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PAPER

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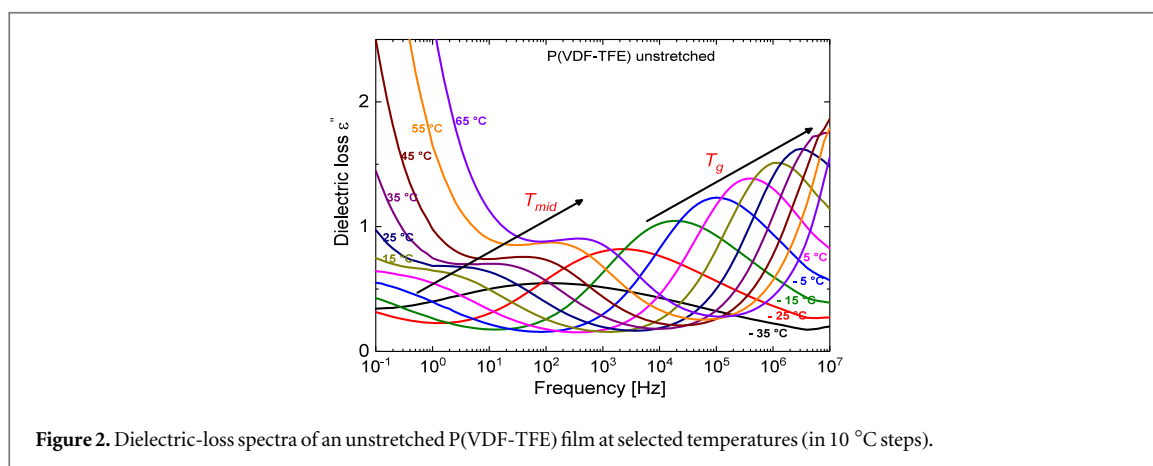
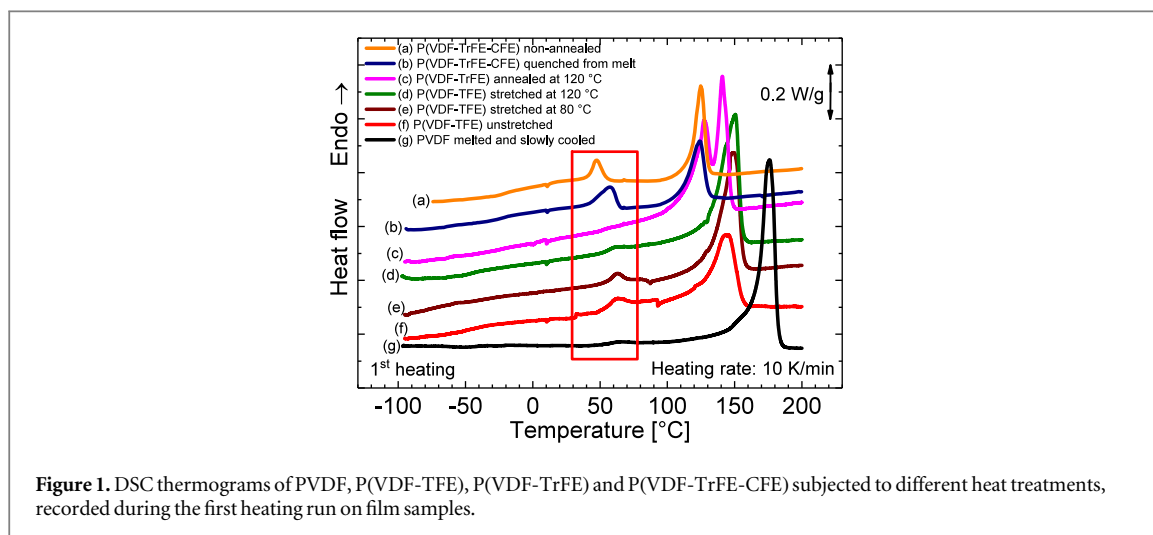
¹ Author to whom any correspondence should be addressed.E-mail: thulasinath.raman.venkatesan@uni-potsdam.de and reimund.gerhard@uni-potsdam.de**Keywords:** mid-temperature transition, vinylidene fluoride (VDF)-based polymers, Differential Scanning Calorimetry (DSC), Dielectric Relaxation Spectroscopy (DRS), ferroelectric polymers, pyroelectric polymers, piezoelectric polymers**Abstract**

