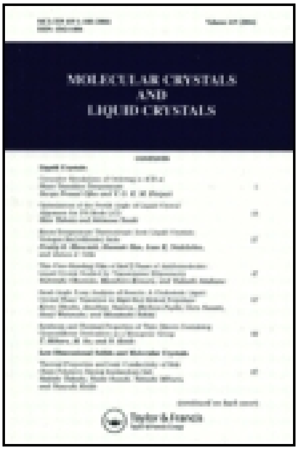

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Curie Temperature Impulse Response of Thin Films of Poly(Vinylidene Fluoride-Co-Trifluoroethylene)

M. Aldissi [a] [b] , W. Bongianni [a] , B. Espinoza [a] & A. M. Nyitray [a]
[a] Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM, 87545
[b] Champlain Cable Corp., P.O. Box 7, Winooski, VT, 05404
Version of record first published: 04 Oct 2006.

To cite this article: M. Aldissi , W. Bongianni , B. Espinoza & A. M. Nyitray (1990): Curie Temperature Impulse Response of Thin Films of Poly(Vinylidene Fluoride-Co-Trifluoroethylene), Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 190:1, 55-61

To link to this article: http://dx.doi.org/10.1080/00268949008047832

Mol. Cryst. Liq. Cryst., 1990, Vol. 190, pp. 55–61
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Curie Temperature Impulse Response of Thin Films of Poly(Vinylidene Fluoride-Co-Trifluoroethylene)

M. ALDISSI*, W. BONGIANNI, B. ESPINOZA and A. M. NYITRAY

Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545

INTRODUCTION

Our current interest focuses on random copolymers of vinylidene fluoride (VF_2) and trifluoroethylene (TrFE). These copolymers have been the subject of an extensive study since the addition of trifluoroethylene produces a *trans* structure similar to the β-phase of PVF_2 and exhibits greater piezoelectric activity.[1] In these materials a Curie phase transition is observed in which the planar *trans* ferroelectric phase containing ordered dipoles undergoes a solid-solid phase transition to a paraelectric phase with conformational disorder and loss of dipole orientation.[2–4] The application of a high electric field is known to raise the Curie temperature[4,5] and is frequently employed to increase peizoelectric activity.

X-ray diffraction measurements showed that in the ferroelectric low-temperature phase, a chain in the crystal has a planar all-*trans* conformation. The degree of order of the crystal depends on the VF_2/TrFE ratio. In the paraelectric high-temperature phase, the conformation of the molecular chain is partially disordered and is packed on an expanded hexagonal lattice.[3–7]

The crystalline structure, and therefore the ferroelectric phase transition, depend normally on the crystallization conditions. This effect is one of the unique characteristics of this class of ferroelectric polymers in contrast to the other ferroelectric materials such as single crystals and ceramics. Such effects in the case of poly(vinylidene fluoride-co-trifluoroethylene) have been studied in detail.[8]

Recently, Bongianni[9] described a process for the manufacture of free standing films of the copolymer in the thickness range 1–10 μm. These films are grown on a substrate and demonstrate volume changes of 25:1 in the thickness direction. Despite growth at temperatures well above the Curie temperature, the films exhibit a high degree of order and crystallinity as indicated by their coupling coefficients. This is in good agreement with work reported by Ohigashi and Koga.[10]

Tajitsu *et al.*[11] reported on the switching characteristics of various copolymer films at room temperature and found that reverse polarization is predicted from

---

*Present address: Champlain Cable Corp., P.O. Box 7, Winooski, VT 05404.

the rigid dipole model with a Lorentz factor close to zero. Assuming a manufacturing process which does not discriminate between crystal phases, crystallization or orientation, their results should find a linear ratio of polarization with dipole density. Reversed polarization is found to increase with VF_2 content with a fair agreement over the range of 50–75 VF_2 mol%.

In this paper, we focus our interest on the potential use of the copolymers for energy storage applications. For this purpose, we have performed impulse response measurements as the film is heated from room temperature through the ferroelectric to paraelectric transition. The reversible energy stored in the film, as indicated by the voltage pulse across a fixed external load, is compared for two commercial copolymers and the materials synthesized by one of us. The effect of film thickness and polymer molecular weight on energy storage is also reported.

