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BRILLOUIN SPECTROSCOPIC STUDIES OF VF₂/TFE COPOLYMERS

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The temperature dependence of sound velocity was studied in thin sheets of isotropic and oriented copolymers of vinylidene fluoride (81 mol%) and tetrafluoroethylene (19 mol%) by Brillouin scattering. For oriented samples, we studied the differences between the sound velocities along the x -axis (chain direction) and y -axis (perpendicular to x in sample plane). The ferroelectric-paraelectric transition points were not observed because this T_c is very close to the melting point of these copolymers. A partial thermal hysteresis loop was observed for all samples. The transitions from paraelectric phase to ferroelectric phase are completed near 85°C for the isotropic sample and the oriented sample with sound propagating along y . For propagation along x -axis, this transition is completed at about 100°C which is very close to results from other methods. The behaviors of temperature dependence of sound velocity along x and y axes are quite different, as we observed also in VF₂/TrFE copolymers. It allows generalization of our conclusions concerning copolymers of vinylidene fluoride and trifluoroethylene.

INTRODUCTION

The polymer vinylidene fluoride (PVF₂) and its copolymers with trifluoroethylene (TrFE) and tetrafluoroethylene (TFE) are ferroelectric.¹⁻³ A copolymer of vinylidene fluoride and tetrafluoroethylene (hereafter abbreviated VF₂/TFE) prepared under any crystallization conditions, possesses the form I (β phase) crystal only, while the form I crystal of VF₂ can be obtained from the form II crystal by stretching a film or by applying a very high electric field.⁴ The ferroelectric to paraelectric (FE-PE) phase transition was never observed in PVF₂ because it may be obscured by melting temperature which caused an argument concerning whether PVF₂ is ferroelectric or not. The FE-PE transition has been commonly observed in copolymers with TrFE, but the introduction of the new chemical species—CHF—created suspicion that the CHF group might cause this transition. Copolymer of TFE are of particular interest because they do not introduce this new chemical species—CHF— or tacticity defects as does TrFE, yet their FE-PE phase transitions have been detected.⁵ They can be viewed simply as VF₂ containing an increased number of head-to-head (CF₂—CF₂—) defects.⁶ Lovinger¹ indicated that the FE-PE transition point is so close to melting point that no transition can be observed. Later, Lovinger *et al.* detected the Curie transition beginning at about 122°C in a differently prepared sample.⁵

Any transitions occurring in the amorphous or crystalline regions in general affect the elastic properties and can therefore be investigated by Brillouin scattering. Krüger *et al.* have studied 70/30 VF₂/TrFE copolymers by Brillouin scattering.⁷ They have detected the FE-PE phase transitions by analyzing kink, between segments with different slopes in the sound velocity vs. temperature curves. Also they observed obvious hysteresis between heating and cooling runs. In this paper we

present the temperature dependence of sound velocity for an isotropic sample and for a stretched sample with sound propagating along the x axis (chain direction) and the y axis (perpendicular to x axis in sample plane). We observed glass transitions and partial FE-PE phase transitions by the same analysis method as Krüger used. The purpose of this work is to compare the different transition behaviors along the chain (intramolecular) direction and along the intermolecular direction. We previously got different transition temperatures from the temperature dependence of sound velocity along the x and y axes for VF₂/TrFE copolymers with various compositions. The present studies of VF₂/TFE will clarify whether that difference is general for VF₂ copolymers or whether it results from introduction of TrFE.