The existence of an intermediate transition between the glass and the Curie/melting temperatures in Poly(vinylidene fluoride) (PVDF) and some of its co- and ter-polymers has been reported by several authors. In spite (or because?) of various different explanations in the literature, the origins of the transition are still not clear. Here, we try to understand the extra transition in more detail and study it with thermal and dielectric methods on PVDF, on its co-polymers with trifluoroethylene (P(VDF-TrFE)) and tetrafluoroethylene (P(VDF-TFE)), and on its ter-polymer with trifluoroethylene and chlorofluoroethylene (P(VDF-TrFE-CFE)). Based on interpretations from the literature and our experimental studies, we propose the new hypothesis that the intermediate transition should have several interrelated origins. Especially since the relevant range is not far above room temperature, better understanding and control of their properties may also have practical implications for the use of the respective polymer materials in devices.

Piezo- and pyroelectricity in poly(vinylidene fluoride) (PVDF) have been extensively investigated since their discoveries in 1969 and 1971, respectively [1]. However, even 5 decades later, a complete understanding of the dielectric and thermal transitions—and in particular of the intermediate transition between the glass (T_g) and the melting (T_m) temperatures [2, 3]—in VDF-based polymers has not been reached. Several authors have reported a similar transition to exist in the copolymers of PVDF with trifluoroethylene (P(VDF-TrFE)) [4, 5], tetrafluoroethylene (P(VDF-TFE)) [2] and hexafluoropropylene (P(VDF-HFP)) [6, 7]. A number of different explanations were put forward for the transition at the intermediate temperature T_{mid} but a true consensus on its exact origin(s) has not been reached so that it remains somewhat mysterious.

In order to obtain new insight into the intermediate transition, which—to our knowledge—has not been exclusively studied before, thermal and dielectric methods were employed on films of PVDF, its co-polymers P(VDF-TrFE) and P(VDF-TFE), and its ter-polymer P(VDF-TrFE-CFE). VDF-based polymer samples were prepared as follows: PVDF powder (SolefTM 1008) was melt-pressed at 220 °C under a pressure of 100 bars and allowed to slowly cool back to R.T. under pressure. Free-standing P(VDF-TrFE) films were cast from an acetonitrile solution of copolymer powder with a VDF/TrFE ratio of 75/25 mol% (Piezotech S.A., France). For the terpolymer samples, P(VDF-TrFE-CFE) powder (Arkema-Piezotech) (VDF/TrFE/CFE ratio of 62.2/29.4/8.4 mol%) was dissolved in acetone and then drop-cast into films with thicknesses between 20 and 40 μm . Extruded P(VDF-TFE) films of 100–200 μm with a VDF/TFE ratio of 70/30 mol% were obtained from F2ME, Russia. Some of the polymer films were annealed (at 120 °C), stretched longitudinally in the direction of extrusion (ratio of 3.6) and/or quenched (in liquid nitrogen) as specified in the text and the figures. For dielectric measurements, aluminum electrodes of 60 nm thickness were evaporated onto both sides of the free-standing polymer films.

In the Differential-Scanning-Calorimetry (DSC) thermograms of figure 1, an additional transition is obvious between (a) the glass-transition step (T_g) at low temperatures (below 0 °C) and (b) the Curie transition (T_C) in P(VDF-TrFE) or the melting transition (T_m) in PVDF, P(VDF-TFE) and P(VDF-TrFE-CFE) at high



temperatures, respectively. Upon first heating, endothermic DSC peaks are found around +50 °C (red box) on all VDF-based homo-, co-, and ter-polymers investigated here—irrespective of preparation conditions.

