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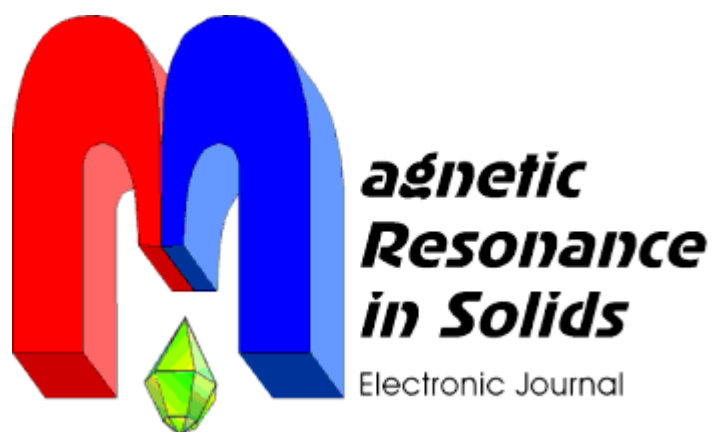
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X-band ESR of chemically dehydrofluorinated poly(vinylidene fluoride) films has been studied in the 150 ÷ 375 K temperature range. Dehydrofluorinated films reveal an ESR signal with g -factor close to that of the free electron. The ESR parameters (integral intensity, width, g -factor) of the samples depend on duration of the chemical reaction, storage conditions and temperature. Heating above 375 K modifies paramagnetic component of the samples stored in air irreversibly, probably, as a result of hydrogenous radicals desorption and/or removal of oxygen, hydroxyl groups and moisture from the samples on heating. The deviation from the Curie law has been revealed for all the investigated samples.

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Keywords: Electron spin resonance, poly(vinylidene fluoride), chemical dehydrofluorination

1. Introduction

Poly(vinylidene fluoride) (PVDF) is a polymer possessing a unique set of physical and chemical properties [1], which allow its numerous technical [2] and biomedical [3] applications. Various approaches to modify PVDF are presently known: chemical treatment, radiation exposure, electron and ion bombardment, etc. Specific properties of the modified polymer are governed by peculiarities of its chemical structure and morphology. For example, it was found that pretreatment of PVDF in alkaline solutions could promote grafting of polystyrene or other monomers to prepare proton exchange membranes [4]. The use of solid polymer surfaces as substrates to create on them nano- and pico-structures of carbon (including quasi-one-dimensional (1D) structures) can be considered as a promising route of modern nanotechnology. Quasi-1D carbon attracts special interest in both academic and practical aspects. On the one hand it may serve as a model substance for experimental probing of various theoretical predictions made in physics of low-dimensional systems. On the other hand it holds promise for potential applications in micro- and nanoelectronics and other fields (optics, medicine, etc.) [5-9].

The formation of nanostructured coatings on the polymer surface requires the development of special technologies. Chemical dehydrohalogenation of some halogen-containing polymers is known to be one of the most convenient and accessible methods of synthesizing conjugated polymers, including carbonyl materials based on quasi-1D carbon structures [10]. The interaction of PVDF with an alcoholic alkali solution results in the formation of a carbon-rich surface layer. Chemical dehydrofluorination leads to the formation of paramagnetic centres of different nature [11], and the task of identifying the nature of species being formed on the polymer surface is still pressing. The temperature dependence of paramagnetic susceptibility can provide important information about atomic and electron structure of these carbonized surface layers.

Ertchak et al. reported the first ESR studies of oriented carbonyl samples prepared by chemical dehydrofluorination of PVDF films. Two types of paramagnetic centres, denoted as C-M1 and C-M2, and an anisotropic broad line were detected. The spectrum of C-M1 is isotropic with g -value of 2.0045 ± 0.0003 . These species can be attributed to either free radical states or pinned quasi-particles similar to topological Su-Schrieffer-Heeger solitons. The ESR spectrum of C-M2 consists of a series of unsaturated anisotropic lines. The C-M2 centres are attributable to mobile quasi-particles (solitons in the spin density wave). It was found that the spin waves associated with C-M2 can be observed in samples heat treated at 120°C for 2 hours [11].

According to our previous study [12], the ESR intensity of dehydrofluorinated PVDF samples increases with duration of chemical treatment. The ESR intensity decreases during the storage of samples in air, whereas its most essential drop occurs within several days after synthesis. Then intensity becomes almost constant thus suggesting the structure stabilization.

