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This is an Accepted Manuscript of an article published in [Ferroelectrics](#) on July 1991, available online: <http://www.tandfonline.com/10.1080/00150199108223322>.

Liu, Zhimin, and V. H. Schmidt. "Studies of 80/20 Mol% Vinylidene Fluoride-Trifluoroethylene Copolymer by Brillouin Scattering." *Ferroelectrics* 119, no. 1 (July 1991): 9–15. doi:10.1080/00150199108223322.

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STUDIES OF 80/20 MOL % VINYLIDENE FLUORIDE-TRIFLUOROETHYLENE COPOLYMER BY BRILLOUIN SCATTERING

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(Received June 1, 1990, in final form March 25, 1991)

The hypersonic behavior of oriented and isotropic copolymer of vinylidene fluoride-trifluoroethylene (80/20 mol%) has been investigated by Brillouin scattering. For the oriented samples, the elastic constants have been measured. For both oriented and isotropic sample, the glass and ferroelectric transitions have been observed. The ferroelectric transition behavior observed in the temperature dependence of sound velocity along the stretch direction (X-axis) seems to be different from that deduced from data of sound velocity along the Y-axis (perpendicular to X but in the plane of the sheet). This behavior is discussed from a structural point of view. An independent transition is suggested.

Copolymers of vinylidene fluoride (VF₂) and trifluoroethylene (TrFE) are semi-crystalline and the crystallites exhibit an order-disorder ferroelectric phase transition for VF₂ content between 60% and 80%.¹⁻³ The ferroelectric phase has an all-trans chain configuration in a pseudohexagonal orthorhombic structure while the paraelectric phase has disordered chains hexagonally arranged. The structure has been studied by X-ray diffraction,¹⁻⁴ while the chain conformation was examined by infrared absorption and Raman scattering.⁵

The phase transition dynamics were studied by dielectric measurements,^{4,6,7} ultrasonic relaxation,⁸ and NMR.^{3,9} However, any transitions of the amorphous or crystalline regions affect the elastic properties and can be investigated by Brillouin spectroscopy.¹⁰ Brillouin scattering is also a powerful tool which provides information on various elastic constants.^{10,11} In this paper, we present the elastic constants of oriented 80/20 mol% VF₂/TrFE copolymer and the results for hypersonic properties of oriented and isotropic copolymers. To explain the different behaviors of temperature dependence of sound velocity along the X and Y axes, a separate transition is suggested.

The oriented copolymer samples in this study were provided by Dr. J. F. Legrand having composition of 80 mol% vinylidene fluoride and 20 mol% trifluoroethylene. The sample was unpoled, was drawn by a ratio of 3.7, and then annealed for several hours. The isotropic copolymer was provided by Solvay Technologies, Inc. in powder form. We dissolved this powder in 50% acetone and 50% tetrahydrofuran, then cast the solution on a piece of glass. The resulting film was put in a vacuum oven to remove remaining solvent and annealed for 10 hours. This sample is denoted as S₁.

To compare results for sound velocities along X and Y, we cut the oriented sample film into two pieces for X-axis and Y-axis experiments to make sure these two samples were exactly the same. They will be denoted as S_{ox} and S_{oy}, respectively. The samples were placed in an optical cell described previously.¹² A Lexel

Model 95-2 argon-ion laser operating in a single mode at a wavelength of 5145 Å was used as a light source. The frequency shift was detected by a Burleigh Model R-140 5-pass Fabry-Perot interferometer. All measurements were performed in the 90° scattering geometry. The temperature was controlled to within $\pm 0.2^\circ\text{C}$. The sound velocity is given¹² by $V(T) = \lambda F_B / \sqrt{2}$, where V is sound velocity, λ is wavelength of light in vacuum and F_B is Brillouin frequency shift.