As shown in the frequency-dependent dielectric-loss spectra of an un-stretched P(VDF-TrFE) film in figure 2, dielectric spectroscopy sheds more light on the extra T_{mid} transition. We can clearly identify two separate relaxation processes—the 1st one at higher frequencies/lower temperatures is assigned to the glass-transition step at T_g with its typical frequency dependence, and the 2nd process at lower frequencies/higher temperatures (above 0 °C) is clearly visible from the intermediate T_{mid} -transition peaks that also shift with frequency.

After stretching, however, we observe (figure 3) that the T_{mid} transition is no longer found [8]. The frequency dependence of the T_{mid} transition, and the fact that it disappears after stretching, can be explained as an upper glass transition ($T_g(U)$) that is associated with the constrained amorphous regions between crystallites. As stretching leads to the removal of the constrained amorphous regions, it is expected to eliminate the $T_g(U)$ associated with it. Boyer was the first to suggest this explanation for PVDF and other semi-crystalline polymers [9]. His proposal was later adopted by several other authors (e.g. [2, 10]). Yet, when the dielectric loss of the stretched sample (figure 3) is plotted as a function of temperature at different frequencies as in figure 4, we observe that—even after stretching—the T_{mid} still exists as a shoulder around 60 °C.

The transition is more clearly seen in the permittivity spectra of figure 4 as a frequency-independent peak—characteristic for a structural transition. From the DSC endotherms shown in figure 1, we notice the T_{mid} transition to be present also in stretched P(VDF-TrFE). Additionally, it was calculated that the specific heat capacity C_p of PVDF already reaches its expected value when PVDF undergoes the conventional glass transition at T_g so that there is no possibility for it to increase further at T_{mid} [3]. All the above observations either contradict the hypothesis of an upper glass transition or at least do not provide a complete picture of the intermediate transition.

It was also suggested that the frequency independence of the T_{mid} transition as seen in figure 4 may indicate a structural transition associated with the melting of secondary crystals formed during storage of the sample above

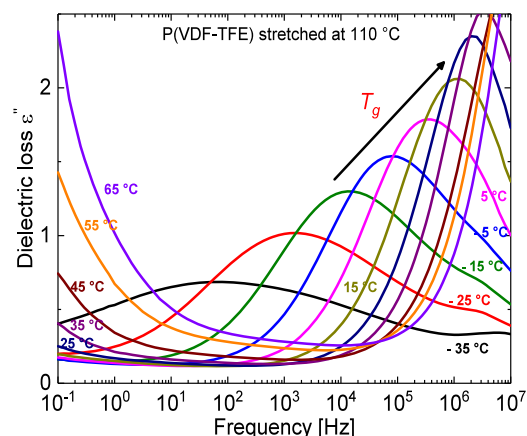


Figure 3. Dielectric-loss spectra of a P(VDF-TrFE) film stretched at 110 °C at selected temperatures (in 10 °C steps).

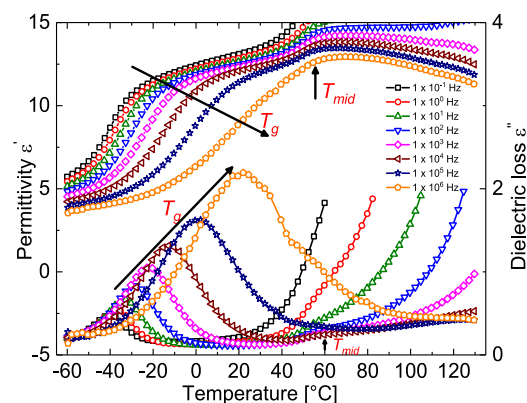


Figure 4. Temperature dependences of the dielectric permittivity (upper half) and the dielectric loss (lower half) at various frequencies in a P(VDF-TrFE) copolymer film stretched at 110 °C.

