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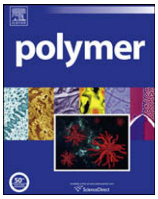

Energy storage study of ferroelectric poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) terpolymers

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A series of P(VDF-TrFE-CTFE)s were synthesized via a well-controlled chemical route including VDF/CTFE copolymerization and dechlorination of P(VDF-CTFE)s to convert CTFE units into TrFE units. The microstructure and properties of the terpolymers were characterized and tested with differential scanning calorimeter (DSC), NMR, dielectric constant and electric displacement–electric field (*D*–*E*) hysteresis loop. Thanks to the clean reaction system and ambient reaction condition of VDF/CTFE copolymerization and the hydrogenation of P(VDF-CTFE)s, the terpolymers obtained with high purity and uniformity exhibit a high electric breakdown field of over 500 MV/m, as a result, the highest energy density is obtained as 10.3 J/cm^3. Via comparing the structure and properties of terpolymers with different compositions and from different preparing processes side-by-side, the TrFE content and the method of TrFE introduced are found to strongly affect the microstructure of the materials and consequently the dielectric properties. The advantages including the lower cost of materials, convenience of the materials preparation and relatively lower energy loss make it possible to be employed as capacitor material.

1. Introduction

As the continuous increasing of energy requirement and exhausting of fossil fuels, improving efficiency of the energy usage becomes more and more urgent and important both in industry and academy as well as seeking new energy. Capacitors are the devices that could take the responsibility, which allow electrical energy to be stored over a long charging time and then released as required far shorter periods under controlled conditions. Polymer film, ceramic, electrolytic and mica were regarded as four classes of materials for the advanced capacitors, especially the polymer film was highly expected to obtain energy density as high as 20 kJ/kg in the future [1]. It is also presently the material choice for energy storage applications due to the relatively high energy density, high electric breakdown field, low dielectric loss, low cost, and graceful failure [2].

As one of the most important dielectric materials in polymers, poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene (TrFE) have attracted a lot of interests both in academy and industry due to their excellent piezoelectricity and pyroelectricity [3]. Especially, P(VDF-TrFE)s are well known ferroelectric polymers and widely used as electromechanical sensors and aculators [4]. Owing to the large remnant polarization, P(VDF-TrFE)s render a small energy density although the polymer displays a high saturation electric displacement (~0.1 C/m^2). Two effective ways are reported to reduce the remnant polarization including the proton irradiation [5] and defects introduction by inserting termonomer [6]. Comparing with the proton irradiation, the polymer prepared via introducing the third monomer such as chlorotrifluoroethylene (CTFE) and 1-chloro-2,2-difluoroethylene (CDFE) as defects possesses the advantages such as high material stability and uniformity and convenience of preparation. The terpolymers could dramatically improve the dielectric constant (from about 10 to 80 at 100 Hz) of the polymer at an ambient temperature and attracted a lot of research interests [7]. The recent energy storage study shows that these terpolymers could store much more energy under a lower electric field (~10 J/cm^3 under a field of 400 MV/m [3c,8], and >12 J/cm^3 at 500 MV/m [9]) than biaxially-oriented polypropylene (BOPP), which has the highest energy density (~2 J/cm^3 under a field of 600 MV/m) in the known polymers used as capacitors.

Comparing with the low-priced homo-polypropylene, two major problems of these terpolymers are concerned. Firstly, the composition of the terpolymers is difficult to control during the polymerization due to the different reaction rate of three different monomers, which is very sensitive to the energy storage. Secondly, the TrFE as comonomer is much more expensive and difficult to be obtained and transported, which would dramatically enhance the

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cost of final materials [10]. Recently, a more convenient chemical route [11] involving the VDF/CTFE copolymerization and partial hydrogenation of P(VDF-CTFE) to convert CTFE units into TrFE units is reported to synthesize this kind of terpolymers with similar structure and slightly lower dielectric properties. In this work, a series of well-controlled terpolymers with designed composition have been synthesized following this procedure and their properties are tested. By comparing the properties and structure of terpolymers with different compositions and from different preparing processes, it is found that the properties of the terpolymers are well dependent on the microstructure of the polymers, especially the TrFE content and how the TrFE units are introduced.

2. Experimental section

2.1. Materials

Triethylboron (TEB) was purchased from Aldrich and used as-received. Tetrahydrofuran (THF) was dried and distilled from sodium benzophenone ketyl under nitrogen. VDF and CTFE were purchased from SynQuest Laboratory, Inc. TrFE was purchased from Halocarbon. All the gas is purified in a freeze–thaw process prior to use. All gas-condense transfer was carried out with rigorous exclusion of oxygen and moisture on a dual-manifold Schlenk line with 50 millitorr high vacuum. All the other chemicals were obtained from commercials and used as-received. All the polymers were prepared in a free-radical polymerization process initiated by TEB/O_2 system [12].

2.2. Preparation of P(VDF-CTFE)

The typical copolymerization was carried out in the following procedure: 0.3 mmol of TEB initiator together with 30 mL acetonitrile as solvent was added into a 75 mL stainless steel autoclave equipped with a magnetic stirrer in an argon-protected dry-box. The autoclave was then cooled by liquid nitrogen before vacuum distilling in certain amount of VDF and CTFE monomers. 0.4 mmol of oxygen was introduced into the autoclave to oxidize organoborane and initiate polymerization before the mixture was warmed to ambient temperature and stirred for 5 h. The resulting polymer was obtained by removing solvent under vacuum, subsequently purified by precipitating from the polymer solution in acetone with excess hexane and washing 3 more times with hexane, and finally dried in a vacuum oven at 70 °C for 8 h. The ^1H NMR (in acetone-d_6) was used to identify the structure of P(VDF-CTFE) as follows: 6.1–6.5 (t, 1H, $-CH_2\mathit{CF_2H}$), 2.6–3.6 (m, 2H, $-CF_2\mathit{CH_2}CF_2-$), 2.2–2.5 (m, 2H, $-CF_2\mathit{CH_2CH_2}CF_2-$), 1.8 (t, 3H, $-CF_2\mathit{CH_3}$), 1.3–1.6 (m, 2H, $-CF_2CH_2\mathit{CH_2}CH_3$), 0.9–1.1 (t, 3H, $-CF_2CH_2CH_2\mathit{CH_3}$). The P(VDF-CTFE)s composition could be conveniently calculated from ^{19}F NMR according to the method described in literature [13].