We measured the sound velocity of the oriented sample by rotating the acoustic wave vector q in the film plane (XY -plane) in 5° steps. The plane wave propagation may be described¹³ by the Christoffel equation $\det(LCL^T - \rho V^2) = 0$, where

$$L = \begin{pmatrix} I_1 & 0 & 0 & 0 & I_3 & I_2 \\ 0 & I_2 & 0 & I_3 & 0 & I_1 \\ 0 & 0 & I_3 & I_2 & I_1 & 0 \end{pmatrix}, \quad C = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ & & & & & C_{66} \end{pmatrix}, \quad C = C^T.$$

Here, C is the elastic stiffness tensor, L is the rotation matrix, I is the unit matrix, I_i ($i = 1, 2, 3$) are direction cosines, ρ is sample density, in our case 1.865g/cm^3 , and V is sound velocity. Considering the symmetry properties of space group $m2m$ of the copolymer in the ferroelectric β phase, for which $I_3 = 0$ in our case and $C_{22} = C_{33}$, $C_{12} = C_{13}$, $C_{55} = C_{66}$, this equation reduces to $(a - \rho V^2)(b - \rho V^2) - d^2 = 0$, with $a = C_{11}I_1^2 + C_{66}I_2^2$, $b = C_{66}I_1^2 + C_{22}I_2^2$, $d = (C_{12} + C_{66})I_1I_2$. We fitted the data to the above equation and obtained the elastic stiffness constants: $C_{11} = 20.31$, $C_{22} = 9.81$, $C_{66} = 3.37$, $C_{12} = 6.17$ in GPa. Comparing with the results for 70/30 mol% copolymer with draw ratio of 3.14¹⁰, $C_{11} = 16.09$, $C_{22} = 9.27$, $C_{66} = 2.07$, and $C_{12} = 6.07$, our results are quite reasonable, because of the high draw ratio in our sample. We have not measured elastic stiffness constants for poled sample because Krüger's work has shown that poling of the oriented sample does not change the elastic properties as far as phonon propagation in the film plane is concerned.¹⁰

Figures 1a, b and c show the behaviors of sound velocity of isotropic and oriented samples for sound propagating along the X and Y axes. We fit the data to the equation¹⁴ $V(T) = a_1 - a_2T - a_3[\text{abs}(T - T_g)]$ which describes sound velocity behavior up to room temperature (23°C). The glass transition temperatures T_g (about -25°C) which concern freezing out of motions in the amorphous part of the copolymer are -31.2°C along X-axis (T_{gx}), -30.0°C along Y-axis (T_{gy}), and -25.2°C for isotropic sample (T_{gi}). T_{gx} and T_{gy} are almost the same. It seems that orientation does not affect T_g very much. The tail of the isotropic sample curve below T_g is much flatter than that of the oriented sample. The kink in the sound velocity curves is attributed to the change in the volume expansion coefficient at T_g .^{14,15} Comparing these curves, the change in expansion for the oriented sample is smaller than for the isotropic one because the oriented sample has more ordered structure.

Above room temperature up to 125°C we have studied the temperature dependence of the longitudinal hypersonic velocity for the isotropic and oriented samples for sound propagating along the X and Y axes. Figures 2–4 show heating and cooling runs together. Above the curved part which corresponds to the mixture

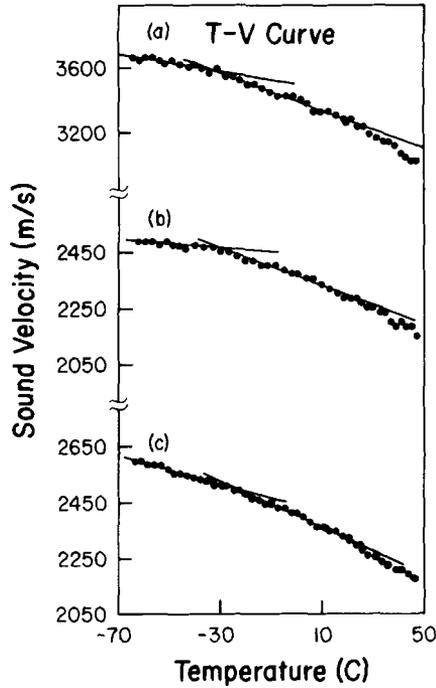


FIGURE 1 Temperature dependence of sound velocity for 80/20 copolymers in temperature range of -65° to 48°C . (a) stretched sample for sound wave propagation along X axis, (b) stretched sample for sound wave propagation along Y axis, (c) isotropic sample.