This paper reports the results of experimental study of the temperature dependence of ESR absorption in chemically carbonized PVDF (*Kynar*) films.

2. Experimental technique

Partially crystalline PVDF films (*Kynar 720*^{*}) ca. $50\ \mu\text{m}$ thick were used as a precursor. The films were treated with a dehydrohalogenating mixture consisting of a saturated (20%) KOH solution in ethanol and acetone (in a 1:9 volume ratio) at room temperature for 3 and 12 hours. Immediately upon synthesis the samples were washed with ethanol, distilled water, acetone, and dried under reduced pressure.

Two sample series were studied. The list of the samples, duration of their chemical dehydrofluorination, storage conditions and reference designations are given in Table I. After preparation all samples were stored at room temperature in darkness. A part of them was stored in air; the others were put in glass tubes just after synthesis, evacuated, and stored under reduced pressure of ca. 1 Pa. Samples 1C, 2C and 2D were heat treated at 393 K for 1 hour in a month and more after the synthesis.

Table I. Description of the samples studied.

Series number	Duration of chemical treatment	Storage conditions	Sample designations	Notes
1	3 hours	air	1A	
		vacuum	1B	
		air	1C	heating
2	12 hours	air	2A	
		vacuum	2B	
		air	2C	heating
		vacuum	2D	heating

ESR measurements were performed using an *ESP 300 Bruker* ESR spectrometer operating at X-band microwave frequencies with 100 kHz magnetic modulation using a TE₁₀₂ cavity. ESR spectra were recorded at different

* Kindly donated by Atofina (since 2004 Arkema, France).

temperatures (the widest temperature range was 120-375 K) repeatedly with increasing and decreasing temperature. All temperature dependencies were measured not earlier than in 25 days after the synthesis.

3. Results and discussion

Pristine PVDF gives no ESR signal. Dehydrohalogenated films reveal an ESR absorption with g -factor close to that of free electron. The spectra of treated samples differ in width, intensity, g -factor, and have the Lorentzian-like shape at room temperature. The spectrum parameters (width and g -factor) for all samples are presented in Table II.

Table II. The spectrum parameters for all the samples at room temperature

Sample ^a	1A	1B	1C	2A	2B	2C	2D
Width, G	15.5	14.1	10.2	13.1	20.4	10.6	17.9
g -value ^b	2.0036	2.0031	2.0035	2.0035	2.0030	2.0036	2.0031

^a See Table I for details; ^b All g -factor values were measured with an accuracy of ± 0.0001 .