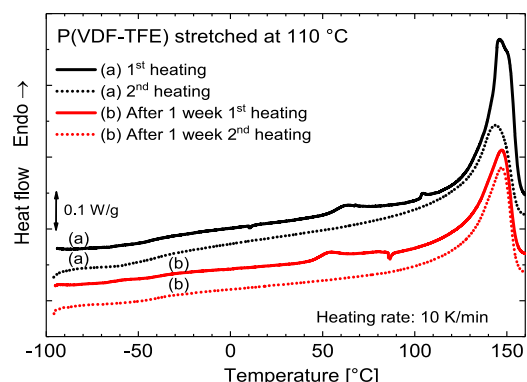


Figure 5. 1st- and 2nd-run DSC thermograms on P(VDF-TrFE) stretched at 110 °C before (upper curves in black) and after (lower curves in red) storage at room temperature for one week.

its T_g [6]. A similar transition was previously observed at 65 °C in our dielectric-loss measurements on P(VDF-TrFE) [11]. Neidhöfer *et al* reported an irreversible heat flow associated with the T_{mid} endothermic peak from their modulated-DSC experiments on α -PVDF, which points towards secondary crystallization. Furthermore, we observe (figure 5) that the T_{mid} endothermic peak seen around 63 °C during the first heating disappears during the second heating. We also notice that the T_{mid} peak reappears upon subsequent cooling and storage of the sample at room temperature for one week. All these findings strengthen the argument that the T_{mid} transition is a result of secondary crystallization. Again, however, looking at the DSC exotherm during cooling

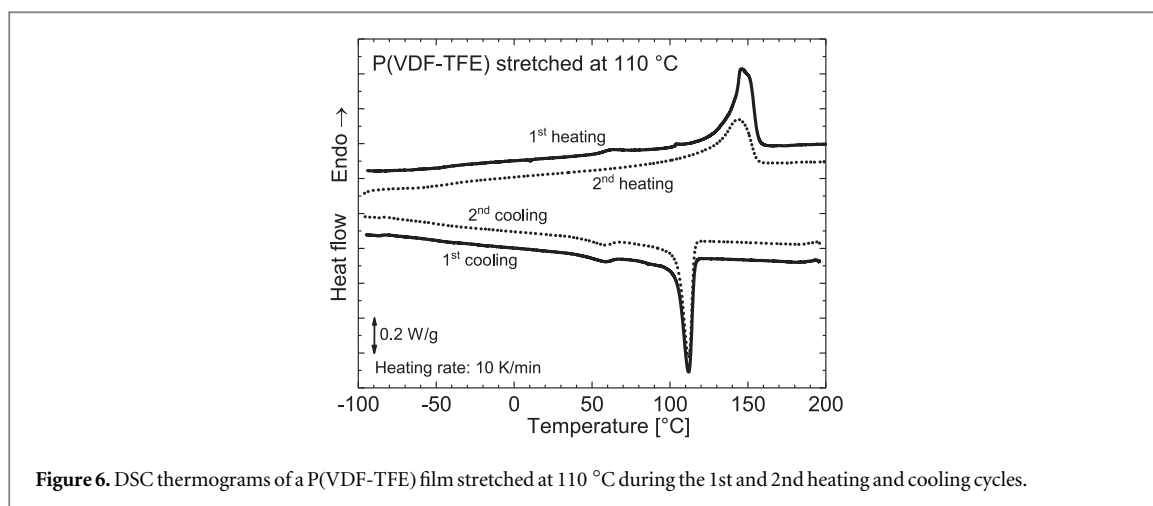


Figure 6. DSC thermograms of a P(VDF-TrFE) film stretched at 110 °C during the 1st and 2nd heating and cooling cycles.

in figure 6 below, we observe a clear peak at 58 °C corresponding to the T_{mid} endothermic peak seen during the first heating. As secondary crystallization is a process that requires time, secondary crystals cannot quickly form during the cooling step seen in the figure.