2.3. Preparation of P(VDF-TrFE-CTFE) from the post-polymerization process [14]

To a 100 mL three-necked flask was added P(VDF-CTFE) copolymers (2.0 g), AIBN (47.6 mg, 0.29 mmol), and then purged with vacuum and argon for 3 times before dry THF (40 mL) was injected and stirred for 30 min at 60 °C to make a homogeneous solution. Then tri(*n*-butyl)tin hydride (0.96 mL, 1.45 mmol) was injected into the mixture by syringe, and the solution was kept stirring at 60 °C for 12 h before it was quenched with methanol. The precipitate was dissolved into THF and stirred with aqueous potassium fluoride to remove the Tin byproduct before washed with hexane and dried under reduced pressure to yield 1.7 g of P(VDF-CTFE-TrFE)s as a white solid. The ^1H NMR (in acetone-d_6) was used to identify the structure of P(VDF-TrFE-CTFE) as follows: 6.1–6.5 (t, 1H, $-CH_2\mathit{CF_2H}$), 5.3–5.7 (m, 1H, $-\mathit{CFH}CF_2-$), 2.6–3.6 (m, 2H, $-CF_2\mathit{CH_2}CF_2-$), 2.2–2.5 (m, 2H, $-CF_2\mathit{CH_2CH_2}CF_2-$), 1.8 (t, 3H, $-CF_2\mathit{CH_3}$), 1.3–1.6 (m, 2H, $-CF_2CH_2\mathit{CH_2}CH_3$), 0.9–1.1 (t, 3H, $-CF_2CH_2CH_2\mathit{CH_3}$).

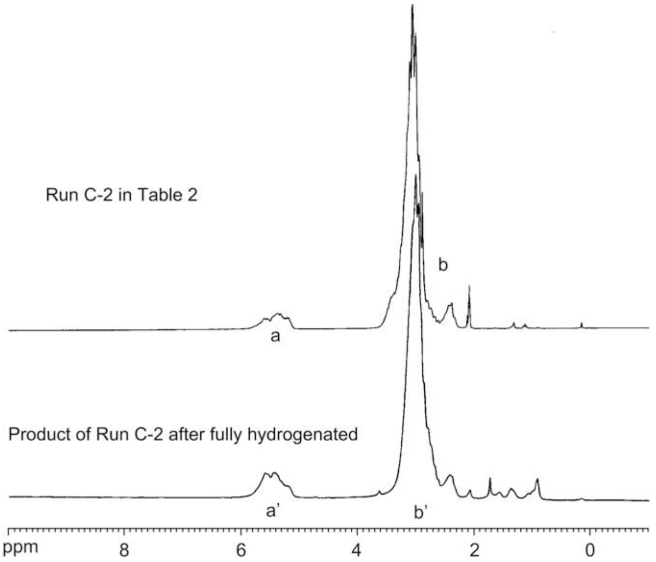


Fig. 1. ^1H NMR of terpolymer (Run 7 in Table 1) and its corresponding product after full hydrogenation.

Combining the ^1H NMR of P(VDF-TrFE-CTFE)s and the composition of the corresponding mother P(VDF-CTFE) copolymers, the composition of P(VDF-TrFE-CTFE)s from post-polymerization process could also be accurately determined as we reported previously [11].

2.4. Preparation of P(VDF-TrFE-CTFE) from direct-polymerization process

The terpolymerization of VDF, CTFE and TrFE was carried out following the same process as the procedure for copolymerization of VDF and CTFE as described above. The ^1H NMR (in acetone-d_6) was used to identify the structure of P(VDF-TrFE-CTFE) in follows: 6.1–6.5 (t, 1H, $-CH_2\mathit{CF_2H}$), 5.3–5.7 (m, 1H, $-\mathit{CFH}CF_2-$), 2.6–3.6 (m, 2H, $-CF_2\mathit{CH_2}CF_2-$), 2.2–2.5 (m, 2H, $-CF_2\mathit{CH_2CH_2}CF_2-$), 1.8 (t, 3H, $-CF_2\mathit{CH_3}$), 1.3–1.6 (m, 2H, $-CF_2CH_2\mathit{CH_2}CH_3$), 0.9–1.1 (t, 3H, $-CF_2CH_2CH_2\mathit{CH_3}$).

The composition of P(VDF-TrFE-CTFE)s form direct-polymerization process used to be calculated by combining the ^1H NMR and element analysis as reported in literature [6]. In this work, the

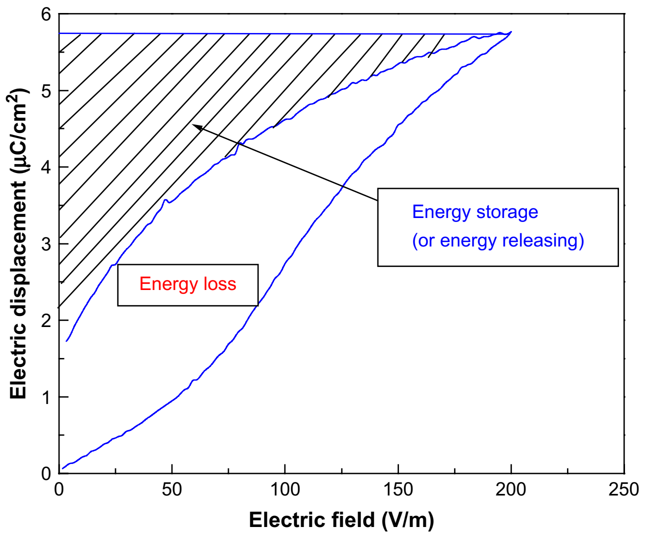


Fig. 2. A typical D–E loop of P(VDF-TrFE-CTFE) measured under unipolar electric field.

composition of direct-terpolymers were calculated via combining the molar ratios of VDF/TrFE (from the integrals of VDF and TrFE units on ^{1}H NMR (Fig. 1)) of P(VDF-TrFE-CTFE)s and P(VDF-TrFE)s (full hydrogenation product of corresponding P(VDF-TrFE-CTFE)s) by the following equations:

$$V_{\mathrm{VDF}}(\mathrm{mol\%}) = \frac{b'}{2a' + b'} \times 100\%$$

$$V_{\mathrm{TrFE}}(\mathrm{mol\%}) = \frac{2a \times \frac{b'}{b}}{2a' + b'} \times 100\%$$

$$V_{\mathrm{CTFE}}(\mathrm{mol\%}) = \frac{2a' - 2a \times \frac{b'}{b}}{2a' + b'} \times 100\%$$

where a, a' are the integrals of the TrFE units from ^{1}H NMR of P(VDF-TrFE-CTFE)s and their corresponding full hydrogenation products (P(VDF-TrFE)s), and b, b' are the integrals of all the VDF units from ^{1}H NMR of P(VDF-TrFE-CTFE)s and their corresponding full hydrogenation products (P(VDF-TrFE)s), respectively.