EXPERIMENT

Copolymer samples were prepared from Kynar 7201, a random copolymer of VF₂/TFE with 81/19 molar ratio in powder form manufactured by Pennwalt Corporation. Light scattering experiments need a transparent film as sample. We prepared this film by the following procedure. First we put the copolymer powder between two pieces of copper with a special plastic film of melting point near 400°C between the copper and powder. The pieces of copper were compressed together by a strong spring. Then we heated the whole fixture to 180°C for several minutes and quenched it in 0°C water. Because the time above melting temperature was not long enough, the powder was melted but had not formed a uniform film. Then we reheated the fixture to 180°C and kept it at this temperature for 15 minutes and quenched it to 0°C to obtain a transparent film. We found that the reheat procedure is necessary to obtain samples with smooth surface and correspondingly good optical properties. A single heating cycle only creates an opaque or translucent film. The samples prepared by this quenching method have melting point of 126°C.⁸ Films thus obtained were stretched by a ratio of 3.5:1 at 65°C, then annealed at 100°C for 24 hours. Annealed samples were cooled naturally under tension. We measured the temperature dependence of sound velocity for three samples. One is isotropic and the other two are stretched samples which were used for measurement of sound velocity along the x and y axes respectively. In the following discussion, we denote them and their transition points by subscripts i , x , y (T_{gi} .. for glass transition and T_{ci} .. for FE-PE transition).

The sample was placed in an optical cell described in a previous paper.⁹ The temperature of the optical cell was controlled within $\pm 0.2^\circ\text{C}$. A Lexel model 95-2 argon-ion laser operating in a single mode at wavelength 5145 Å was used as a light source. The frequency shifts were measured by a piezoelectrically scanned Burleigh 5-pass Feby-Perot (F-P) interferometer. The sound velocity V was related to the frequency shift F_B by¹⁰

$$V = \lambda F_B / \sqrt{2},$$

in the case of 90° scattering geometry, where λ is the laser wavelength. We used one sample for both heating and cooling runs. First we cooled the sample to about -65°C without measurement, then heat it with heating rate of about 0.5°/minute.

The temperature steps varied between 1.5° and 2.5°. Each step lasts about 25 minutes for a number of scans by the F-P interferometer. When the temperature is just close to copolymer melting point at about 120°C, the sample becomes soft which can be observed from the optical windows and from the degraded Brillouin spectrum. We held this temperature for about 10 minutes, then reduced temperature to start the cooling run.

RESULTS AND DISCUSSION

Figure 1a–c shows the temperature dependence of velocity of sound propagating along the x (Figure 1a) and y (Figure 1b) axes for stretched samples, and for an isotropic sample (Figure 1c), in the temperature region from -65° to 40°C where the glass transitions occur. We fit these data to the equation¹¹

$$V(T) = a_1 - a_2 T - a_3[\text{abs}(T - T_g)] ,$$

which describes sound velocity up to room temperature. The fitting procedure determined the glass transitions T_g which concern freezing out of motions in the amorphous part of the copolymer. The parameters of $a_i = (i = 1,2,3)$ describe the slopes of sound velocity *vs.* temperature curves in this temperature region. The $T_{gx} = -45^\circ\text{C}$ and $T_{gy} = -47^\circ\text{C}$ values for the stretched sample are very close to the values near -50°C obtained by other methods.^{5,8} They are almost the same because these transitions correspond to the same physical process in similar samples. Significant differences were found in T_{cx} and T_{cy} for similar samples, which will be discussed later in detail. The value $T_{gi} = -40^\circ\text{C}$ is a little higher than T_{gs} and T_{gy} . The stretched (oriented) copolymers have more orderly structure than isotropic ones and may have lower glass transition. The rates of decrease of sound speed *vs.* temperature in copolymers of VF₂/TFE are 5.5 m/s per degree along x , 3.5 m/s per degree along y and 3.75 m/s per degree for the isotropic sample. The decrease rate for the isotropic sample is between those along x and y because the crystal cells take random directions. These results are similar to those of 4.6 m/s, 2.1 m/s and 2.9 m/s per degree in 80/20 VF₂/TrFE copolymers.¹²