In a third explanation found in the literature, it is assumed that the fluorine atoms in the $TGT\bar{G}$ chains of the non-polar α -phase in VDF-based polymers either flip from up to down or vice versa ($TGT\bar{G} \rightarrow GT\bar{G}T$) at T_{mid} . The process was first proposed by Miyamoto *et al* to describe the dielectric (α_c) transition which they observed around 90 °C in α -PVDF [12]. Later, Loufkis and Wunderlich adopted the same explanation to describe the T_{mid} transition observed between 47 and 77 °C on the DSC endotherms in their quenched α -PVDF samples [3]. Based on previous dielectric and x-ray diffraction results [13, 14], Loufkis and Wunderlich expected conformational disorder (*condis*) to occur between 87 and 97 °C. They also showed that slow cooling from the melt freezes the up-down equilibrium associated with *condis* between 77 and 87 °C—observed as a DSC exotherm with a corresponding T_g -like relaxation step during heating. However, upon quenching, the *condis* peak was reported to shift to lower temperatures. Finally, subsequent heating was claimed to lead to un-freezing and re-organization of *condis* with an endothermic peak in the T_{mid} temperature range. It was stated that the endothermic T_{mid} peak can only be observed in quenched samples. Once the lower-temperature conformation relaxes with a *condis* reorganization, it cannot be re-introduced into the already grown crystals. Hence, the relaxation should be irreversible. Several authors agree with a *condis* relaxation (see e.g. [7] and [6]). Frübing *et al* associated the frequency-dependent (α_c) peaks in the dielectric spectra of P(VDF-HFP) (similar to the T_{mid} peaks of P(VDF-TrFE) seen in figure 2) to *condis* and found that the peaks disappeared after stretching [6].

Even though the last explanation seems more convincing, certain aspects of our experimental results are still contradictory in themselves if we adopt the *condis* hypothesis. In figure 1, we can clearly see that the endothermic peak is not only observed in quenched samples, but also in a PVDF sample that was slowly cooled from the melt. Also, as explained before, we see in figures 5 and 6 that the process is reversible, as it re-appears in the DSC heating cycle after one week and as it is always present in the cooling cycle as an exotherm.

In addition to the above three alternative explanations for the T_{mid} transition, we should also consider interface effects. In the same temperature range where we observe the T_{mid} transition, a depolarization peak was found in thermally stimulated depolarization-current (TSDC) experiments on PVDF [15]. A very similar peak was also observed in our previous TSDC experiments on P(VDF-TrFE) and P(VDF-TrFE-CFE) films [11]. The peak had been attributed to a Maxwell-Wagner (MW) interface polarization which occurs as a result of injected charges trapped at the amorphous-crystalline (a-(c)) interfaces. Therefore, we also need to look at interface effects when we try to identify the origins of the T_{mid} transition.

Going through the available extensive literature (partially cited above), we find several hints that the different processes reported by various authors as being behind the T_{mid} transition could be interrelated. In view of the literature and our detailed experiments, the T_{mid} transition may also be the result of all the different processes occurring together in the relevant temperature range between 35 and 80 °C. On this basis, we propose a new hypothesis: first, we consider the amorphous-crystalline interfaces where we have tie molecules, i.e. amorphous molecular-chain sections that continue at both ends into the adjacent crystalline lamellae that are typically found in semi-crystalline polymers [16, 17]. Below the conventional T_g , the tie molecules remain frozen along with the other amorphous chains. Furthermore, at or just above T_{mid} , tie molecules that are constrained between crystalline lamellae will un-freeze and undergo an upper glass transition at $T_g(U)$, after which they attain sufficient energy for conformational disorder (crystalline regions might also undergo *condis* in