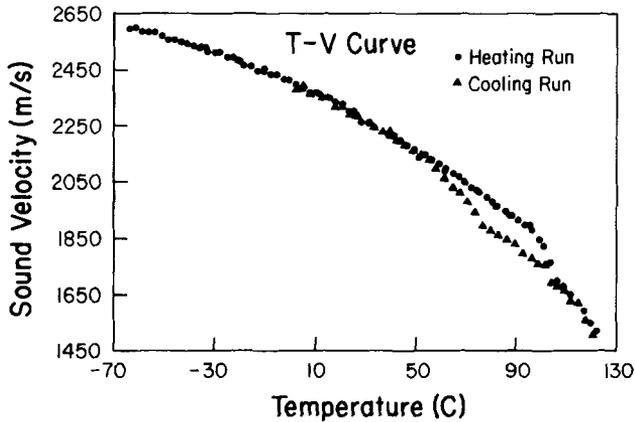


FIGURE 2 Sound velocity for isotropic sample.

of two coexisting phases, the temperature dependence of sound velocity is essentially linear.¹⁰ For the isotropic sample, the transition temperature from ferroelectric to paraelectric T_{ci} is about 107°C , while for the oriented sample with sound propagating along the Y axis, the transition point T_{cy} is about 102°C . The behavior of sound velocity along the X axis is quite strange and we will discuss it in detail later. On the cooling runs, the paraelectric to ferroelectric transitions are completed

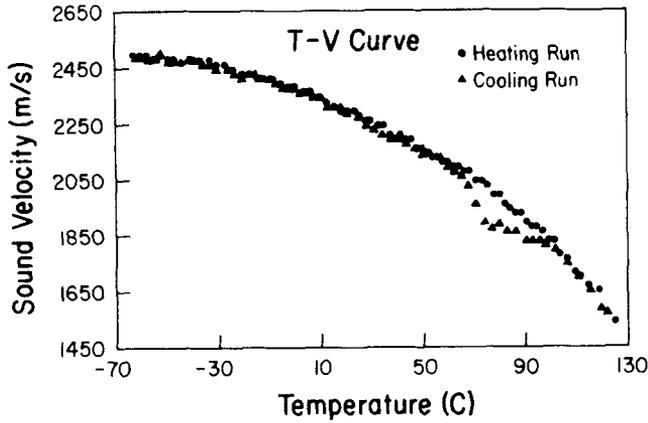


FIGURE 3 Sound velocity for stretched sample for sound wave propagation along Y axis.

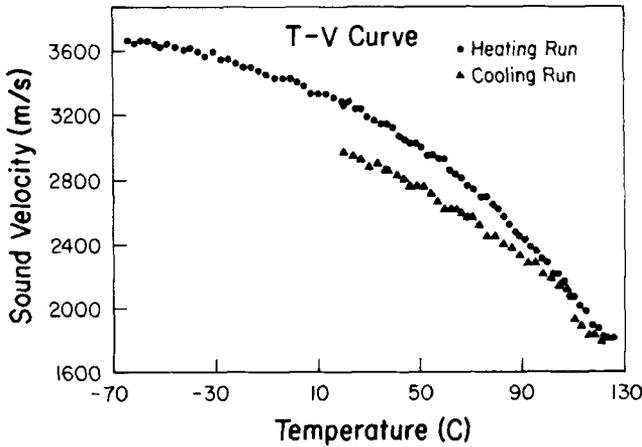


FIGURE 4 Sound velocity for stretched sample for sound wave propagation along X axis.

at about $T_{\text{cic}} = 55^{\circ}\text{C}$ for S_i and $T_{\text{cyc}} = 60^{\circ}\text{C}$ for sample S_{oy} . These transitions show about 50 K broad hysteresis, close to Krüger's results for 70/30 mol% copolymers.¹⁰

