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Naser Pouriamanesh, Florian Le Goupil, Natalie Stingelin, Georges Hadziioannou. Limiting Relative Permittivity “Burn-in” in Polymer Ferroelectrics via Phase Stabilization. ACS Macro Letters, 2022, 11 (4), pp.410-414. <10.1021/acsmacrolett.2c00022>. <hal-03996577>

HAL Id: hal-03996577

<https://hal.science/hal-03996577v1>

Submitted on 20 Feb 2023

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Limiting relative permittivity ‘burn-in’ in polymer ferroelectrics via phase stabilization

Naser Pouriamanesh[†], Florian Le Goupil[†], Natalie Stingelin^{‡*} and Georges Hadziioannou^{†*}

[†] Université de Bordeaux, CNRS Bordeaux INP/ENSCBP, Laboratoire de Chimie des Polymères Organiques, UMR 5629, Allée Geoffroy Saint-Hilaire, 33615, Pessac Cedex, France

[‡] School of Materials Science & Engineering and School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA

KEYWORDS: *ferroelectric polymers, energy storage, electrocalorics, phase transitions, stability*

ABSTRACT: VDF-based polymers, such as poly(vinylidene fluoride) (PVDF) and its copolymers, are well-known ferroelectrics of interest for numerous applications, from energy storage to electrocaloric refrigeration. However, their often complex thermal phase behavior that typically leads to a low phase stability can drastically affect the long-term dielectric properties of this materials family. Here, we demonstrate on the example of the ter-polymer P(VDF-*ter*-TrFE-*ter*-CFE) (molar ratio: 64/29/7) that by limiting mass transport/segmental chain-motion both during solidification and in the solid state, a drastically smaller ‘burn-in’ in relative permittivity, ϵ_r , is observed. Indeed, ϵ_r decreases little over time and saturates rapidly at 96-97% of its initial value. Mass transport thereby is manipulated by controlling the number of chain entanglements per macromolecule, achieved via selection of a suitable polymer solution concentration and molecular weight. In addition, rapid solvent extraction assists in reducing unwanted relaxation processes. Accordingly, increased control of the phase stability of P(VDF-*ter*-TrFE-*ter*-CFE) is gained. Moreover, pathways are opened to reliably identify processing routes for any given VDF-based polymer with critical information being obtained from thermal analysis and viscometry data only, enabling rapid feedback to materials design, including prediction of required molecular weights, without the need for use of complex characterization methodologies.

Ferroelectric polymers are materials that can be spontaneously polarized under application of an electric field.¹ This phenomenon can be exploited and used in electrostrictive actuators, energy storage and electrocaloric refrigeration.²⁻⁷ The most common family of ferroelectric polymers are vinylidene fluoride (VDF)-based materials, such as PVDF and its copolymers (see inset of Figure 1 for an example),^{1,6-9} where local re-arrangements of the C-F dipoles along the backbone lead to the desired ferroelectric behavior. Because of the relative ease of chain rearrangement, however, multiple structures can be adopted, leading to polymorphism and a complex phase behavior.¹⁰⁻¹² Since different phases can co-exist or readily transform into slightly different molecular arrangements, with often drastic effects on the ferroelectric properties of the material including the relative permittivity, this behavior can result in long-term stability issues when such polymers are used in devices. For instance, in electrocaloric devices, the adiabatic temperature change, ΔT_{EC} , typically decreases within a few days of film deposition as the example of the ter-polymer P(VDF-*ter*-TrFE-*ter*-CFE) (64/29/7), cast at commonly used conditions^{13, 14} and shown in Figure 1, illustrates.