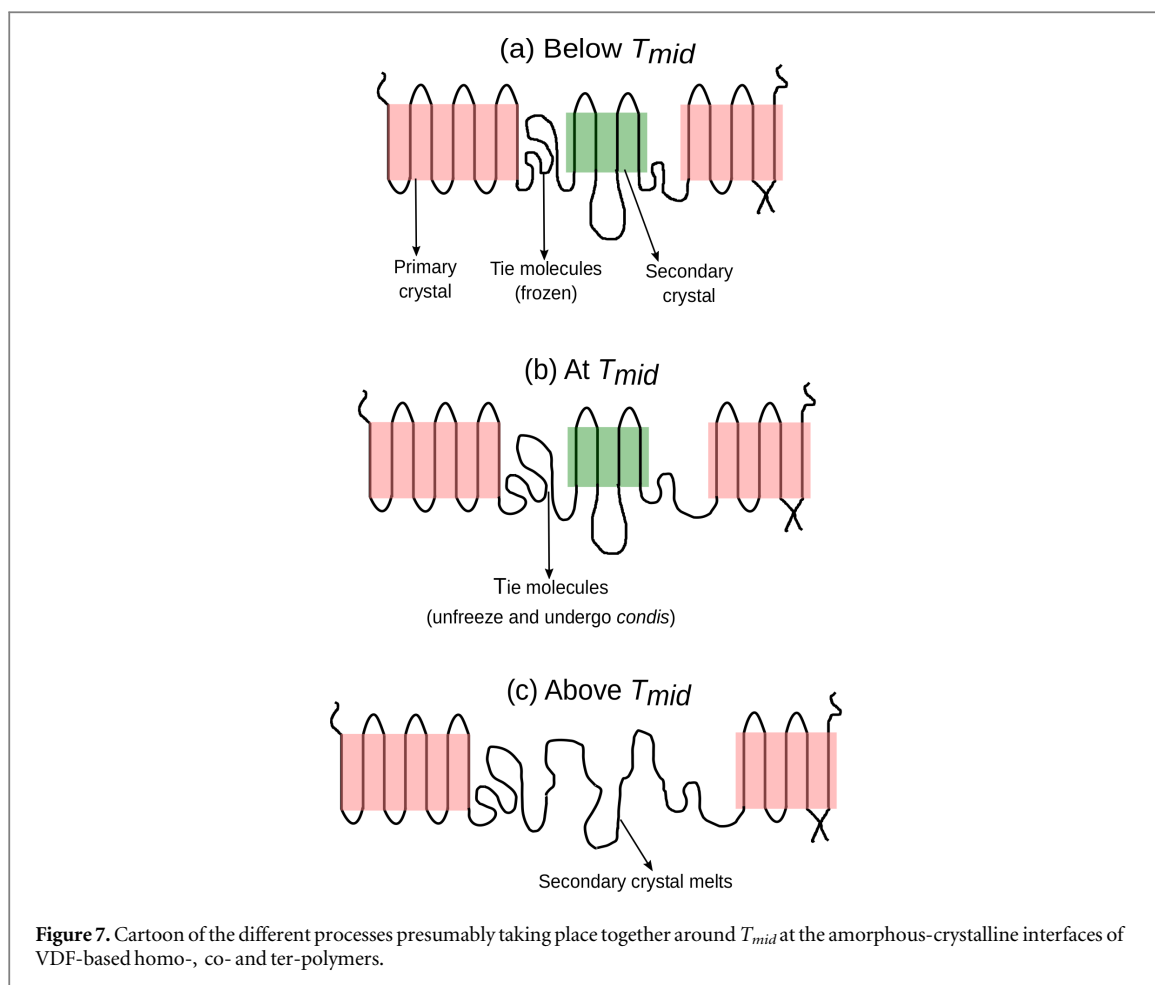


Figure 7. Cartoon of the different processes presumably taking place together around T_{mid} at the amorphous-crystalline interfaces of VDF-based homo-, co- and ter-polymers.