EXPERIMENTAL

Materials used in this study were (i) two copolymer samples whose VF_2/TrFE molar ratios were 75/25 and 69/31, purchased from Daikin Kogyo Co. Ltd.; (ii) three copolymer samples whose VF_2/TrFE molar ratios were 73/27, 66/34 and 62/38, kindly provided by Solvay Co.; and (iii) various samples synthesized by us.

In our synthesis, VF_2 and TrFE gases, purchased from PCR Specialty chemicals and Aldrich, were passed through molecular sieves to remove the inhibitor. The gases were then condensed separately at liquid nitrogen temperature then submitted to dynamic pumping to remove traces of oxygen before the appropriate amounts are transferred into the polymerization reactor. The copolymers were prepared by an emulsion technique using a standard procedure[12] at temperatures between room temperature and 60°C. The reaction was done in a stainless steel autoclave fitted with a mechanical stirrer and a temperature probe to regulate the polymerization temperature desired. The reactor was charged under nitrogen with 200 ml of oxygen-free de-ionized water, 0.50 g sodium sulfite, 0.11 g sodium phosphate buffer, 1.22 g ammonium peroxodisulfate initiator and 2.97 g ammonium perfluorooctonate emulsifier. Ammonia solution was added to bring the pH into the range 8.9–9.0. The reactor was then frozen at liquid nitrogen and the nitrogen gas pumped out under high vacuum before distilling in the two monomers. The reactor was then warmed to room temperature or the desired polymerization temperature at which point stirring was started. The copolymerization was stopped after 30 min. to 1 hr. and the excess monomers vented, after which the copolymer was recovered by coagulation in water containing some aluminum sulfate. Conversions of 50 weight% were generally obtained. The copolymer was then repeatedly washed with deionized water and filtered yielding a white material.

Films 5–10 μm thick were metallized with 1000 Å of vacuum-deposited aluminum. One side was coated through a mask so that a $\frac{1}{4}$ inch diameter contact area was produced. Capacitance of this structure was measured at room temperature on an HP8754A Network Analyzer. The resultant room-temperature relative dielectric constant was 6 over a frequency range of 3–10 MHz, regardless of comonomer ratio, molecular weight or film thickness.

The impulse response of a given film is measured by charging the film through a 100 KΩ input resistor and rapidly discharging through a low output impedance resistor. The switching is performed by a Unitrode GA301 silicon controlled rectifier (SCR). Care is taken to limit the PRF to values allowing full charging to take place, and lead lengths are minimized to reduce inductive ringing.

The film is mounted on a thermocooler to allow for rapid heating and cooling with respect to room temperature. A thermocouple is placed adjacent to the film to measure the substrate temperature.

RESULTS AND DISCUSSION

Figure 1 shows a multiple exposure photograph of the impulse response of a Solvay 66/34 mol% film into a 2.2 Ω output impedance over a temperature range of 20–90°C. The lowest trace represents the response at 20°C and each additional trace represents an incremental increase in temperature of 10°C. The 10 nsec. rise time of the pulse is a result of the switching of the SCR, and the 15–20 nsec. fall time is consistent with the dielectric relaxation for this material reported over this temperature range.[13]

The stored charge, as represented by the discharge voltage across the output resistor, increased dramatically as the film temperature increased through the ferroelectric to paraelectric transition. With an output impedance of 25 Ω, voltage peaks greater than 3 times room temperature are usually recorded. This implies an effective relative dielectric constant and energy storage increases of 10, all recorded with pulse widths of less than 50 nsec.

Figure 2 shows the relative voltage impulse response with rising temperature of commercial films into a 25 Ω output impedance. With the exception of the materials

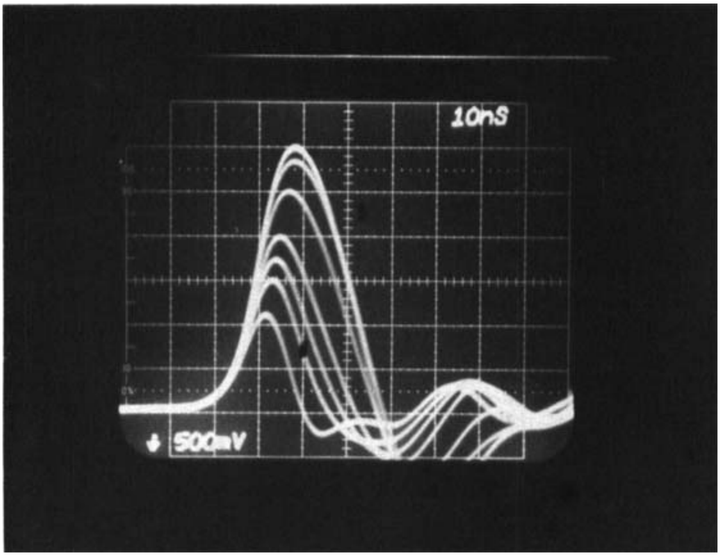

FIGURE 1 Impulse response of a Solvay poly(VF_2/TrFE) film :66/34 molar ratio over ferroelectric to paraelectric transition.