Infrared spectroscopic and other methods indicate that with increasing VF_2 content the transition point shifts to higher temperature^{4,9,16} and the thermal hysteresis becomes larger.⁴ Our Brillouin spectroscopic results are consistent with the above conclusion about transition points. For the isotropic sample, the T_c of 80/20 copolymer (107°C) is about 7 K higher than its counterpart of 70/30 copolymer (100°C).¹⁷ For the oriented sample, our T_{cy} (102°C) is about 5 K higher than that for 70/30 copolymer (97°C).¹⁰ The differences of hysteresis range between the counterparts are not clear partially because of some difficulties in determining them accurately.

Figure 4 shows the temperature dependence of velocity of sound propagating along the X axis. First we have not seen any obvious F-P (ferroelectric to paraelectric) transition point, not only because there is no obvious border between the straight line in the paraelectric phase and curved line in the coexisting phase

but also because we cannot determine the hysteresis range. Above 125°C, the sample suffered a premelting effect and the Brillouin spectrum became very bad, so we had to stop at 125°C. The T_c values for 80/20 copolymer obtained previously are 121°C by dielectric constant measurement for an unstretched but poled sample,¹⁸ 138°C by x-ray diffraction and infrared spectroscopy,² and 138°C according to manufacturer's product data.¹⁹ Apparently, T_c is above 125°C for 80/20 copolymers, so we can reach this temperature but can not determine T_c because Brillouin scattering requires a range of T about T_c so a slope change at T_c can be observed. In our experiment, we got different T_c along different axes for similar samples. The same thing happened in Krüger's work.¹⁰ In his 70/30 copolymer results the T_c obtained from Y-axis sound velocity data is 97°C and that from X-axis data is 117°C. Krüger identified both of them as the same F-P transition points and explained the 20°C difference between them as due to the different annealing times used in preparing the samples. But this explanation can not be used in our case because our two samples for measurements of sound along the X and Y axes are exactly the same. Even if the annealing process affects the T_c value, it is hard to believe this effect is great enough to make a 20°C difference between T_{cx} and T_{cy} .

For the cooling run the sound velocity temperature dependence is strange, too. The cooling curve separated from the heating curve at the beginning of the cooling run and did not rejoin the heating curve until below T_g (the data below 15°C have not been shown in Figure 4). We used similar samples (cut from one piece) to make several measurements in the following ways: 1) Heated sample up to 125°C directly in 2.5 hours without stopping to minimize the effect of heating time, then started cooling run measurement, as shown in Figure 4. 2) Heated the sample only up to 110°C and to 100°C respectively to see the effect of premelting on cooling behavior. All three cooling curves have similar behavior. After these runs, we measured the X-axis sound velocity for these samples at room temperature. It had decreased permanently compared with that for the unused sample, but surprisingly, along the Y axis the sound velocity has almost the same value as for the unused one. The reason is not clear yet, but we believe that the behaviors of sound velocity vs. temperature along the C—C bonded polymer chains and perpendicular to these chains are quite different.

It has been thought that T_{cy} should be the same as T_{cx} because both should correspond to a single ferroelectric to paraelectric phase transition.¹⁰ The question arises as to which one, T_{cx} or T_{cy} , has the same physical significance as the ferro/para transition point T_c measured by other methods. Also if T_{cx} is T_c , then what kind of transition does T_{cy} (102°C) correspond to?