Since the number of entanglements in solution and the solid state can be expected to have notable influence on

chain mobility and the segmental chain motion in a macromolecular material,^{15, 16} and hence its phase stability, we set out to explore how this characteristic affect the evolution of certain solid-state dielectric properties over time, with focus on the relative permittivity, using a P(VDF-*ter*-TrFE-*ter*-CFE) ter-polymer with a 64/29/7 ratio (by mol) of VDF/TrFE/CFE as a model system. The reason for this selection is that this VDF-based polymer is well studied,^{12-14, 17-19} and it displays promising dielectric properties including a high dielectric constant (>50 at 100 Hz) and a low dielectric loss, which is as desired for energy storage applications.^{19, 20} Moreover, this P(VDF-*ter*-TrFE-*ter*-CFE) features a polar to non-polar phase transition around ≈ 20 °C, which promises realization of room temperature electrocaloric functions.¹³

Critically, we chose a relatively high molecular weight material (weight-average molecular weight, $M_w \approx 335$ kg mol⁻¹; number-average molecular weight, $M_n \approx 92$ kg mol⁻¹; provided by Arkema-Piezotech, France) because we have to consider that the number of entanglements per chain, N , is proportional to the molecular weight M ; i.e. $N \propto M$. This means that higher molecular-weight materials allow for more entanglements per macromolecules (a higher N) in the melt, and it enables access to a broader range of N

by selecting suitable solution processing conditions. Indeed, when solution processing macromolecular materials, as is often the case in the fabrication of polymer ferroelectric devices, N can be manipulated via the polymer concentration in the solvent, c (vol%). Thereby, one has to take into account that N depends on c approximately as $N \propto M \cdot c$; which implies that at constant overall M , if c is decreased (leading to dilute solutions), N is lowered. As a consequence, the molecular weight between entanglement M_e increases, providing the material with more molecular mobility and segmental motion in the solid state, likely increasing the probability for molecular re-arrangements and, thus, decreasing phase stability.

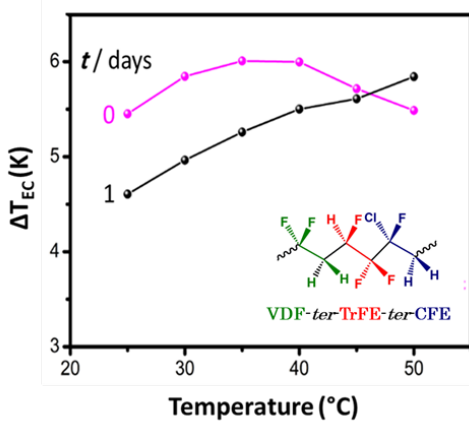


Figure 1. Evolution over time of the adiabatic temperature change, ΔT_{EC} , relevant in electrocaloric applications, measured for a model polymer, the ter-polymer P(VDF-*ter*-TrFE-*ter*-CFE) (molar ratio: 64/29/7) at 110 MV m^{-1} , as cast (pink) and after 1 day of film fabrication (black). The films were cast at 90°C from 10 vol % solutions in cyclopentanone and were then annealed at 105°C , according to procedures reported in literature.¹³ The inset shows the chemical structure of P(VDF-*ter*-TrFE-*ter*-CFE).

In order to assess the effect of polymer concentration in solution on N , we performed rheometry on a range on systems [0.1, 1, 2.5, 5, 10 and 15 vol% P(VDF-*ter*-TrFE-*ter*-CFE) in cyclopentanone], using a cone-plate configuration (see the SI for details). This method allows for measuring the specific viscosity, η , and thus allows to identify the critical overlap concentration, c^* , i.e., the concentration above which chain entanglements occur ($N > 0$).