2.5. Characterization

^{1}H and ^{19}F NMR spectra were recorded on a Bruker AM-300 spectrometer instrument. The thermal transition data were obtained by a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min after a circle of quick heating (20 °C/min) and cooling (20 °C/min) to remove the thermal history. Size exclusion chromatography (SEC) was performed in a THF mobile phase with a Waters1515 isocratic pump. The dielectric constants of the polymers were acquired using an HP multifrequency LCR meter (HP 4284A) scanned at increasing temperature from 0 °C to 120 °C and at different electric frequency from 10 Hz to 1 MHz with a 1 V bias. The polymer films with 15–25 μm in thickness are obtained via casting their solution in acetone on a Teflon substrate followed by solvent evaporation at room temperature. The polymer films are annealed at 180 °C for 6 h then cooled to room temperature before peeled off from the substrate. The energy density storage and loss of dielectric materials could be calculated from the D–E loop measured by the traditional Sawyer–Tower circuit [15] under a unipolar electric field as shown in Fig. 2. Energy density discharged is equal to integral $U_e = \int E\mathrm{d}D$ (E is the electric field and D is the electric displacement) and energy loss is equal to integral of the area enclosed by charge and discharge curve and y-axis. U_l was calculated using the following equation:

$$U_1 = \int \left[D_{\mathrm{discharge}}(E) - \int D_{\mathrm{charge}}(E) \right] \mathrm{d}E = \int D_{\mathrm{discharge}}(E)\mathrm{d}E - \int D_{\mathrm{charge}}(E)\mathrm{d}E$$

E is the electric field, $D_{\mathrm{charge}}(E)$ and $D_{\mathrm{discharge}}(E)$ are the functions of electric displacement against electric field, which could conveniently calculated from the integral of discharge curve subtracted by the integral of charge curve along the electric field.

Table 1
Copolymerization results of VDF, CTFE and TrFE initiated with TEB/O_2.

Run	B/O_2 (mmol/mmol)	VDF/CTFE (mL)	TrFE (mL)	Time (h)	Conversion (%)	CTFE (%)	TrFE (%)	M_w(M_w/M_n)
A-1	2.4/2.0	25.0/5.0	0	0.25	2.3	27.5	0	N.A.
A-2	2.4/2.0	25.0/5.0	0	0.5	21.2	24.3	0	N.A.
A-3	2.4/2.0	25.0/5.0	0	0.75	40.1	23.2	0	N.A.
A-4	2.4/2.0	25.0/5.0	0	1.0	67.2	21.5	0	N.A.
A-5	2.4/2.0	25.0/5.0	0	2.0	88.7	19.1	0	N.A.
A-6	2.4/2.0	25.0/5.0	0	4.25	98.0	18.0	0	N.A.
B-1	0.3/0.4	25.0/1.5	0	4	26.4	8.0	0	48,300 (1.7)
B-2	0.3/0.4	25.0/2.5	0	4	29.8	12.0	0	42,700 (1.5)
B-3	0.3/0.4	25.0/2.0	0	3.5	24.4	16.0	0	39,800 (1.8)
B-4	0.3/0.4	25.0/4.0	0	3	31.6	19.6	0	38,700 (1.6)
B-5	0.3/0.4	25.0/5.0	0	3	34.7	23.0	0	N.A.
B-6	0.3/0.4	25.0/5.5	0	3	35.2	24.8	0	N.A.
B-7	0.3/0.4	25.0/8.4	0	2.5	29.7	31.4	0	N.A.
B-8	0.3/0.4	25.0/11.0	0	2.5	33.3	34.0	0	34,900 (1.9)
B-9	0.3/0.4	25.0/14.0	0	2.5	36.8	37.3	0	35,300 (1.6)
C-1	1.2/1.0	20.0/1.5	11.6	1	23.6	7.7	26.7	28,600 (1.8)
C-2	0.3/0.4	24.0/1.0	4.5	4	27.3	7.7	11.6	35,100 (1.5)

Reaction conditions: 30 mL acetonitrile as solvent, room temperature.

3. Results and discussions

3.1. Synthesis and characterization of the co- and terpolymers

In commercials, the fluoro polymers/copolymers are prepared in emulsion or suspension at elevated temperature initiated with free radical initiators [16]. The reaction temperature should be well controlled when thermal initiators are utilized due to the potential crosslinking of resulting polymer at elevated temperature in the present of free radicals, especially for the monomers containing chlorine, bromine or iodine atoms. Even during the hydrogenation process, the reaction temperature has to be carefully controlled to prevent the crosslinking of these polymers induced by AIBN [17] as well. At this point, the trialkylboron/O_2 initiator system possesses incomparable advantage, which could initiate the polymerization of fluoro monomers at ambient temperature as reported by us recently [12].

Initiated with triethylboron/O_2, P(VDF-CTFE)s with different compositions were prepared in acetonitrile solution and listed in Table 1. Although close reactivity ratios of VDF ($r_1 = 0.70$) and CTFE

Table 2
The composition and thermal properties of co- and ter-polymers.

Run	Mother polymer (g)	AIBN (mL)	$(Bu)_3SnH$ (mg)	VDF/TrFE/CTFE	T_c (°C)	T_m (°C)	ΔH (J/g)
B-9A	B-9 (1.5)	1.20	71.5	62.7/29.3/8.0	N.A.	106.8	13.1
B-9B	B-9 (1.5)	1.44	86.2	62.7/33.5/3.8	N.A.	133.3	19.3
B-8A	B-8 (1.5)	1.30	78.0	66.0/26.6/7.4	N.A.	124.8	15.6
B-8B	B-8 (1.5)	1.47	89.0	66.0/29.3/4.7	N.A.	133.3	17.6
B-7A	B-7 (2.0)	0.75	45.0	80.4/11.8/7.8	50.5	111.3	19.7
B-7B	B-7 (2.0)	0.96	47.6	80.4/14.8/4.8	70.8	128.5	25.6
B-2A	B-2 (1.5)	0.23	14.0	88.0/5.2/6.8	N.A.	144.1	34.5
B-1	B-1	N.A.	N.A.	92.0/0.0/8.0	N.A.	146.1	25.9
C-1	N.A.	N.A.	N.A.	65.6/26.7/7.7	23.8	123.6	21.0
C-2	N.A.	N.A.	N.A.	80.7/11.6/7.7	N.A.	119.2	29.2

Hydrogenation reaction conditions: 40 mL THF as solvent, at 50–60 °C, overnight.