Figures 2–4 show temperature dependence of sound velocity up to about 120°C for the above-mentioned three samples. Determining the FE-PE phase transitions is very difficult by Brillouin scattering because this transition beginning at 122°C is thwarted by the onset of melting for quenched samples with melting temperature $T_m = 126^\circ\text{C}$.⁵ In the studies of this copolymer by Brillouin scattering, we identified FE-PE phase transitions by detecting kinks between basically linear parts with different slope of sound velocity *vs.* temperature curves.⁷ It is difficult to observe the completed phase transition in these samples by Brillouin scattering. In our experiment, the samples suffered premelting effects at temperatures above 110°C and the Brillouin spectra become so bad above 120°C that the data seem untrustworthy. We have not observed a completed phase transition but have seen some clues of this transition. In Figures 2 and 3, the temperature dependence of sound velocity along y and in the isotropic sample show a clear tendency toward finishing the transitions, which appear likely to be completed not very above from the temperature where we stopped. We have determined that the paraelectric to fer-

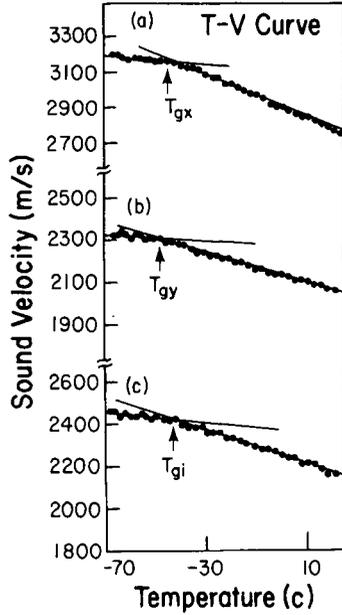


FIGURE 1 Temperature dependence of sound velocity for 81/19% VF₂/TFE copolymers in temperature range of -65° to 23°C (a) stretched sample for sound propagation along x axis, (b) stretched sample for sound propagation along y axis, (c) isotropic sample.

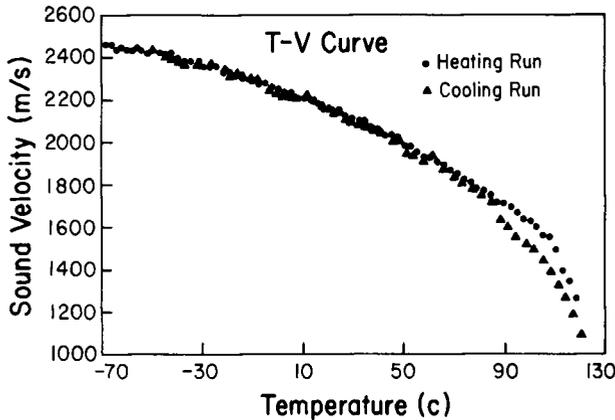


FIGURE 2 Sound velocity for isotropic sample, ○: heating run, △: cooling run.

roelectric phase transition is completed at about 85°C upon cooling and have seen obvious hysteresis.

In Figure 4 showing the velocity of sound propagating along x, we could not see any tendency toward completing the FE-PE transition near our highest temperature. We consider the junction point where the cooling run coincide with heating run as the para/ferro transition T'_c , at about 100°C which is close to Lovinger's result of 95°C¹ and 110°-115°.⁵ Comparing Figure 4 with Figures 2 and 3, we conclude that the transition behaviors of this copolymer along x and y axes are quite different even though the transition points have not been determined accu-

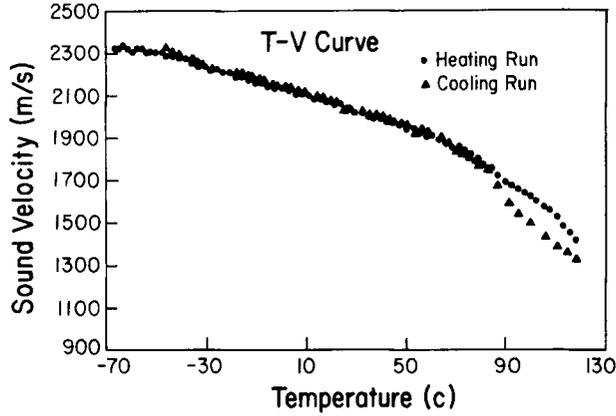


FIGURE 3 Sound velocity for stretched sample for sound wave propagation along y axis. \circ : heating run, \triangle : cooling run.