Figure 2A displays the measured reduced viscosities at various polymer concentrations. As expected, two different

viscosity regimes can be identified: $c_1 < 2 \text{ vol\%}$ P(VDF-*ter*-TrFE-*ter*-CFE) in cyclopentanone, and $c_2 > 5 \text{ vol\%}$, as deduced from the difference in the slope obtained for η vs. c . At $c < 2 \text{ vol\%}$, the system is in the dilute regime where polymer chains are essentially isolated (no entanglements occur), while at $c > 5 \text{ vol\%}$ chain entanglements form, increasing in number when c is increased. Accordingly, c^* is in the regime of 2-5 vol% polymer. Hence, we selected one system with $c < c^*$ (non-entangled, highly mobile) vs. $c > c^*$ (highly entangled, low molecular mobility), green and blue areas indicated in Figure 2A, as representative samples to assess the influence of chain entanglements on phase stability. Specifically, we worked with materials and films cast from 0.5 vol% and 10 vol %. As casting temperature, we chose 90°C , that is a temperature well below the boiling temperature of cyclopentanone (which is around 130°C), while being well above the observed solid-solid phase transitions identified in differential scanning calorimetry (DSC; see endotherms at around 20°C and 45°C in the DSC provided in Figure 2B and highlighted with blue dotted lines) where we can expect relative rapid molecular re-arrangements.

A few observations can be readily made comparing our DSC data on material obtained from films cast at 90°C that were aged at room temperature for periods of 2 hrs to one week after casting at 90°C (Figure 2C). First heating scans were used for this purpose to reflect the nature of the cast films rather than melt-processed systems.

Firstly, a clearly different phase behavior is observed depending whether the polymer chains are entangled in solution ($c > c^*$, i.e., 10 vol% polymer; right panel) or not ($c < c^*$, i.e., 0.5 vol% polymer; left panel). While the latter shows the rapid evolution of two clearly detectable endotherms at around 18°C and 37°C , which are attributed to solid-solid phase transitions (including from a polar to a non-polar polymorph, as alluded to above), systems with a higher number of entanglements initially only displayed one endotherm (around 18°C) with a higher temperature endotherm around $35\text{-}37^\circ \text{C}$ appearing only when the sample was aged for more than 8 hrs at room temperature. This finding already indicates a reduced molecular mobility in the latter system due to an increased entanglement density that limits the structural arrangements that P(VDF-*ter*-TrFE-*ter*-CFE) chains can undergo, while in the films cast from dilute systems, chains seem to re-arrange more easily due to the lack of entanglements that can act as 'loci of friction'.