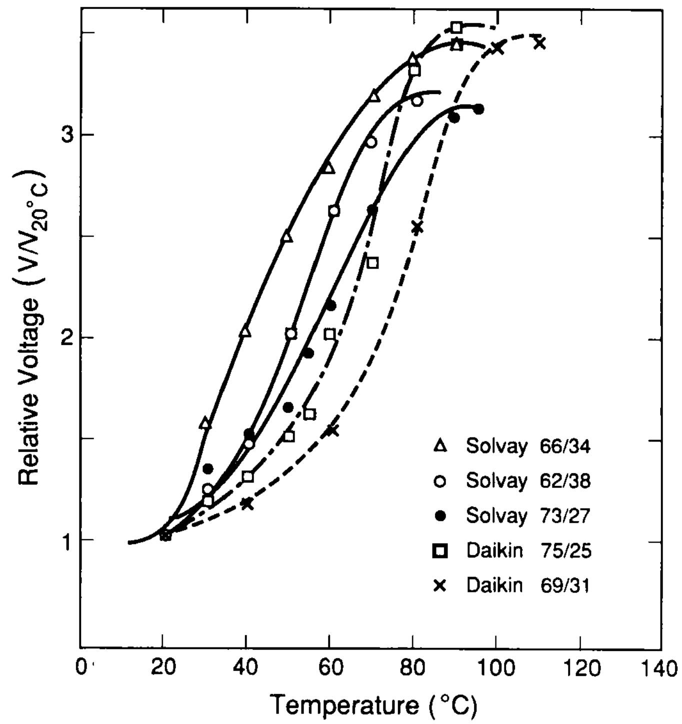

FIGURE 2 Impulse response of commerical poly(VF_2/TrFE) films near Curie temperature normalized to voltage at 20°C.

of 62/38 and 69/31 molar ratios, the curves shift to the right with copolymer temperature dependence. The highest voltage increase of 3.5 was obtained with the Daikin 75/25 molar ratio (for an energy density increase of 12). The film with the lowest temperature is the Solvay 66/34 with a 3-fold voltage increase at 65°C.

Since all films were grown at 130°C for 3 hours, departure from a simple Curie temperature dependence may be due to non optimal growth conditions for a given copolymer ratio and molecular weight. It is known that the time/temperature history is critical for the production of high quality films of a given thickness. For example, if not enough time is allowed, the complete conversion of amorphous to crystalline materials will not take place. If too much time is taken, the biaxial stress will force an isothermal crystal-crystal transition to a second ferroelectric phase.

Figure 3 shows the impulse response of a 65/35 film for two different thicknesses. The 8.2 μm-thick film demonstrates a behavior similar to the 66/34 Solvay film (see Figure 2), with a 3-fold voltage increase at 67°C (compared with 65°C for the Solvay film). The 5.3 μm-thick film moves up in temperature to 80°C and has a lower maximum. Differential scanning calorimetry (DSC) of the thinner film exhibited "splitting" of the Curie and melting temperatures, which is usual evidence of a crystal-crystal transition.

The effect of molecular weight on the impulse response is shown in Figure 4. The two 73/27 films, however synthesized using two different techniques, were of