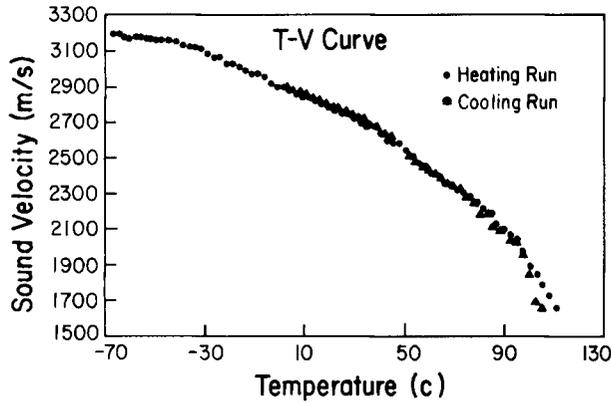


FIGURE 4 Sound velocity for stretched sample for sound wave propagation along x axis. \circ : heating run, \triangle : cooling run.

rately. We see that T'_{cx} is not equal to T'_{cy} , and can infer that T_{cx} is not equal to T_{cy} from the Figures.

The difference between T_{cx} and T_{cy} in a similar sample is not a new discovery. Krüger *et al.*⁷ found 20°C difference between T_{cx} and T_{cy} in their Brillouin scattering studies for 70/30 mol% VF_2/TrFE copolymers. They thought that T_{cx} and T_{cy} correspond to the same physical process and explained this difference as an annealing effect, but this conclusion is open to question because the samples they used in measurements along x and y were prepared with different annealing times. We found the same thing happened for copolymers of VF_2/TrFE with various compositions from 80/20, to 60/40 mol%.¹² The x and y samples used in our measurements were cut from the same piece so they have the same annealing history. The difference between T_{cx} and T_{cy} can not be explained as an annealing effect. We believe that this difference means that T_{cy} and T_{cx} represent total different physical processes or transitions. This difference is also reflected in the para/ferro

phase transitions. As mentioned above, T'_{cy} is about 85°C and T'_{cx} is about 100°C

Brillouin scattering has the unique characteristic that allows one to study the properties related to the special direction we are interested in. The sound velocity along y axis mainly reflects the change of intermolecular van der waals bonding. The sound velocity along x axis mainly reflects the change of intramolecular, C—C bonds. There is no reason to presume T_{cx} and T_{cy} should be the same. The FE-PE phase transition in ferroelectric copolymers is caused by intramolecular change from the all-trans conformation to irregular TGT \bar{G} conformations. So the T_{cx} in Brillouin scattering should correspond to the well-known Curie temperature found in other measurements. T_{cy} corresponds to a transition in the intermolecular direction, and may reflect a discrete structural change in the ferroelectric phase.

We review, for comparison with our VF₂/TFE copolymer data, other results indicating two transitions which, however, are all for 70/30 VF₂/TrFE copolymers. Faria and Latour¹³ 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. Delzenne¹⁴ 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.

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 interchain direction which happen at different temperatures. 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 the 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.

We attribute the similar transition behavior for VF₂/TFE copolymers to similar phenomena as in VF₂/TrFE even though the ferro/para transitions have not been observed completely. Our results for VF₂/TFE allow generalization of our conclusions about two transitions obtained from the copolymers of VF₂/TrFE and exclude any possible effect of the atomic group CHF found only in VF₂/TrFE copolymers. Because VF₂/TFE copolymer is equivalent to VF₂ containing a higher percentage of head-to-head defects, it is a reasonable inference that two-transition behavior should be possible in PVF₂ homopolymer, to the extent that it is not obscured by melting.

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