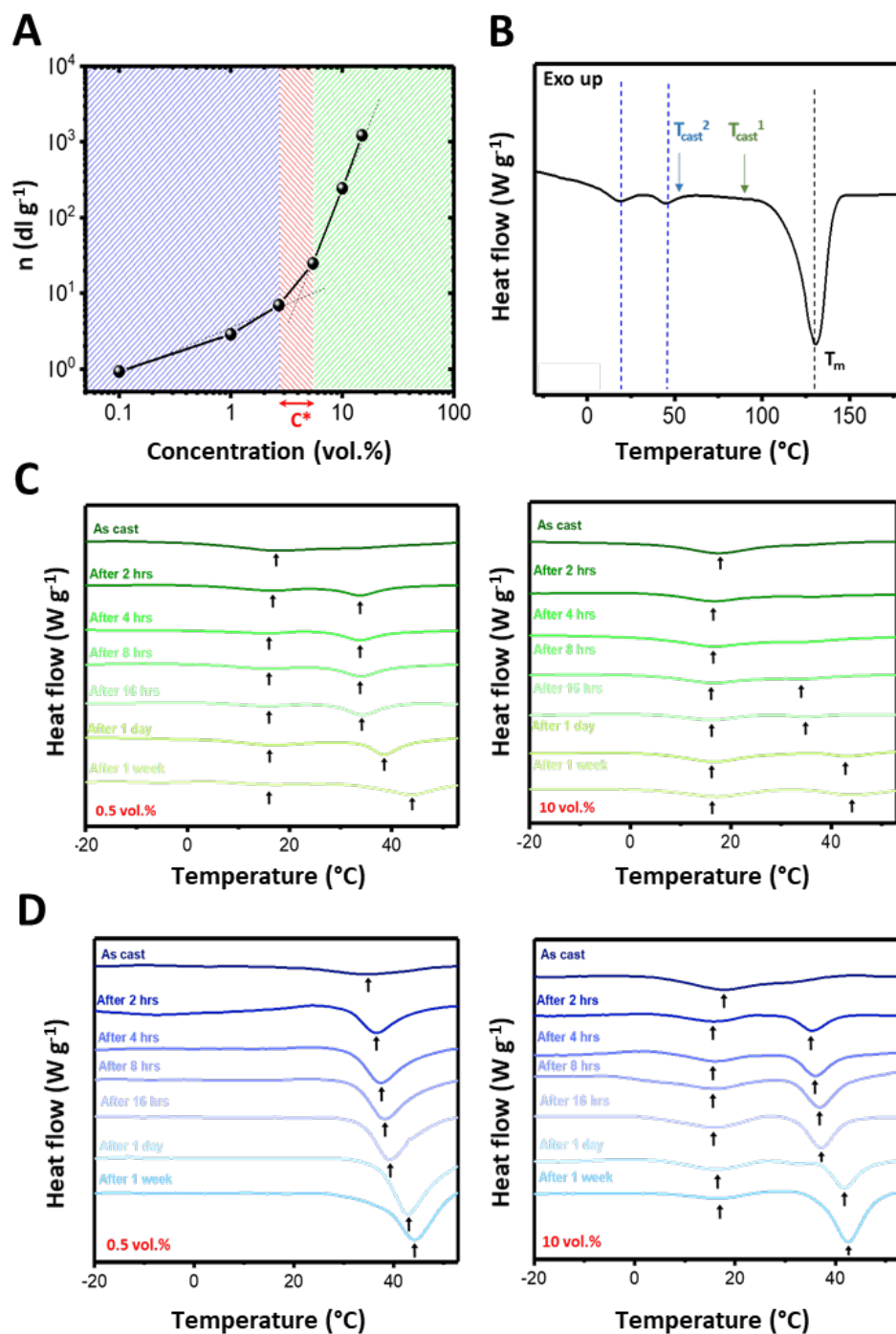


Figure 2. A. Rheometry data identifying the different concentration regimes for P(VDF-*ter*-TrFE-*ter*-CFE) (64/29/7). Regimes where the P(VDF-*ter*-TrFE-*ter*-CFE) chains are relatively isolated (dilute regime) or entangled (concentrated regime) can be clearly identified (blue and green areas, respectively). Given is the reduced viscosity (n) as function of P(VDF-*ter*-TrFE-*ter*-CFE) concentration in cyclopentanone and measured at room temperature. The critical overlap concentration, c^* , where entanglements set in, is found around 2-5 vol% polymer. B. Differential scanning calorimetry (DSC) first heating thermograms, measured on material obtained from P(VDF-*ter*-TrFE-*ter*-CFE) films cast at 90 °C, revealing notable phase transitions of this polymer, including solid-solid phase transitions (blue dotted lines) and melting (black dotted line). A heating rate of 20 °C min⁻¹ was used; measurements were conducted in N₂ atmosphere. C,D. Phase evolution of P(VDF-*ter*-TrFE-*ter*-CFE) films cast, respectively, at 90 °C (C) and 55 °C (D) from 0.5 and 10 vol% cyclopentanone solutions and, then, aged at room temperature for periods of 2 hrs to one week, as measured with DSC (first heating scans; taken at 20 °C min⁻¹; N₂ atmosphere), using the prominent endotherms indicated in B as indicators.

Secondly, the difference between films cast at $c < c^*$ vs. $c > c^*$ is more pronounced when depositing solutions of the two concentrations at lower temperatures, allowing time for mass transport and diffusion (Figure 2D). We used 55 °C, which is at the higher end of the observed second endotherm in the thermogram displayed in Figure 2B. In this scenario, the diluted system, where essentially no entanglements occur, only displays the higher temperature endotherm (around 37 °C), which rapidly evolves over time, shifting to higher temperatures (≈ 44 °C) within a short period of time (1 week). Concentrated, chain-entangled systems display a similar shift, however a persistent low temperature endotherm is observed around 17 °C, suggesting a stronger structural stability.