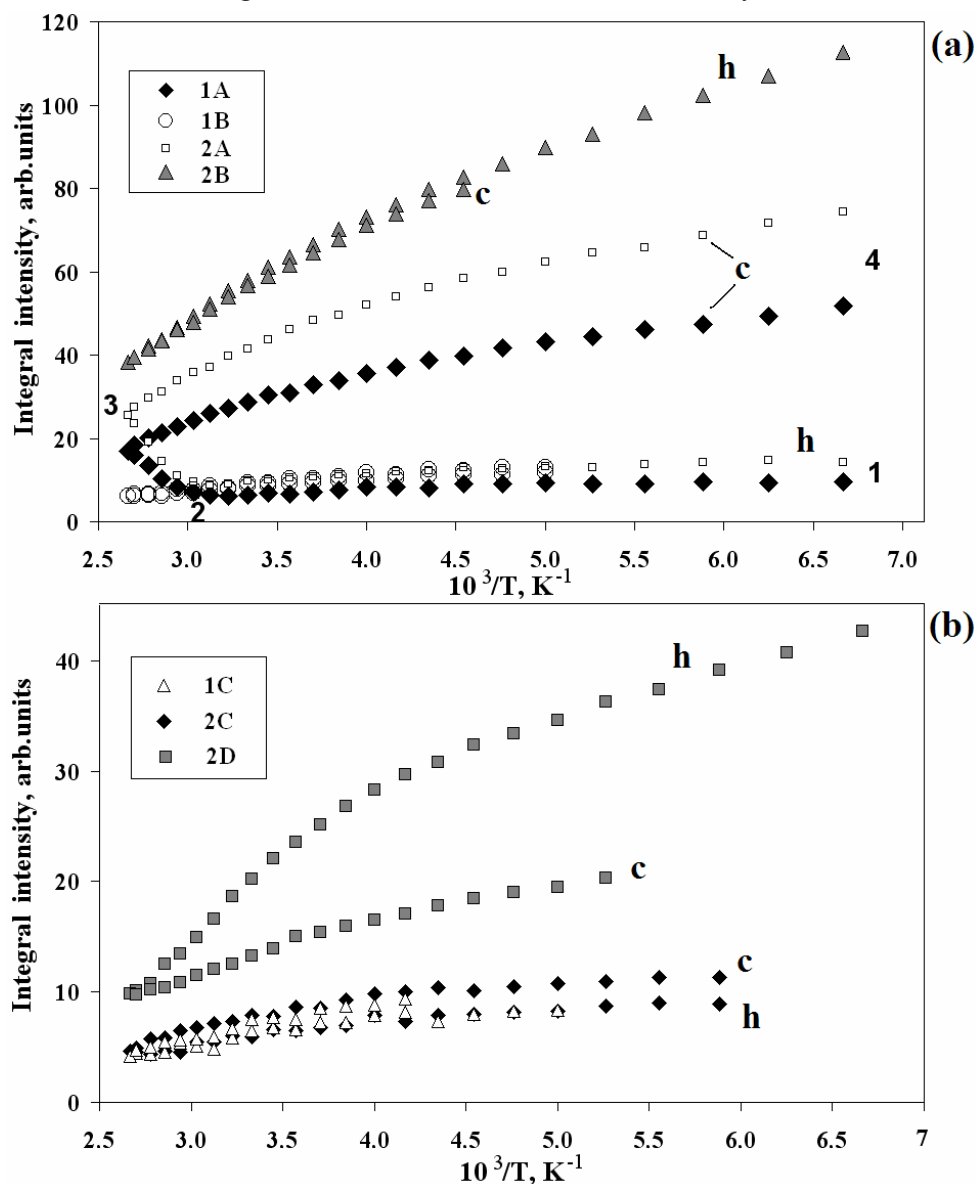


Fig. 1. Temperature dependencies of the ESR integral intensity for the samples studied. Letters “h” and “c” denote correspondingly heating and cooling in this and the following figures. Numbers 1-4 denote three regions of the heating-cooling cycle: heating from 150 to 320 K (region 1–2), heating from 320 to 375 K (region 2–3), and cooling from 375 to 150 K (region 3–4).

One can see from the data presented in Table II that ESR parameters of the samples kept in air differ from those kept under reduced pressure. The value of g -factor is lower in samples 1B and 2B. The spectrum width of sample 1B is smaller than that of 1A, but the spectrum of sample 2B is broader than 2A. Additional thermal treatment at 393 K for 1 hour (samples 1C, 2C and 2D) leads to narrowing of the ESR line and it does not change g -value.

Figure 1 shows the temperature dependencies of the ESR integral intensity. This parameter was measured using a double integration routine. For the sake of convenience the overall heating-and-cooling cycle of the samples kept in air

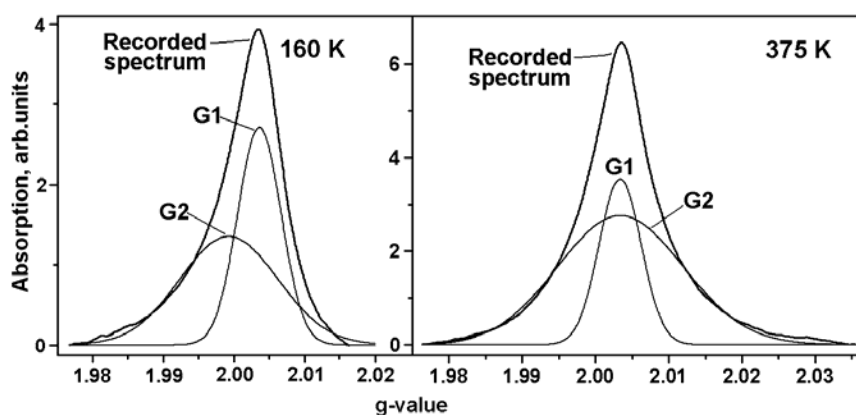


Fig. 2. ESR spectra of sample 1A at 160 and 375 K recorded on heating and their expansion into two Gaussians *G1* and *G2*.