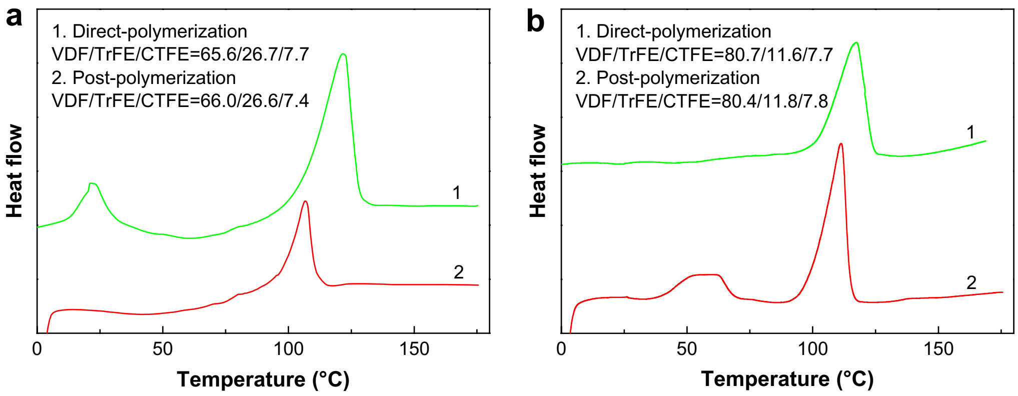


Fig. 3. Effect of preparing process on the thermal property of the terpolymers (a) terpolymers with a TrFE content about 27 mol%; (b) terpolymers with a TrFE content about 12 mol%.

($r_2 = 0.72$) in free radical polymerization at low conversion have been reported in the literature [18], more or less difference of the reactivity ratios could also lead to huge difference in resulting polymer compositions at different conversion with the same monomers ratio in feed. As shown in Table 1 from A-1 to A-5, the CTFE content of the copolymer decreases as conversion increases. This indicates that the effect of monomer conversion on the composition of resulting polymers, caused by the continuous concentration decreasing of the monomer with higher reactivity ratio, has to be considered especially at a higher conversion. In order to keep the polymers with well-controlled composition and distribution, the monomer conversions of all the copolymerization have been carefully controlled in 30–40% via altering the reaction time as shown in Table 1 from B-1 to B-9. All the conversions of terpolymers (C-1 to C-2) are controlled in 20–30% because of the bigger reactivity ratio difference of VDF and TrFE [19]. Via controlling the hydrogenation reaction, two series of terpolymers with about 8% and 4% of CTFE and variable content of TrFE from 5.2–33.5% were prepared and are listed in Table 2. For the sake of clear comparison, 2 typical direct-terpolymers C-1 and C-2 together with a P(VDF-CTFE) sample (B-1) are listed in Table 2 for the comparison study of all the properties.

3.1.1. *Thermal property*

As we reported previously [6], appropriate content of defects provided by CTFE could help to shift the Curie temperature of P(VDF-TrFE)s to ambient temperature. With the same content of VDF and in a certain range, the melting and Curie temperatures and crystallinity are increased with the increasing of TrFE content as shown in Table 2. It is well known that more TrFE units result in more all-*trans* conformation of β-phase than tttg$^+$tttg$^-$ conformation of γ-phase formed in the terpolymers. The phase transition of longer sequence β-phase needs more energy than the relative shorter sequence of γ-phase, which results in the higher melting and Curie temperature.

It is surprised to note that the preparing process exhibits great effect on the thermal properties of the terpolymers as well as the composition. The DSC curves of two pairs of terpolymers with close composition but from different preparing process are shown in Fig. 3. In most of the cases, the melting point and fusion value of direct-terpolymers are higher than that of the corresponding post-terpolymers with the same composition. With a higher TrFE content (27 mol%), the sample prepared from direct-polymerization process possesses a Curie temperature around 20–25 °C, and no obvious Curie temperature is found in the sample prepared from post-polymerization process. When the TrFE content is reduced to 12 mol% (Fig. 3(b)), the Curie temperature disappears in direct-terpolymer but appears in post-terpolymer at 60–70 °C. The same phenomenon has also been obtained in the dielectric constant measurement, which will be discussed later on. And all the results indicate that the different process might result in different microstructure of the polymer.

3.1.2. *Dielectric constant*

In general, the energy storage of dielectric materials could be estimated with the equation: $U_e = 1/2\varepsilon_0\varepsilon_r(V/d)^2$, where ε_0 is vacuum permittivity ($= 8.82 \times 10^{-12}$ F/m), ε_r is the dielectric constant and V/d is the electric field applied which is equal to the voltage applied divided by the thickness of film. Indicated by this equation, both the electric field and dielectric constant of material are directly related to the energy storage of material. Although the effective dielectric constant calculated from some fluoro polymers reported recently is not a real constant but continuously decreasing as the increasing of the electric field [3c]. The dielectric constant scanned under a low electric field at elevated temperature still could help to understand the energy barrier of ferroelectric–paraelectric transition (F–P transition) and the Curie temperature, which influence the energy storage as well as energy loss greatly. Following the previous report [11], a more detailed study of TrFE content on the dielectric constant against temperature at 1 kHz frequency is shown in Fig. 4. As the decreasing of TrFE content, the dielectric constant peak gradually shifts from about 40 °C to beyond 100 °C and the peak shape shifts from a broad flat into a narrow peak at about 90 °C and

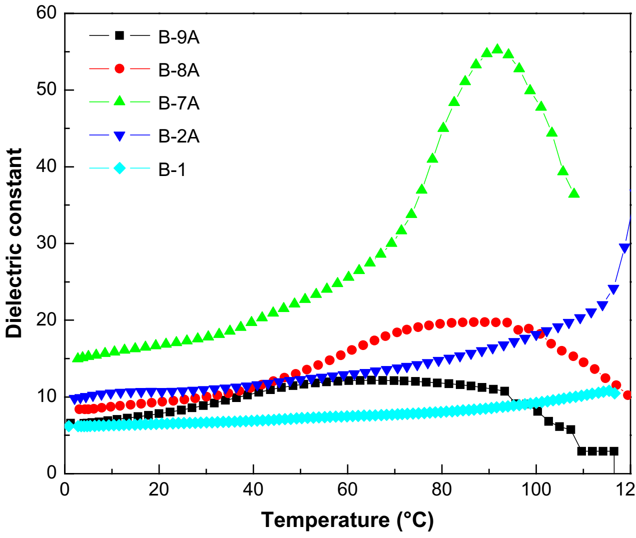


Fig. 4. Effect of composition on the dielectric constant as a function of temperature.