The effect of casting temperature and, thus, solidification rate on the phase stability of films cast from solutions of $c > c^*$ can be readily followed by the evolution of relative permittivity over time of films cast at 55 and 90 °C, respectively, and then aged at 20 °C (Figure 3A). A rapid and notable decrease in relative permittivity is observed when films are cast at 55 °C; within less than 2.5 hrs, ϵ_r is reduced to ≈ 70 % of its initial value, reaching 65 % after 25 hrs, while still decreasing. In notable contrast, when casting films at 90 °C, leading to rapid solvent extraction, the relative permittivity only decreases slightly in the initial 5 hrs to ≈ 95 % its initial value, rapidly saturating there, in agreement with our observations made in thermal analysis.

From the above, we conclude that the use of classical polymer science approaches to reduce molecular mobility and/or segmental chain-motion (increase of chain entanglements; rapid solidification to limit chain relaxation processes) can be highly successful to introduce a structural (phase) stability in VDF-polymers such as P(VDF-*ter*-TrFE-*ter*-CFE), that is in turn reflected in the material's long-term dielectric properties. Accordingly, one would expect higher molecular-weight materials and/or film deposition from more highly concentrated solutions to lead to even higher phase/property stability. However, increasing the polymer concentration above 10 vol% (at the same molecular weight) leads to a viscosity of ≈ 48 Pa s¹, which can be a challenge for uniform film deposition. A similar behavior is expected when selecting a higher molecular weight material, while keeping the polymer concentration constant. We thus scrutinized the generality of our approach by increasing the solvent evaporation rate in order to more rapidly quench the material into the solid state, thus, limiting molecular relaxation during drying. This can be achieved by selecting a higher casting temperature. We chose a temperature of 105 °C, just at the onset of melting, to avoid undesired dewetting effects, using a relatively highly chain-entangled solution ($c > c^*$).

We first tested the phase stability of such films, using again differential scanning calorimetry (Figure 3B). Only one endotherm around 17 °C is initially recorded, very similar to films cast at these concentrations at 90 °C. The second endotherm that is observed in materials from films cast at 90 °C to evolve over time at ≈ 37 °C, does also appear in films cast at 105 °C after room-temperature storage. Yet, reassuringly, it is very weak and seems to shift notably less

over time, indicative of an even higher phase stability — a conclusion that is supported by the evolution of the relative permittivity over time (Figure 3A) where only a 3 % loss in the normalized relative permittivity values is recorded after 1 day compared to 8 % observed for the films cast at 90 °C.