(Fig. 1a) can be divided into three parts: heating from 150 to 320 K, heating from 320 to 375 K and cooling from 375 to 150 K. The paramagnetism of these samples decreases on heating from 150 to 320 K (region 1–2 in Fig. 1a), whereas on heating above 320 K (region 2–3) it increases. On cooling down (region 3–4) the ESR intensity increases again and the rate of this variation becomes higher than in the 1–2 temperature range. These effects are more pronounced in the second sample series. The ESR parameters before and just after recording the

temperature dependence were found to change greatly. For example, the intensity and the width of the spectrum of sample 1A at room temperature increase by 73 and 20%, respectively.

The ESR peak for samples 1A, 2A, 1C, 2C is asymmetric at low temperatures. Therefore the spectra were expanded into two Gaussians (Fig. 2). For other samples kept in air the temperature dependencies of the Gaussian parameters are qualitatively the same. The area, width and the peak position (*g*-value) of the Gaussians were measured at different temperatures.

The temperature dependencies of the peak area are similar for both Gaussians, they differ in the rate of variations. Figure 3a shows the temperature dependence of the *G1* and *G2* peak area. On heating from 150 to 320 K the area decreases twofold for *G1* and by a factor of 1.5 for *G2*. On heating above 320 K this parameter grows ca. 2.5 times for *G1*, whereas the *G2* peak area increases ~4-fold. On cooling down the values rise 3- and 3.5-fold for *G1* and *G2*, respectively. The areas of both Gaussians were close to each other before recording of the temperature dependencies.

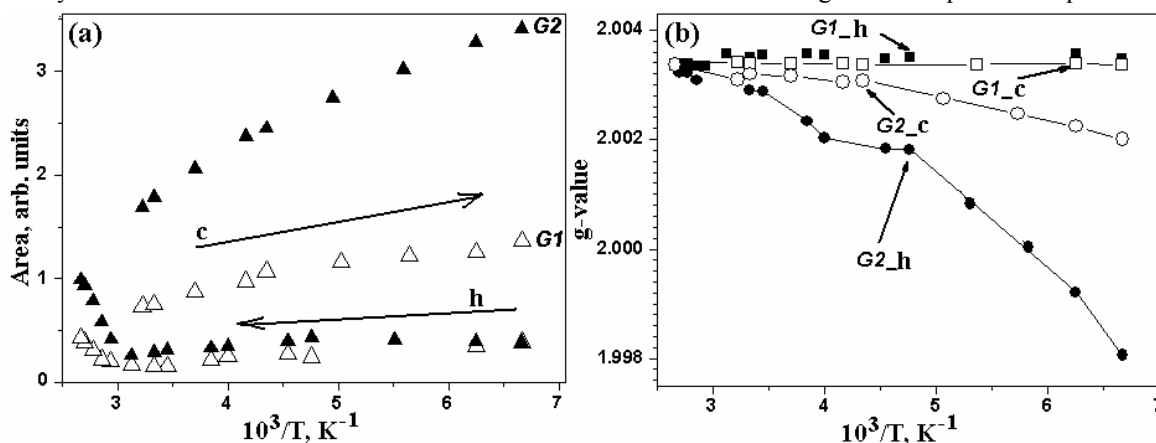


Fig. 3. Temperature dependencies of the area (a) and *g*-factor (b) for *G1* and *G2* in sample 1A.

The width of *G1* remains constant (9.5 ± 0.5 G) within the whole temperature range. The *G2* width value was found to be 23.7 ± 1.3 G on heating from 150 to 320 K. On heating to 375 K it monotonously increases up to 29.0 ± 0.4 G and remains constant on cooling down. The *g*-value of *G1* was 2.0035 on heating from 150 to 320 K, it decreased to 2.0034 on heating up to 375 K, and did not change on cooling down (Fig. 3b).