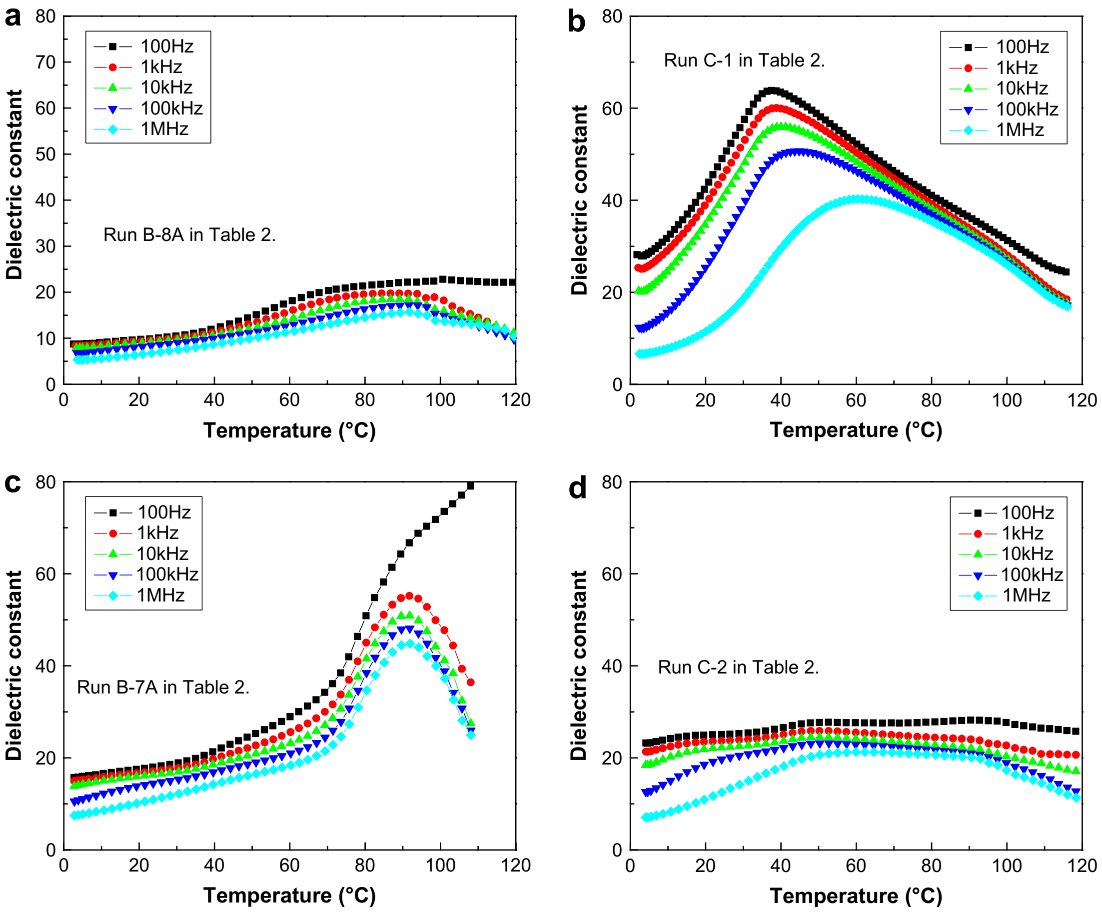


Fig. 5. Comparison of dielectric constant of terpolymers from different preparing process measured at different frequency as a function of temperature.

then broadens and fades gradually. With the increasing of TrFE content, the highest dielectric constant value appears in the sample with the composition of VDF/TrFE/CTFE = 80.4/11.8/7.8, which agrees very well with the results as we reported [11].

It is interesting to note that the dielectric constant spectrum obtained in two kinds of terpolymers (prepared from different process) with the same composition is completely different as shown in Fig. 5. With a composition around VDF/TrFE/CTFE = 65/27/8 the direct-terpolymer (Fig. 5(b)) possesses lower Curie temperature and higher dielectric constant peak value at Curie temperature than the terpolymer from hydrogenation (Fig. 5(a)). And if the composition is about VDF/TrFE/CTFE = 80/12/8, the Curie temperature of terpolymer from hydrogenation (Fig. 5(c)) shifts to 90 °C with a narrow peak of dielectric constant, while no obvious peak is obtained in the direct-terpolymer (Fig. 5(d)). The results agree well with the Curie temperature obtained from DSC curve and indicate the F–P transition of terpolymers prepared from different processes is totally different even the compositions are very close.

3.1.3. *D–E hysteresis loops*

It has been well studied that the P(VDF-TrFE)s possess relatively high displacement (about 0.1 C/m^2), but most of which is remnant polarization once the electric field is removed. That means this part

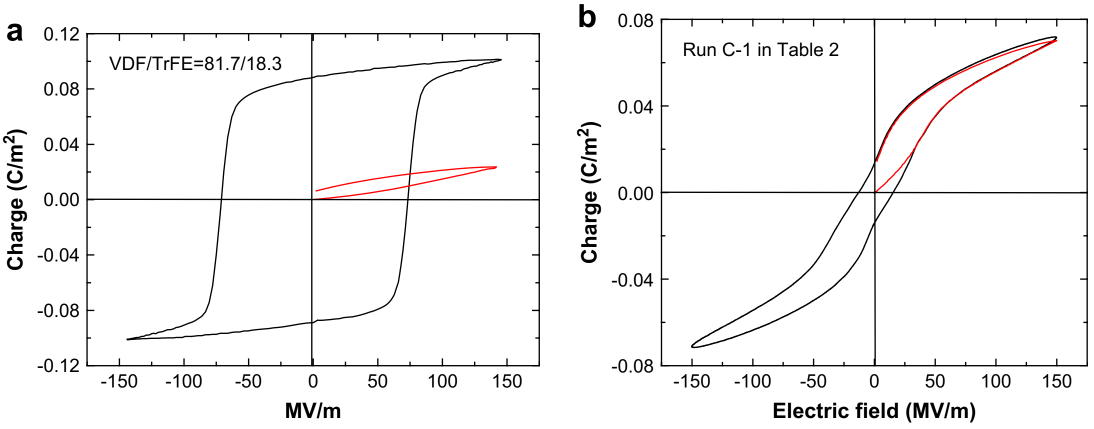


Fig. 6. The D–E hysteresis loops of P(VDF-TrFE) (a) and direct-P(VDF-TrFE-CTFE) (b) measured under uni- and dipolar electric field.