We review, for comparison with our 80/20 copolymer data, other results indicating two transitions which however are all for 70/30 VF₂/TrFE copolymers. Brillouin scattering for oriented samples¹⁰ yielded $T_{cx} = 117^\circ\text{C}$ and $T_{cy} = 97^\circ\text{C}$ while our result for an isotropic sample¹⁷ is $T_{ci} = 100^\circ\text{C}$. Dielectric constant measurement¹⁸ indicated $T_c = 99^\circ\text{C}$ while other methods gave $T_c = 105^\circ\text{C}$. Faria and Latour²⁰ made thermally stimulated depolarization (TSD) measurements on poled but unstretched samples with applied mechanical vibration which gave superimposed electrical noise from the piezoelectric effect but only when the sample was in a piezoelectric (probably ferroelectric) phase. They found two peaks upon heating, first an "A" peak near 100°C which they attributed to a ferro-ferroelectric transition

of unspecified nature, and then a sharper “B” peak at 108°C where the piezoelectric noise ceased, which they consider to be the ferro-paraelectric transition. Delzenne²¹ reported that the ferro-paraelectric transition takes place in two stages, or that perhaps there are two transitions. From these results, we conclude that the process of transition from ferro to paraelectric phase is unclear.

Considering the unique property of being able to choose wave vector q direction in Brillouin scattering, one can study independently the sound velocity behavior along the oriented axis (C—C bonds) and along the Y-axis (C—H, C—F bonds). According to our data and the above review, we believe that the supposedly existing two transitions are transitions in the C—C bond direction and in the C—H, C—F bond direction which happens at different temperatures. We suggest here a model to explain our experimental results. With increasing temperature the crystal cell expands continuously, until at some temperature the copolymer exhibits a structural transition. This transition is mainly related to *intermolecular* change. It corresponds to a discrete change in crystal cell dimension as reported for 52/48 copolymers by Lovinger.²² Above this transition point, the sound velocity temperature dependence has a different slope. As discussed above, in this temperature range the copolymer is ferroelectric and keeps the all-trans conformation. This is why this transition was observed only in the Y-axis sound velocity which mainly reflects the intermolecular bonding and is insensitive to intramolecular change. Even at temperatures above 138°C, for which the all-trans conformation becomes disordered helical, we expect that the ferro/para transition will not be observed in the Y-axis sound velocity because the intermolecular bonding in that direction is similar for all-trans and helical conformations for stretched but unpoled samples. So we identify T_{cy} to be a structural transition point which has totally different physical significance from T_{cx} . By similar reasoning, if there is a structural transition in the X (C—C bond) direction, sound waves propagating along Y will not see it. Only T_c (T_{cx}) which corresponds to transition from all trans to disordered helical conformations is observed because this sound wave is only sensitive to change in the X direction, *intramolecular* change. So we consider the T_{cx} in Krüger’s work for 70/30 copolymer to be the Curie point T_c .

To confirm the above model, we recommend further Brillouin scattering study of more samples with different compositions and measurement of temperature dependence of sound velocity along the X and Y axes simultaneously. In addition, further X-ray diffraction studies may provide more information about structural transitions along different axes. There are very different lattice constant changes along the X and Y axes. In the ferroelectric phase the unit cell dimensions of 52/48 mol% copolymer crystals are $a = 9.12 \text{ \AA}$, $b = 5.25 \text{ \AA}$, and c (in our case x) $= 2.55 \text{ \AA}$. They become $a' = 9.75 \text{ \AA}$, $b' = 5.63 \text{ \AA}$, $c' = 4.60 \text{ \AA}$ (cell doubling along c) in the paraelectric phase.² The changes are +6.9%, +7.2% and -9.8% (considering cell doubling) respectively. The increases for a and b are almost the same, while c decreases. Unfortunately, although a , b , c vs. T data exist for other compositions,^{2,22} none exist for the 80/20 composition. Such data might show a and b changes occurring at a different temperature than c changes. Accordingly, continuous temperature dependence study of X-ray diffraction of lattice constants is also recommended.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. J. F. Legrand and Solvay Technologies, Inc. for kindly providing samples, and Dr. G. F. Tuthill for useful discussions. This work was supported by Department of Energy Grant No. DE-FG06-87ER45292.

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NOTE ADDED TO PROOF

After this manuscript was submitted, Brillouin scattering results on 80/20, 70/30, and 60/40 copolymers were published by J. K. Krüger, M. Prechtel, and J. F. Legrand, *Ferroelectrics*, **109**, 315 (1990).