Table 1. Individual contributions to the T_{mid} transition expected from the different processes after different heat treatments.

Heat treatment	Number of tie molecules	$T_g (U)$	Conformational disorder (<i>condis</i>)	Secondary crystallization	T_{mid} expected in DSC as
Stretched (at high temperature)	Low	↓	↑	↓	Relaxation step
Annealed/slowly cooled	Lowest	↓	↓	↓	Weakest relaxation step
Quenched/un-stretched/non-annealed	High	↑	↑	↑	Large endothermic peak
Stretched (at low temperature)	Moderate	↑	↑	↑	Small endothermic peak

the vicinity of T_{mid}). Finally, slightly above the onset of the intermediate transition at T_{mid} , the imperfect or secondary crystals that formed either during rapid quenching and/or storage will melt, which leads to an endothermic DSC peak. A schematic diagram of the proposed hypothesis is shown in figure 7.

With our new hypothesis, we can predict the individual contributions of the different processes to the collective T_{mid} transition for the heat treatments shown in table 1:

1. In films stretched at high temperature, the amount of tie molecules would be less. Stretching will stabilize the crystalline phase—thus hindering the formation of secondary crystals during storage. In this case, the

main contribution to the T_{mid} transition would be due to *condis*. Hence, the T_{mid} transition is expected to be seen only as a small relaxation step in the DSC endotherm.

2. In films annealed or slowly cooled from the melt, the number of tie molecules would be the lowest, as annealing and slow cooling relieve and limit, respectively, constrained regions. In addition, annealing decreases the α -phase fraction in VDF-based polymers [18, 19]. Thus, the contribution from *condis* would also be minimal, resulting in the weakest T_{mid} transition.
3. In films that are quenched or non-annealed and un-stretched (e.g. drop-cast), the number of tie molecules would be the maximum, resulting in a $T_g(U)$ transition. In addition, the α -phase fraction and the chances of secondary crystallization would be higher. This will result in a T_{mid} transition with contributions from all the three different processes outlined before—manifesting itself as a strong endothermic DSC peak.
4. In films stretched at low temperature, the lower stretching temperatures would allow for only a moderate number of tie molecules. Although contributions from all three processes would be present, the overall magnitude would be less than in the case of quenched/non-annealed/un-stretched samples. Thus, we would expect a smaller endothermic peak at T_{mid} .

Finally, looking at figure 1 again, we can simply apply our above predictions to the various VDF-based homo-, co- and ter-polymers subjected to the different heat treatments as mentioned in table 1, which may serve as a direct proof of our hypothesis for the origins of the mid-temperature transition.

Even though the T_{mid} transition was first observed on VDF-based polymers several decades ago, its origins remained a mystery. So far, the transition had been attributed to several different processes—some apparently contradictory to each other—to explain the behaviour at the T_{mid} transition. Explanations include (1) an upper glass-transition step, (2) a relaxation of the conformational disorder associated with $TGT\bar{G}$ chains in α -crystals, and (3) a structural transition as a result of secondary crystal melting. Furthermore, interface effects in the vicinity of the T_{mid} transition complicate the situation.

Here, detailed thermal and dielectric investigations of the T_{mid} transition were carried out on VDF-based homo-, co- and ter-polymers subjected to different heat treatments. Based on the existing literature and on our new results, we demonstrated that the T_{mid} transition should have several interrelated origins. The individual contributions from the processes at the amorphous-crystalline interfaces in the temperature range from 35 to 80 °C vary according to the thermal sample histories. Our new understanding of the origin(s) behind the T_{mid} transition shows that the MW polarization at (a)–(c) interfaces may be controlled and enhanced via appropriate heat treatments, which may help to optimize (relaxor-)ferroelectric and other applications-relevant properties in VDF-based polymers. Thus, a better fundamental understanding of the microscopic processes in VDF-based polymers can also lead to significant improvements in their potential for practical device applications under various environmental conditions.

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