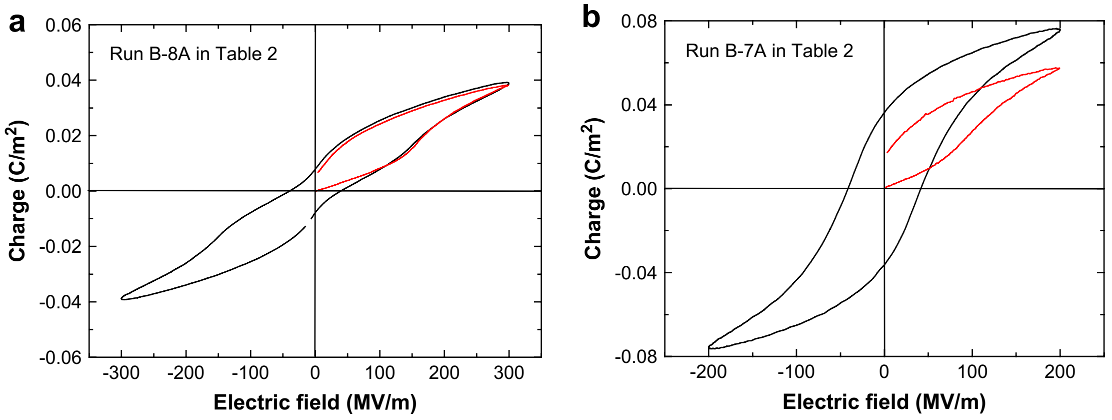


Fig. 7. The D–E hysteresis loops of post-terpolymers under uni- and dipolar electric field. (a) 2A in Table 1; (b) 3A in Table 1.

of polarization has no contribution to the energy storage if the materials are utilized as capacitors. As shown in Fig. 6(a), the D–E hysteresis loops of P(VDF-TrFE) measured under uni- and dipolar electric field could help to identify this part of polarization. Under unipolar electric filed, the displacement is quite low (0.02 C/m^2) comparing with which measured under dipolar electric field (0.10 C/m^2). That means about 80% of the polarization contributes nothing to the energy storage since this part of polarization could not reverse automatically unless an inverted electric filed applied. It was well known that the crystal size of P(VDF-TrFE) is so big that the polarization formed under electric field is trapped by the big crystal sheet, which means most of the polarization induced by electric field is not reversible. Our study [6] has shown that the introduction of termonomer containing chlorine atom could effectively reduce the crystal size and the crystals with reduced-size are easier to reverse. As a result, almost no remnant polarization is obtained in the resulting P(VDF-TrFE-CTFE)s, and the D–E curves under uni- and dipolar electric field coincide very well as shown in Fig. 6(b).

In the case of direct-terpolymers, it has been known that the TrFE units are controlling the conformation of crystal and about 30% of TrFE is efficient to keep the conformation in all-*trans* structure, which is favorable for the dipole aligning and reversing under electric field. The similar TrFE content effect was obtained in the post-terpolymers as shown in Fig. 7. When about 27% TrFE was introduced, the D–E loops of uni- and dipolar electric field coincide very well. A lower TrFE content (11%) is inefficient to keep well-organized conformation, and much more remnant polarization would be obtained and the remnant polarization under dipolar electric field was much higher than that measured under unipolar electric field.

TrFE content dominates not only the dielectric constant but also the polarization of the post-terpolymers. The D–E loops of post-terpolymers under unipolar electric field (400 MV/m) are given in Fig. 8(a). As TrFE decreases from 33.5% to 5.2%, the displacement is continuously enhanced from 0.04 C/m^2 to 0.09 C/m^2. In addition, if the D–E loops of post-terpolymers and direct-terpolymers are compared side-by-side as shown in Fig. 8(b), it is interesting to note that the displacement of direct-terpolymer is higher than that of post-terpolymer and higher the TrFE content, the more difference obtained, although the compositions are consistent. According to the calculation method presented in literature [20], the polarizations of P(VDF-TrFE)s are 0.103 C/m^2 (VDF/TrFE = 63/37) and 0.107 C/m^2 (VDF/TrFE = 80/20), and the close polarization values are expected in terpolymers with the same VDF content if the CTFE units are assumed to contribute the negative dipole moment in the same amount as TrFE units. The polarization of saturated direct-terpolymer (Run C-1 in Table 2) matches the calculation perfectly and indicates that the polarization (0.095 C/m^2) of the other direct-terpolymer (Run C-2 in Table 2) is not saturated. But for the terpolymers from post-polymerization process, the results obtained (0.059 and 0.086 C/m^2) are totally off the prediction although both of them are already saturated.

In order to give these interesting results a scientific explanation, more careful study of the polymers microstructure has been carried out by comparing the ^{19}F NMR of the two terpolymers (Run B-7A

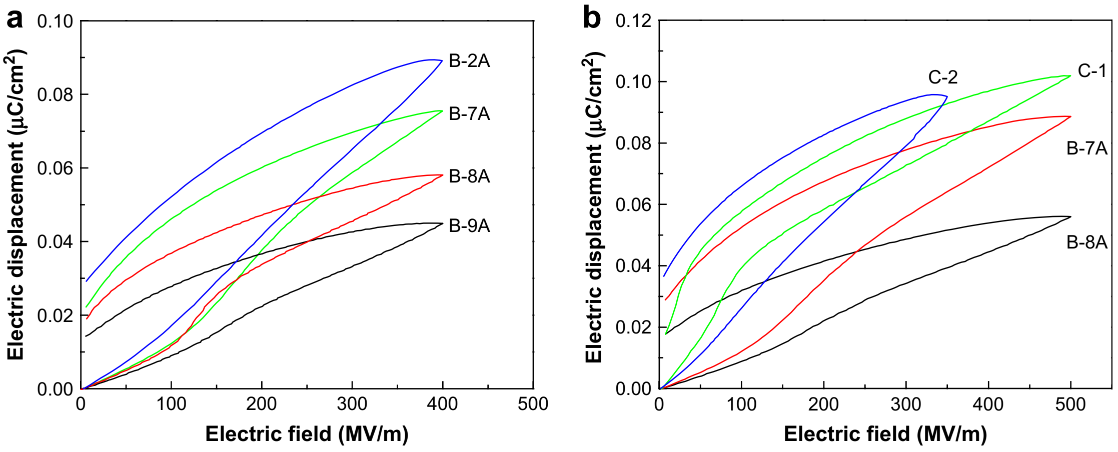


Fig. 8. D–E hysteresis loops of terpolymers under unipolar electric field (a) effect of TrFE content on D–E curves of post-terpolymers; (b) effect of preparing process.

