

The Mystery Behind the Mid-Temperature Transition(s) in Vinylidene fluoride-based Homo-, Co- and Terpolymers – Has the Puzzle Been Solved?

Thulasinath Raman Venkatesan

University of Potsdam, Institute of Physics and Astronomy
Karl-Liebknecht-Strasse 24-25, 14476 Potsdam, Germany
and

KU Leuven, Department of Physics and Astronomy
Celestijnenlaan 200D, 3001 Leuven, Belgium

Michael Wübbenhorst

KU Leuven, Department of Physics and Astronomy
Celestijnenlaan 200D, 3001 Leuven, Belgium

Bernd Ploss

University of Applied Sciences Jena, Department of SciTec
Carl-Zeiss-Promenade 2, 07745 Jena, Germany

Xunlin Qiu

Technical University of Chemnitz, Institute for Print and Media Technology
Reichenhainer Straße 70, 09126 Chemnitz, Germany

Takashi Nakajima

Tokyo University of Science, Department of Applied Physics
6-3-1 Nijuku, Katsushika-ku, 125-8585 Tokyo, Japan

Takeo Furukawa

Kobayashi Institute of Physical Research
3-20-41 Higashi-Motomachi, Kokubunji, 185-0022 Tokyo, Japan

Reimund Gerhard

University of Potsdam, Institute of Physics and Astronomy
Karl-Liebknecht-Strasse 24-25, 14476 Potsdam, Germany

ABSTRACT

Over the last half century, the existence of an additional thermal transition in between the glass transition and the Curie/melting transition has been frequently observed on vinylidene fluoride-based ferro-, pyro- and piezoelectric homo- and co-polymers. The transition has also been observed recently in some of the related relaxor-ferroelectric terpolymers. Despite its well-known existence and the rich history of its treatment in the literature, the origin(s) and a more or less complete picture of the mid-temperature transition have remained elusive until now. Over the years, several authors have put forth various explanations for the so-called mid-temperature transition – some complementary and some contradictory to each other. At the 17th IEEE International Symposium on Electrets (ISE-17) in Limerick, Ireland, in September 2019, the mysterious mid-temperature transition and its possible mechanism(s) became the subject of a panel discussion ^{a)} to mark the Golden Jubilee of the discovery of piezoelectricity in polyvinylidene fluoride (PVDF) by Heiji Kawai of Kobayashi Institute of Physical Research, Japan, as well as the Centennial of the first recognition of ferroelectricity in piezoelectric Seignette's or Rochelle salt. The panel put forward a new hypothesis that the mid-temperature transition is most likely a result of several

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interrelated processes that take place within the respective temperature range. The relevant processes include an upper glass transition or relaxation, a relaxation related to conformational disorder, possible imperfect/time-dependent structures formed as a result of thermal processing and secondary crystallization, as well as interface polarization effects at crystalline-amorphous boundaries. The article captures the essence of the panel discussion and the perspectives obtained therefrom to elucidate the complex mid-temperature transition in vinylidene fluoride-based ferro-, pyro- and piezoelectric homo-, co- and ter-polymers.

Index Terms — vinylidene fluoride-based polymers, ferro-, pyro- and piezoelectric polymers, mid-temperature transition, dielectric relaxation spectroscopy, nonlinear dielectric spectroscopy, differential scanning calorimetry

1. INTRODUCTION

SINCE the discovery of piezoelectricity in poly(vinylidene fluoride) (PVDF) fifty years ago by Kawai in Japan [1], the relevant properties of the homopolymer PVDF and of various co- and ter-polymers with VDF have attracted considerable interest. While pyroelectricity was already known in ancient Greece [2] and probably in China more than two thousand years ago, piezoelectricity had only been discovered in France by Jacques and Pierre Curie in 1880 on tourmaline, quartz, Seignette's (or Rochelle) salt and other crystals [3] and quickly became a "hot topic" [4]. On piezoelectric Rochelle salt, ferroelectricity was finally recognized and described by Valasek one hundred years ago in 1920 [5]. At the same time, *i.e.* in the year 1920, synthetic polymers were first postulated by Staudinger [6], but piezoelectricity in natural and synthetic polymers was only investigated by Fukada in Japan in the 1950s and 1960s [7]. Soon after the discovery of piezoelectricity in PVDF [1], the related properties of pyroelectricity and optical second-harmonic generation in PVDF were reported by a team from Bell Laboratories [8]. In several studies mainly by a Japanese research team around Fukada and Furukawa, ferroelectricity in PVDF was clearly demonstrated between 1975 and 1980 [9].

Nevertheless, the origin of the unexpected ferroelectric and electret properties in PVDF was debated quite intensively – in particular the question whether charges or dipoles or both were essential for the observed piezo-, pyro- and ferroelectric phenomena. The discussion about charges and/or dipoles had accompanied modern experimental electret research since its beginnings one century ago with the seminal work on carnauba-wax electrets started by Eguchi in 1919 [10] and summarized in 1925 [11]. The observation of charges and dipoles and their interaction on and in electrets led to the introduction of the concept of hetero-charge (internal space charge and dipole charges; polarity opposite to the polarity of the adjacent electrode) and homo-charge (injected charge; the same polarity as that of the adjacent electrode) [12]. With respect to PVDF, it was proposed that the orientation of dipoles in the crystalline β -phase was necessary for piezoelectricity – but only for providing the trapping sites for

the charges that caused the polarization component which leads to piezo- and pyroelectricity [13–15]. Today, it is instead accepted that the ferro-, pyro- and piezoelectricity of PVDF and related polymers originate from the polarization of its ordered crystallites, but also that the amorphous phase around the crystallites and the interface charges at crystalline-amorphous "boundaries" can play significant roles in the piezoelectric response and its stabilization [16–18].

The complexity of PVDF and its copolymers with trifluoroethylene (TrFE), tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) is not only a consequence of the interplay between molecular dipoles and internal plus injected charges, but also of a semi-crystalline morphology with up to five different crystalline modifications – some polar and some non-polar – and of several transitions and thus a strong influence of the respective thermal histories on a given polymer sample. The crystalline phases of PVDF [19] itself are usually designated as α , β , γ , δ and ϵ with three different chain conformations that can be arranged with different dipole orientations: (I) all-trans or $TTTT$, a highly polar zig-zag chain, (II) trans-gauche or TG^+TG^- , a polar helical chain, and (III) trans-trans-trans-gauche or $T_3G^+T_3G^-$, a polar chain with alternating zig-zag and trans-gauche monomers (*cf.* Figure 1). For historical reasons, the anti-parallel dipole arrangement of the TG^+TG^- chains is called α -phase, as it is the non-polar phase that is formed upon crystallization from the melt or from solution without further treatment. Upon stretching at a high ratio, the α -phase may be transformed into the highly polar β -phase in which the $TTTT$ chains are arranged with all dipoles in parallel. By means of high-field poling under suitable conditions, the α -phase can be transformed into the polar α_p - or δ -phase that was discovered in 1977/78 by Das-Gupta [20] and quickly confirmed by several other research groups. Thermal treatment (annealing) may convert the TG^+TG^- chains of the α -phase into $T_3G^+T_3G^-$ chains that may again be arranged either with their dipoles all in parallel (polar γ -phase) or with anti-parallel dipoles which constitute the non-polar ϵ -phase discovered by Lovinger at Bell Laboratories in 1981/82 [21].

In the P(VDF-TrFE), P(VDF-TFE) and P(VDF-HFP) copolymers [22, 23], the VDF co-monomer segments are usually already found in the highly polar zig-zag conformation so that no further processing is required before electrical