The ESR parameters of sample 1A stored in darkness at room temperature were found to keep changing. The intensity and the width decreased by 54 and 28%, respectively, within the first 20 hours, and by 5 and 3% during the following 30 hours. Thus, during the storage of samples the ESR parameters tend towards original values that were measured before the heating-cooling experiments. Nevertheless, after each heating run the material was found to modify irreversibly. As one can see from Fig. 4 the difference between the ESR intensity before and after heating at the same temperature becomes smaller. The heating at 393 K for 1 hour prior to measurements eliminates the hysteresis effect. The temperature dependencies of samples 1C and 2C on heating and cooling were found to nearly replicate (Fig. 1b).

For sample 1C the spectrum width was measured to be 10.4 ± 0.4 G and it changed neither on heating nor on cooling. The *g*-value monotonously increased while heating and decreased while cooling, it was found to be 2.0034 at 200 K and 2.0036 at 375 K.

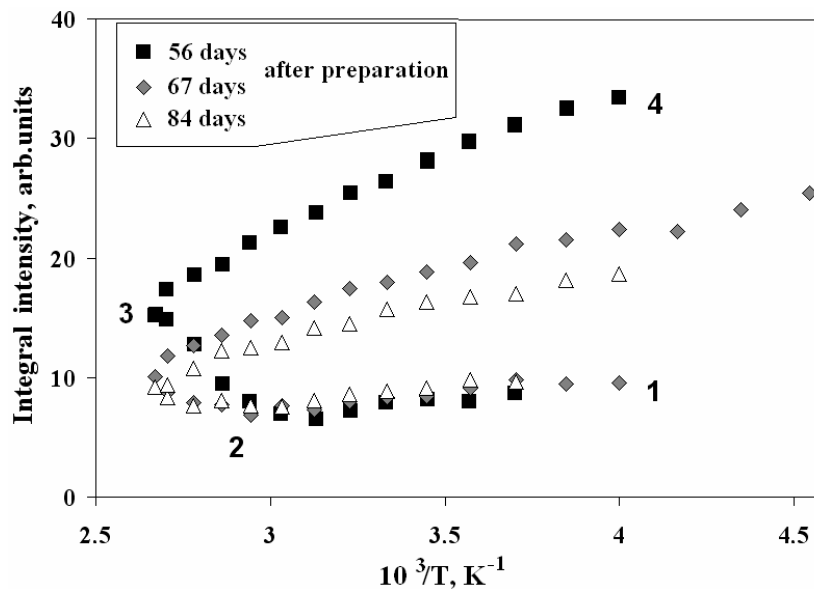


Fig. 4. Temperature dependences of the ESR integral intensity for sample 1A in 56, 67 and 84 days after its preparation.

Probably, the observed phenomena of decrease (Fig. 4) or almost complete elimination of the hysteresis effect (Fig. 1b, samples 1C and 2C) might be caused by removal of oxygen, hydroxyl groups and moisture from the samples on heating.

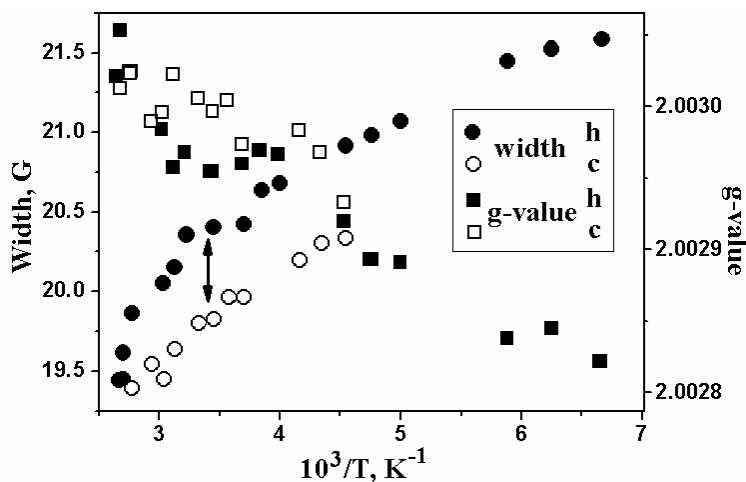


Fig. 5. Temperature dependence of the spectrum width and g-value for sample 2B.