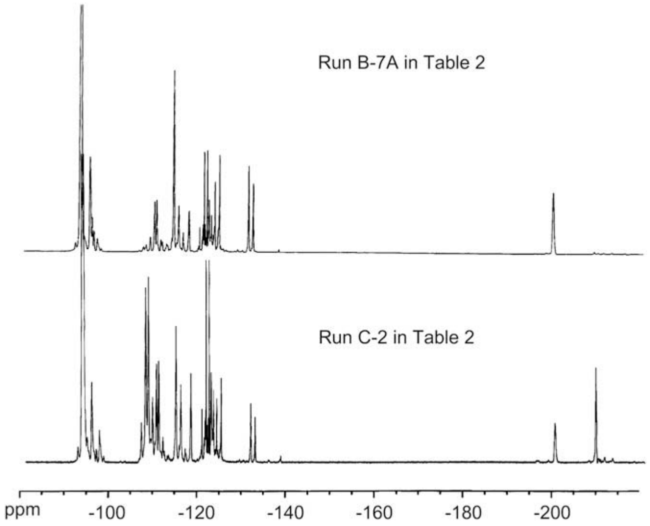
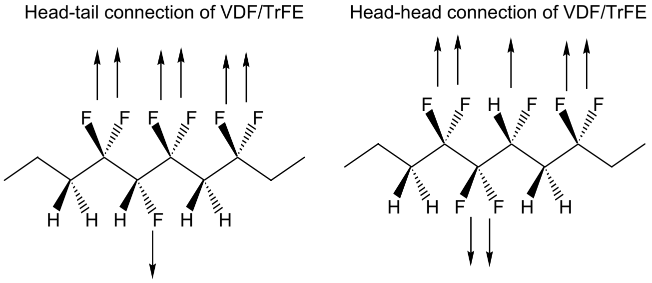


Fig. 9. ^{19}F NMR of terpolymers with same composition from different preparing process.



Scheme 1.

and Run C-2) as given in Fig. 9. The assignment of all the peaks in the spectra has been reported in literature [11b,11c]. The major difference of two ^{19}F NMR spectra is the peak at about −210 ppm, which is assigned to the head–tail connection of VDF and TrFE units. Only head–head connection of VDF and TrFE units was found in the post-terpolymer (at about −132 ppm), while about 70% head–tail connection together with the other 30% head–head connection of VDF-TrFE units exists in the direct-terpolymer. The structure of the head–head connection and head–tail connection is depicted in Scheme 1, where the arrows denote the directions and amounts of dipole of C–F bond. As shown in Scheme 1, the dipole moment of one unit of TrFE is one-half that of VDF unit, and the head–tail connection of VDF-TrFE contributes it in the same direction as VDF while the head–head connection provides the dipole in the opposite direction, which will cancel the dipole from VDF sequences in the same amount. In other words, the major difference between head–tail and head–head connection of TrFE units is contributing the dipole in positive or negative direction of the overall dipole. Following this direction, the calculation of the different terpolymer should be corrected as follows: the polarization of terpolymer (P_{ter}) is equal to $P_{\mathrm{VDF}} \times V_{\mathrm{VDF}} + P_{\mathrm{TrFE}} \times V_{\mathrm{TrFE}} - P_{\mathrm{CTFE}} \times V_{\mathrm{CTFE}}$ if the VDF-TrFE connection is in head–tail sequence, otherwise $P_{\mathrm{ter}} = P_{\mathrm{VDF}} \times V_{\mathrm{VDF}} - P_{\mathrm{TrFE}} \times V_{\mathrm{TrFE}} - P_{\mathrm{CTFE}} \times V_{\mathrm{CTFE}}$, where P_{VDF}, P_{TrFE} and P_{CTFE} are the polarization of PVDF, PTrFE and PCTFE sequence, V_{VDF}, V_{TrFE} and V_{CTFE} are the molar contents of VDF, TrFE and CTFE, respectively. If the dipole moment of CTFE is calculated the same as TrFE in amount and equal to one-half that of one VDF unit, the terpolymer's polarization could be estimated as $P_{\mathrm{ter}} = P_{\mathrm{VDF}} \times V_{\mathrm{VDF}} - 1/2(P_{\mathrm{VDF}} \times V_{\mathrm{CTFE}}) \pm 1/2(P_{\mathrm{VDF}} \times V_{\mathrm{TrFE}})$. For example, for the terpolymers (Run B-9A and Run B-7A in Table 2) from post-polymerization process, the polarizations calculated by the corrected equation are 0.061 C/m^2 and 0.091 C/cm^2 respectively, which agree perfectly with the results obtained (0.059 C/m^2 and 0.086 C/m^2, correspondingly). This means the different connection of VDF-TrFE sequences in the terpolymers from different process could successfully explain the difference of polarization as well as the thermal properties and dielectric constants.

3.1.4. Energy storage and loss

As a function of electric field applied and electric displacement, the energy storage of the terpolymers from post-polymerization process with various TrFE content (from 33.5% to 0) and same CTFE content (about 8%) were calculated from the polarization curve and plotted in Fig. 10(a). Thanks to the clean reaction process, the energy density could be tested under a very high electric field (>500 MV/m) until saturated, which is higher than reported [8]. As a result, the highest energy storage of 10.3 J/cm^3 is obtained, which is not limited by electric breakdown field but the saturation. In addition, the TrFE content plays an important role in the energy storage of post-terpolymer as well as in the thermal and dielectric properties. When the TrFE content decreases, the energy density under the same electric field is dramatically enhanced and the maximum value is obtained in the VDF-CTFE copolymer where there is no TrFE unit. Calculated from the integral of electric field employed and the electric displacement measured, the energy density depends on the overall dipole moments aligned and released during the charge and discharge process, which is controlled by the TrFE content as discussed above. Therefore the