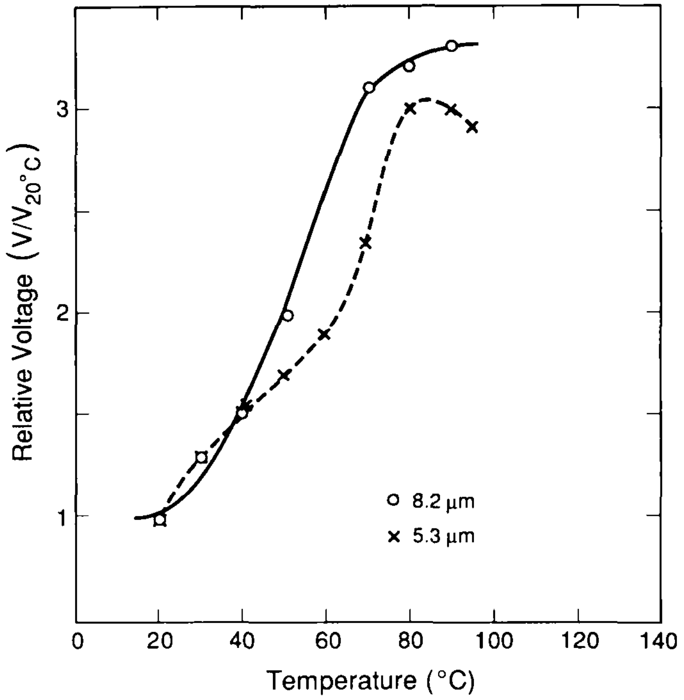

FIGURE 3 Impulse response of Los Alamos poly(VF_2/TrFE) film :65/35 molar ratio near Curie temperature normalized to voltage at 20°C for two different thicknesses.

a comparable quality: the Solvay film had a coupling coefficient of 27% compared with 24% for the Los Alamos film, but the thermal history of the two films was very different. The thermal hysteresis of the 550,000 molecular weight film showed a transition upon heating as much as 40°C higher than upon cooling. The only point of similarity between the two films is a cooling transition of about 90°C.

As a pulse power storage medium, the final question to be addressed is the breakdown field (E_B). For a parallel plate capacitor, the maximum energy density is given by

$$\epsilon_{max} = \int E.D\, dv / \int dv = \kappa\, \epsilon_0\, E_B^2, \qquad (1)$$

where κ is the relative dielectric constant and ϵ_0 is the permitivity of free space and equals 8.85×10^{-12} farad/m.

Figure 5 shows the breakdown field measured on a Solvay 62/38 film of 9 µm thickness using the electrode geometry already described. For comparison, the breakdown field of a 6 µm-thick film of commercial mylar is shown using the same electrode geometry. Since breakdown field is thickness-dependent, the difference between the two materials is somewhat overstated in this figure. In fact, going from 9 to 6 µm, Bongianni[17] measured an increase of dielectric strength of about $\frac{1}{3}$, yielding about the same strength as mylar.

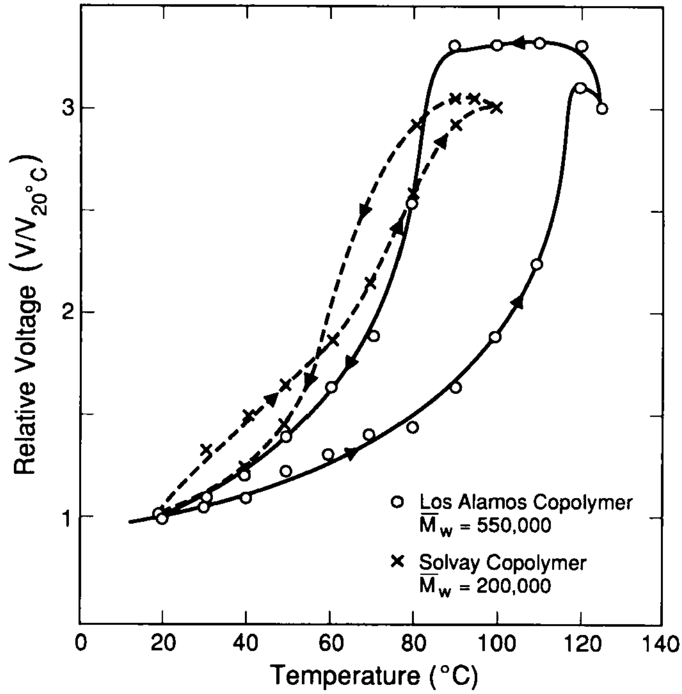

FIGURE 4 Impulse response of poly(VF_2/TrFE) films :73/27 molar ratio at ferroelectric to paraelectric transition for two different molecular weights.

To address the energy density question, we can expect a 100 MV/m breakdown field for a 6 μm-thick (Solvay 66/34) film at 65°C. With a relative dielectric constant of 60, equation (1) yields an $\epsilon_{max} \approx 5$ MJ/m^3, which can be delivered in 30–50 nsec. Considering the speed of delivery of this energy, and that the latter is already in an electrical form, this material is comparable with explosive-driven generators for pulse power applications.