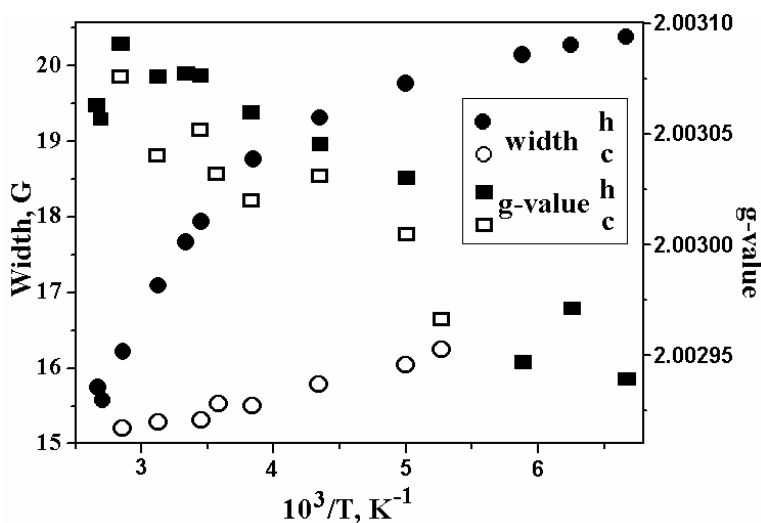


Fig. 6. Temperature dependence of the spectrum width and g-value for sample 2D.

Paramagnetism of samples 1B and 2B kept in vacuum was lower at higher temperatures within the whole temperature range. The temperature dependence of ESR in sample 2D additionally heated in vacuum was different: the heating curve is located above the cooling one (Fig. 1).

The spectra of samples 1B, 2B and 2D show the Lorentzian-like shape within the whole temperature range. The g-factor value increased on heating and decreased on cooling. Conversely, the spectrum width decreased on heating and increased on cooling. The dependence of the spectrum width and g-value on temperature for sample 2B is shown in Fig. 5. The sample 1B qualitatively showed the same pattern. The width and g-factor values in 1B were, respectively, 14.7 G and 2.0031 at 200 K before heating, and 13.3 G and 2.0032 at 375 K. The temperature dependencies of the spectrum width and g-value for sample 2D are shown in Fig. 6.

The temperature dependencies of the ESR intensity revealed deviation from the Curie law in all the samples studied (Fig. 1).

Our qualitative interpretation of the experimental results is based on ideas evolved in studies of chemical dehydrofluorination of PVDF [e.g. 9]. The interaction of the polymer with alcoholic alkali solution results in the successive elimination of hydrogen and fluorine atoms from the polymer chain to yield a fluorine-substituted polyene structure. Further elimination brings about the formation of nanofragments of linear carbon chains in various configurations. Side

reactions such as nucleophilic substitution of fluorine atoms by ethoxy-groups may also occur. The g -factor in the observed ESR spectra is close to that of π -radicals in linear π -conjugated polymer *trans*-polyacetylene (2.0026). Such position of the ESR signal can be associated with a system of unpaired π -electrons delocalized over conjugated fragments [13-15]. Presumably, the main mechanism for the formation of these paramagnetic centers can be an inter- and/or intramolecular transfer of electrons to the sites of impurities and/or lattice damage localization [16]. Free radicals also reveal g -factor close to that of free electron (2.0023). The emergence of the ESR signal in chemically treated PVDF suggests the formation of free radicals during dehydrofluorination. Presumably, the paramagnetic centers observed are carbon-centered radicals containing hydrocarbon groups and/or fluorine atoms. Some of radicals become oxygenated in the air and, for example, peroxide radicals ($-\text{CH}_2\text{-CF}(\text{OO})\text{-CH}_2-$) can be formed. The ESR spectra are described as composed of one or more types of radicals mentioned above as well as long-life polyenyl ($-\text{CH}_2\text{-(CF=CH)}_n\text{-C}^{\cdot}\text{F-CH}_2-$) radicals with free electrons delocalized over several C=C bonds [17-19].

Thus, the observed ESR absorption can be associated with a system of unpaired electrons delocalized over conjugated fragments and/or with free radicals, which may appear due to oxidation reactions and some secondary transformations of the π -conjugated structures formed on the polymer surface during and after chemical dehydrofluorination.

Probably, water vapor adsorbed on the material surface as well as hydrogenous radicals might be of considerable importance. In this case heating to 370 K and above may change the paramagnetic component of the material as a result of H-radicals desorption. The ESR spectrum shape may also modify (see, for example, Fig. 6).