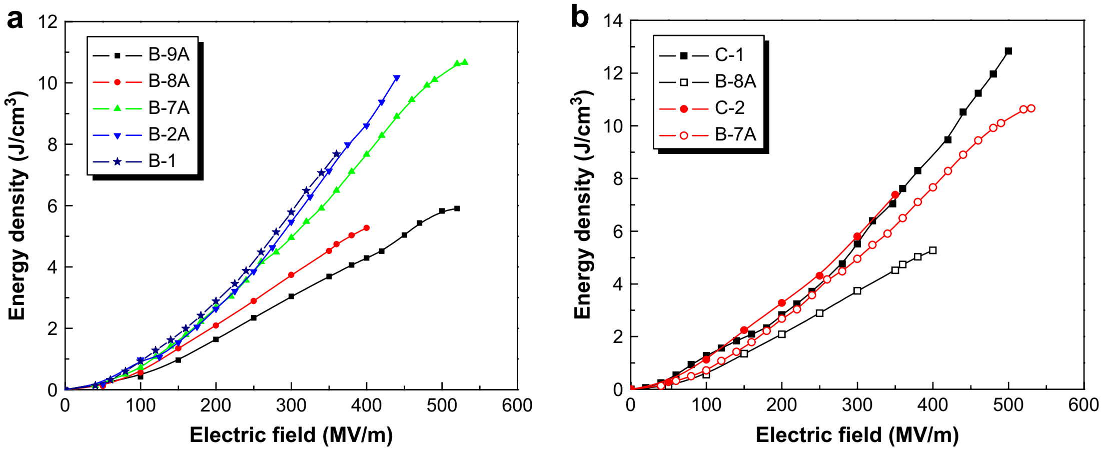


Fig. 10. (a) The energy density of co- and ter-polymers under increasing electric field. (b). Energy density comparison of terpolymers from different preparing process.

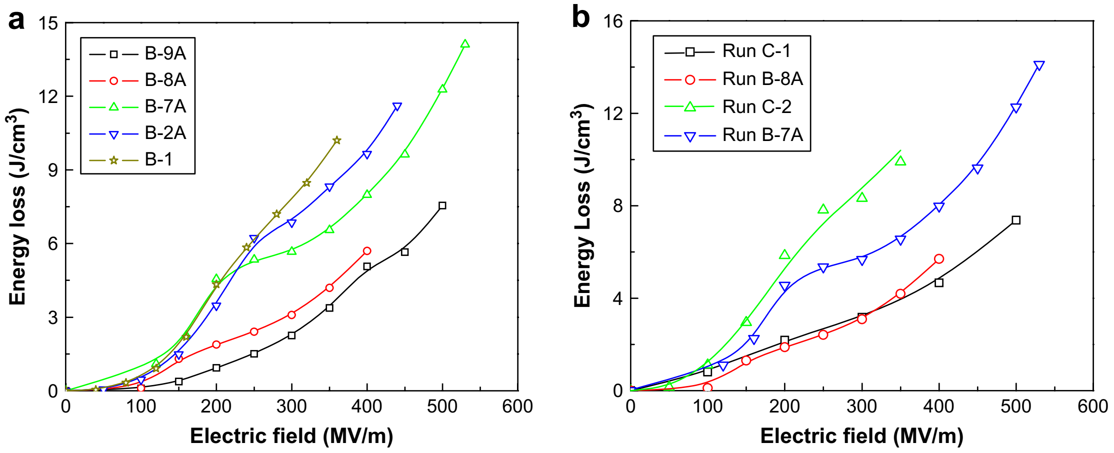


Fig. 11. (a) Energy loss observed in the terpolymers from hydrogenation under elevated electric field. (b) Energy loss comparison of terpolymers from different preparing process.

content of TrFE units introduced as head–head connection exhibits negative influence on the energy density discharged as obtained. This could further be proved by comparing the energy density measured in terpolymers prepared from different process as plotted in Fig. 10(b). As a result of more dipole cancelled by more TrFE introduced in post-terpolymers, the energy density of post-terpolymer is more or less lower than that of the corresponding direct-terpolymer depends on the amount of TrFE introduced. The more TrFE introduced in head–head connection (post-terpolymer), the lower energy density is measured than that of introduced in head–tail connection (direct-terpolymer).

As a parameter to evaluate the efficiency of capacitors, energy loss of the dielectric materials is as important as energy storage. Performing like the typical dielectric polymers, the energy loss of P(VDF-TrFE-CTFE)s keeps increasing as electric field applied increases. The energy loss of terpolymers and copolymer with different TrFE contents measured under different electric fields are depicted in Fig. 11(a). As the TrFE content decreases, the energy loss of polymers under the same electric field is increasing and reaches maximum in P(VDF-CTFE) copolymer (TrFE content is zero). That indicates more TrFE units in the terpolymer help the terpolymer keep in all-*trans* conformation, which is not only easier for the dipole moments to be polarized but also more readily to be released once the electric field is removed. The results agree well with the FTIR, DSC and dielectric constant results discussed above. A comparison study of energy loss between the terpolymers prepared from direct- and post-processes was also carried out as shown in Fig. 11(b). Almost the same energy loss in the terpolymers with higher TrFE content (Run C-1 and Run B-7A in Table 2) is obtained, but at a lower TrFE content, the post-terpolymer possesses a lower energy loss than the corresponding direct-terpolymer. When enough TrFE units are introduced into the polymer, the conformation will be kept in all-*trans* ($t > 4$) structure and all the polarization is reversible, consequently, the energy loss of polymer is the lowest. When the TrFE content is reduced, the conformation starts to change from all-*trans* to $tttg^{+}tttg^{-}$ and even $tg^{+}tg^{-}$, whose polarization is not totally reversible and remnant polarization appears. As a result, the energy loss is increasing. The lower energy loss obtained in post-terpolymer could be attributed to the lubricant effect of $-CF_2-CF_2-$ sequence from the head–head connection of VDF and TrFE units.

4. Conclusions

A series of ferroelectric P(VDF-TrFE-CTFE)s terpolymers with high energy density (10.3 J/cm^3) and low energy loss (5 J/cm^3) are successfully synthesized via well-controlled dechlorination of P(VDF-CTFE)s. The properties of these terpolymers, such as thermal properties, dielectric constant, polarization and energy storage and loss, were systematically investigated. By comparing the NMR spectra and the properties of the terpolymers prepared from direct- and post-process side-by-side, the relationship between the microstructure and the properties of the terpolymers has been well illuminated in detail. It was surprised to note that the connection sequence of TrFE and VDF units is another important factor influencing the properties of the resulting polymer as well as the TrFE and CTFE content. Although the energy density is slightly lower than direct terpolymer, the post-terpolymers are still acceptable for the capacitor material if the lower cost of the materials and relative lower energy loss are considered.

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