CONCLUSIONS

We have demonstrated in this study that copolymers of vinylidene fluoride and trifluoroethylene, which have high crystal polarization and switching speeds, may become an important energy source for pulse power applications, perhaps better than any known polymer. The energy storage capability of this class of material, which is the highest obtained on any polymer, is characterized by (i) high coupling coefficient and dielectric strength resulting in a high breakdown field, and (ii) a low Curie temperature. In our measurements, we have shown that some discrepancies exist between the various materials. As explained in the text, the film growth conditions (time, temperature) and the film thickness are factors that influence the impulse response of the materials. Furthermore, the materials studied here come from three different sources obtained using different synthesis techniques. The

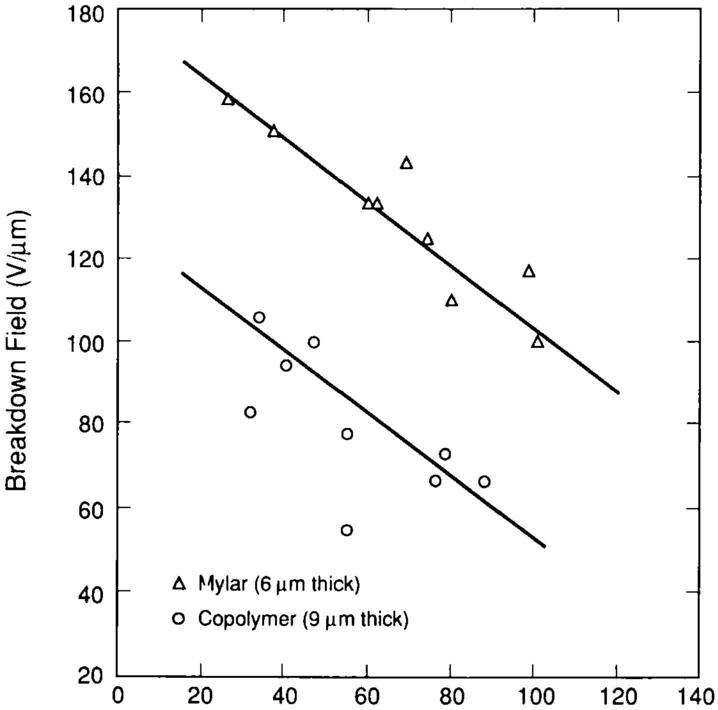

FIGURE 5 Breakdown field *versus* temperature for thin films of mylar and poly(VF_2/TrFE) :62/38 molar ratio.

result of this is materials with different molecular weights and crystallinity due to the chain conformation. However, whatever technique is employed for the synthesis and film growth, optimal conditions should be well defined in order to assess quantitatively the materials properties.

References

1. T. Yagi, M. Tatemoto and J. Sako, *Polymer J.*, **12**, 209 (1980).
2. K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani and H. Tadokoro, *Polymer*, **22**, 1312 (1981).
3. A. J. Lovinger, G. T. Davis, T. Furukawa and M. G. Broadhurst, *Macromolecules*, **15**, 323 (1982).
4. G. T. Davis, T. Furukawa, A. J. Lovinger and M. G. Broadhurst, *Macromolecules*, **15**, 329 (1982).
5. A. J. Lovinger, T. Furukawa, G. T. Davis and M. G. Broadhurst, *Polymer*, **24**, 1233 (1983).
6. K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani and H. Tadokoro, *Polymer*, **25**, 195 (1984).
7. K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani and H. Tadokoro, *Ferroelectrics*, **57**, 297 (1984).
8. H. Tanaka, H. Yukawa and T. Nishi, *Macromolecules*, **21**, 2469 (1988).
9. W. Bongianni, to be published in Ferroelectrics.
10. H. Ohigashi and K. Koga, *Jpn. J. Appl. Phys.*, **21**, L455 (1982).
11. Y. Tajitsu, H. Ogura, A. Shiba and T. Furukawa, *Jpn. J. Appl. Phys.*, **26**, 554 (1987).
12. L. A. Wall, "Fluoropolymers," Wiley-Interscience, New York, 1972.
13. T. Furukawa and Y. Tajitsu, *Ferroelectrics*, **76**, 403 (1987).