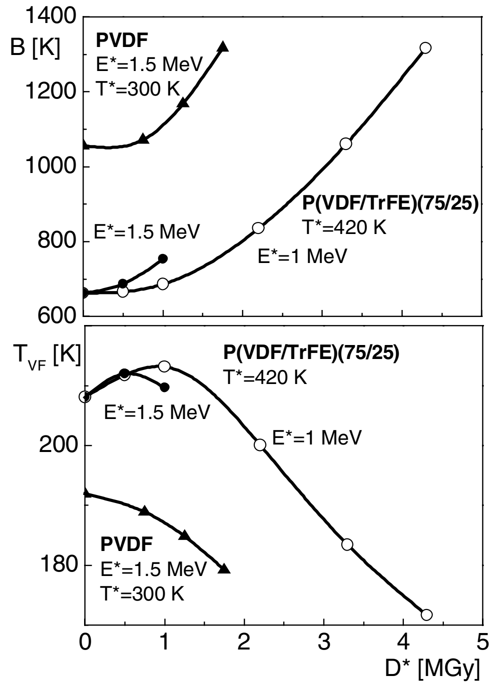


Figure 14 Dose dependences of the parameters B and T_{VF} obtained on fitting the temperature variation of dielectric relaxation times to Vogel–Fulcher equation for PVDF and P(VDF/TrFE)(75/25) irradiated with electrons of incident energy E^* at the temperature T^*.

Brownian dipolar motions in the amorphous phase of the copolymer increases and the static freezing temperature T_{VF} shifts towards lower temperatures for irradiation with doses higher than 1.5 MGy. However, it should be observed that the values of the parameters are affected by an overlapping of the Curie point dielectric anomaly with that of the glass transition and thus the radiation-induced changes in B and T_{VF} can be considered qualitative only. Moreover, the interpretation of the experimental data of samples irradiated above the Curie point is complicated due to the fact that heating the samples at temperatures in the ferroelectric–paraelectric transition region leads to conformational changes [8] and in consequence, changes in the dielectric response [24].

4. Conclusions

Dielectric response of semicrystalline PVDF-type ferroelectric polymers contains contribution of the response related to dipolar freezing in the amorphous phase and contributions of the local mode and changes from ferroelectric all-trans conformation to non-polar TGTG′ conformation in the crystalline phase. The aim of the paper was to show the way in which the dielectric response can be transformed in a single, diffuse and dispersive dielectric anomaly, characteristic of ferroelectric relaxors. The Curie point anomaly appears in PVDF at temperatures ∼150 K higher than the dynamic glass transition but the Curie point can be shifted downward by loading the planar zigzag chains with units having the dipole moment different than that of VDF [8, 14] or by introducing random field in form of radiation-induced defects [34–40]. It has been shown that relaxor-like dielectric anomaly can be obtained in P(VDF/TrFE) copolymers by fast electron irradiation [18–27] or by loading either with CTrFE or with CFE [15–17].

We studied modification of the dielectric response of PVDF and P(VDF/TrFE) copolymers by fast electron irradiation as well as radiation damage to the materials by ESR, IR and Raman spectroscopy. The results show that three processes are involved in electron-induced functionalization of the ferroelectric polymers. Fast electron irradiation in a Van de Graaff accelerator breaks the C–H, C–F and C–C bonds and creates various types of in-chain and end-chain alkyl radicals in the polymer films. Some of the radicals become oxygenated when the samples are transferred from the high vacuum of the accelerator into the air. The kinetics of formation and decay of alkyl and alkyl peroxy radicals is determined mainly by the VDF content in the sample and by the temperature and dose of irradiation. As the hydrogen fluoride is desorbed the decay of the radicals is accompanied by creation of isolated and conjugated C=C bond in the PVDF-type chain and polyenyl radicals with unpaired electron delocalized over several C=C linkage appear. Such defects as double C=C bonds, polyenyl radicals and non-polar TGTG′ conformations are sources of random field, which in the case of P(VDF/TrFE) copolymers adds to the random field due to intrinsic statistical disorder. Moreover, it should be observed that C=C bonds present in the polyvinylidene chains break the coherence of ferroelectric all-trans conformation into regions of shorter trans-sequences, which can be thought as polar nanoclusters.

The radiation-induced functionalization of the ferroelectric polymers of PVDF-type may be considered as consisting of two effects. The first one is similar to that observed in crystalline ferroelectrics [46] where the downward shift of the Curie temperature is related to a decrease in the density of ferroelectrically active dipoles and random field (defects) result in rounding and decrease of the Curie point anomaly. Thus the relaxor-like dielectric response with a single broad and dispersive anomaly appears in semicrystalline ferroelectric polymers as a result of defect-induced merging of the Curie point anomaly with the response of the amorphous phase. The second effect is related to a contribution of the response of polymer chain fragments with short trans coherence (polar nanoclusters) to the dielectric response of irradiated samples and causes an increase of the dielectric dispersion.

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