4. Conclusions

The absence of the ESR signal in pristine PVDF and increase of its intensity in dehydrofluorinated PVDF samples with duration of chemical treatment show that ESR technique is useful for the investigation of PVDF carbonization.

The ESR parameters of chemically dehydrofluorinated derivatives of PVDF depend on ambient and heat treatment temperatures and duration of the chemical reaction. The hysteresis effect is inherent in the ESR parameters of the samples kept in air. Heating above 375 K modifies paramagnetic properties of these samples irreversibly eliminating the hysteresis effect. Moreover in the samples stored in vacuum temperature variations of the ESR intensity while heating and cooling were found to be very close to each other. The deviation from the Curie law has been revealed in all of the investigated samples.

The observed ESR absorption can be associated with a system of unpaired electrons delocalized over conjugated fragments and/or with free radicals, which may appear due to oxidation reactions and some secondary transformations of the π -conjugated structures formed on the polymer surface during and after chemical dehydrofluorination.

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References

1. Jungnickel B.-J., in *Polymeric Materials Encyclopedia*, edited by J.C. Salamone (CRC Press, Boca Raton, 1996) **9**, 7115.
2. *Ferroelectric polymers: chemistry, physics and applications*, edited by H.S. Nalwa (Marcel Dekker, New York, 1995).
3. Laroche G., Marois Y., Guidoin R., King M.W., Martin L., How T., Douville Y. *J. Biomed. Mater. Res.* **29**, 1525 (1995).
4. Zhang S., Shen J., Qiu X., Weng D., Zhub W. *J. of Power Sources* **153**, 234 (2005).
5. *Carbyne and Carbynoid Structures*, Eds. R.B. Heimann, S.E. Evsyukov, L. Kavan. (Kluwer Academic Publishers, Dordrecht, the Netherlands, 1999).
6. Kudryavtsev Yu.P., Heimann R.B., Evsyukov S.E. *J. Mater. Sci.* **31**, 5557 (1996).
7. Babaev V.G., Guseva M.B., Savchenko N.F., Khvostov V.V., Bugrov S.G. *Poverhnost'. Rentgenovskie, sinhrotronnye i nejtronnye issledovaniya* **3**, 100 (2005) (in Russian).
8. Babaev V., Guseva M., Khvostov V., Novikov N., Flood P., in: *Polyynes: Synthesis, Properties, and Applications*, edited by F. Cataldo (CRC Press, Boca Raton, 2005) p. 219.
9. Babaev V.G., Khvostov V.V., Guseva M.B., Savchenko N.F., Belokoneva Yu. *Poverhnost'* **5**, 89 (2007) (in Russian).
10. Evsyukov S.E., in: *Polyynes: Synthesis, Properties, and Applications*, edited by F. Cataldo (CRC Press, Boca Raton, 2006) p. 253.

11. Ertchak D.P., Kudryavtsev Yu.P., Guseva M.B. Alexandrov A.F., Evsyukov S.E., Babaev V.G., Krechko L.M., Koksharov Yu.A., Tichonov A.N., Blumenfeld L.A., Bardeleben H.J. *Journal of Physics: Condensed Matter*, **11(3)**, 855 (1999).
12. Pesin L.A., Khayrullina N.A., Evsyukov S.E., Shvachko J.N., Fedij A.A. *Proc. of the IX Int. Youth Scientific School "Actual problems of magnetic resonance and its application"*, edited by M.S. Tagirov (Kazan, 2005) p. 104.
13. Berlin A.A. *Journal of Polymer Science* **55**, 621 (1961).
14. Lewis I.C. *Carbon* **20**, 519 (1982).
15. Lebedev Yu.A. *Pisma v ZhTF* **30**, 72 (2004).
16. Blumenfeld L.A., Benderskiy V.A., Lyubchenko V.A., Stunzas P.A. *Zhurnal strukt. khimii* **8**, 829 (1967) (in Russian).
17. Goslar J., Hilczer B., Smogór H. *Acta Polonica A* **108**, 89 (2005).
18. Le Moël A., Duraud J.P., Lemaire I., Balanzat E., Ramillon J.M., Darnez C. *Nuclear Instruments and methods in Physics Research B* **19/20**, 891 (1987).
19. Adem E., Burillo G., Munoz E., Rickards J., Cota L., Avalos-Borja M. *Polymer Degradation and Stability* **81**, 75 (2003).