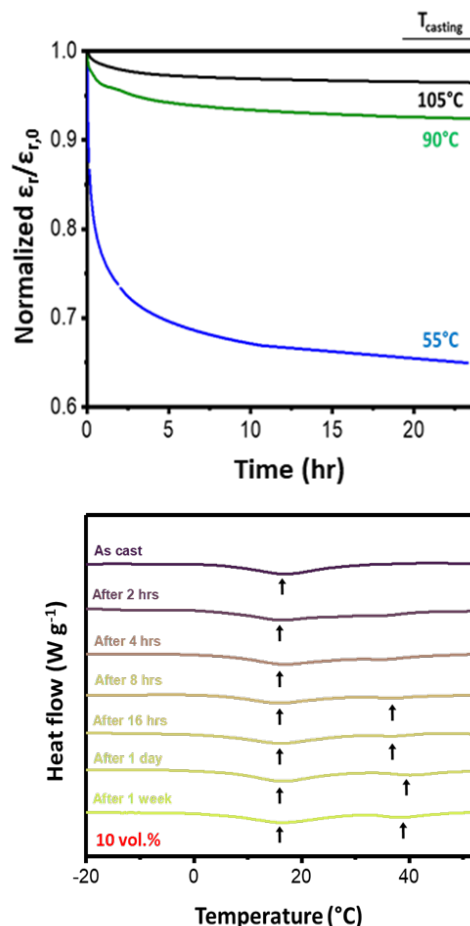


Figure 3. A. Evolution over time of the relative permittivity normalized to the permittivity at $t = 0$ hr, $\epsilon_{r,0}$, measured at 20 °C for P(VDF-*ter*-TrFE-*ter*-CFE) (64/29/7) films cast at 55 °C, 90 °C and 105 °C ($c > c^*$: i.e., at 10 vol% polymer content). B. Phase evolution over time of P(VDF-*ter*-TrFE-*ter*-CFE) (64/29/7) films cast at 105 °C using also 10 vol% polymer solutions in cyclopentanone, which were then aged at 20 °C, as assessed with DSC (first heating scans; taken at 20 °C min⁻¹; N₂ atmosphere), using the prominent endotherms indicated in Figure 2B as indicators. The observed endotherms are notably weaker than for films cast at lower temperatures (Figure 2C,D), and seem to shift less significantly over time.

Our work shows that mass transport and segmental motion, manipulated via selection of high molecular weight materials and use of concentrated solutions, assisted by rapid solvent evaporation that limits molecular relaxation during solidification, leads to a notably increased structural phase stability of a P(VDF-*ter*-TrFE-*ter*-CFE) *ter*-polymer. This strategy is expected to be broadly applicable to other VDF-based materials as it relies on general polymers physics frameworks. This strategy is also superior com-

pared to approaches frequently used in literature that employ post-film-deposition treatments such as thermal annealing.²¹⁻²² This is highlighted in Figure S3. We like to note, however, that likely compromises will need to be sought with respect of N, M and solvent evaporation rate to induce a desired materials property set. Choosing, for instance, a too high N and/or M will result in an amorphous material. To identify optimum parameters, straightforward methodologies such as thermal analysis and rheometry/viscometry can be combined for rapid screening with view of realizing the targeted property set. Our work thus will underpin future materials discovery, assisting materials design and processing activities with respect to needed molecular weight, entanglement density and solidification rate.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at <http://pubs.acs.org>.

All experimental details are included, with the description of the materials used, the methods for film and device fabrication, as well as detailed procedures and lists of the instruments and characterization techniques used to obtain the results presented here.

AUTHOR INFORMATION

Corresponding Authors

* **Natalie Stingelin** – School of Materials Science & Engineering and School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA
<https://orcid.org/0000-0002-1414-4545>

Email: natalie.stingelin@mse.gatech.edu

* **Georges Hadziioannou** – Université de Bordeaux, CNRS Bordeaux INP/ENSCBP, Laboratoire de Chimie des Polymères Organiques, UMR 5629, Allée Geoffroy Saint-Hilaire, 33615, Pessac Cedex, France;

<https://orcid.org/0000-0002-7377-6040>

Email: georges.hadziioannou@u-bordeaux.fr

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

N. P. and N. S. acknowledges the IDEX Associated International Chair entitled MARBLE. F. L. G. acknowledges funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement n. PCOFUND-GA-2013-609102, through the PRESTIGE programme coordinated by Campus France. This work was performed within the framework of the Equipex ELORPrintTec ANR-10-EQPX-28-01 with the help of the French state's Initiative d'Excellence IdEx ANR-10-IDEX-003-02.

ABBREVIATIONS

VDF, vinylidene fluoride; TrFE, trifluoroethylene; CFE, chlorofluoroethylene; M_w , molecular weight; M_n , number-average molecular weight; M_e , molecular weight between entanglement; c , concentration; c^* , critical overlap concentration; DSC, differential scanning calorimetry

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