



Phase transition studies of vinylidene fluoride copolymers with trifluoroethylene and tetrafluoroethylene using brillouin scattering
by Zhimin Liu

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University
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Abstract:

The hypersonic behaviors of copolymers of vinylidene fluoride with trifluoroethylene (VF₂/TrFE) and tetrafluoroethylene (VF₂/TFE) of various compositions have been investigated by Brillouin scattering in the temperature range from -65° to 125° C. We present a theoretical explanation of the transition behavior for this kind of semicrystalline material. For VF₂/TrFE and VF₂/TFE copolymers, the glass transitions are clearly seen. An anomaly of sound attenuation near the paraelectric/ferroelectric transition was first studied in 70/30 mol% VF₂/TrFE copolymers. Split Brillouin peaks were observed near that transition point. For stretched 80/20 and 60/40 mol% samples, the temperature dependence of sound velocity along x (chain) and y (interchain) directions has been studied separately. The phase transitions obtained from measurement along x and y directions are certainly different. We present a model which suggests two transitions in this temperature range. T_{cy} is identified as a transition only related to interchain change and T_{cx} as the ferro/para transition. Studies of VF₂/TFE copolymers yield similar results. This suggests that conclusions concerning 81/19 mol% VF₂/TrFE may be generalized to include VF₂ homopolymer since VF₂/TFE can be viewed simply as VF₂ containing an increased number of head-to-head (CF₂-CF₂-) defects.

PHASE TRANSITION STUDIES OF VINYLIDENE FLUORIDE
COPOLYMERS WITH TRIFLUOROETHYLENE AND
TETRAFLUOROETHYLENE USING BRILLOUIN SCATTERING

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APPROVAL
of a thesis submitted by
Zhimin Liu

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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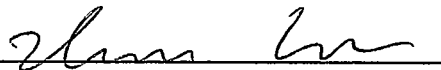
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ABSTRACT

The hypersonic behaviors of copolymers of vinylidene fluoride with trifluoroethylene (VF_2/TrFE) and tetrafluoroethylene (VF_2/TFE) of various compositions have been investigated by Brillouin scattering in the temperature range from -65° to 125° C. We present a theoretical explanation of the transition behavior for this kind of semicrystalline material. For VF_2/TrFE and VF_2/TFE copolymers, the glass transitions are clearly seen. An anomaly of sound attenuation near the paraelectric/ferroelectric transition was first studied in 70/30 mol% VF_2/TrFE copolymers. Split Brillouin peaks were observed near that transition point. For stretched 80/20 and 60/40 mol% samples, the temperature dependence of sound velocity along x (chain) and y (interchain) directions has been studied separately. The phase transitions obtained from measurement along x and y directions are certainly different. We present a model which suggests two transitions in this temperature range. T_{cy} is identified as a transition only related to interchain change and T_{cx} as the ferro/para transition. Studies of VF_2/TFE copolymers yield similar results. This suggests that conclusions concerning 81/19 mol% VF_2/TrFE may be generalized to include VF_2 homopolymer since VF_2/TFE can be viewed simply as VF_2 containing an increased number of head-to-head ($\text{CF}_2\text{-CF}_2\text{-}$) defects.

CHAPTER I

INTRODUCTION

The polymer polyvinylidene fluoride (PVF₂), formula (CH₂-CF₂)_n, and its copolymers (VF₂/TrFE) with trifluoroethylene, monomer CHF-CF₂ and P(VF₂/TFE) with tetrafluoroethylene, monomer CF₂-CF₂, exhibit a variety of scientifically interesting and technologically important properties which have made it the most widely investigated piezoelectric polymer.¹ Ferroelectricity in semicrystalline polymers and copolymers has been revealed.²⁻⁴ The appearance of ferroelectricity in PVF₂ and its copolymers is closely related to the structural characteristics of the β crystalline phase (point group m2m) of PVF₂.⁵ This structure consists of aligned all-trans (TT conformation) chains which aligns the CH₂-F₂ dipoles perpendicular to the chain axis. Ferroelectric models predict existence of a Curie temperature for this polymorph above which the all-trans conformation transforms to a paraelectric phase which has irregular TGT $\bar{G}$ helical conformation (point group probably 6/mmm). However, such a Curie temperature has not been found, and it is generally believed⁶ that this

temperature may lie within the region of melting of polyvinylidene fluoride. A lot of evidence such as its pyroelectricity, and field-induced reorientation of VF_2 dipoles with corresponding hysteresis curves, points clearly to the ferroelectric nature of VF_2 . However, arguments to the contrary have invoked absence of a clearly discernible Curie temperature (i.e. the temperature of the ferroelectric-paraelectric phase transition). The strongest evidence so far for existence of a Curie temperature has come from the work on copolymers of vinylidene fluoride and trifluoroethylene. Attention has also been directed toward copolymers of vinylidene fluoride with other fluorocarbons, partially in the hope that Curie transitions would be unequivocally observed. Extensive studies on phase transitions of copolymers of VF_2/TrFE and VF_2/TFE with various compositions have been conducted by a number of authors using x-ray diffraction^{7,8}, NMR⁹, thermally stimulated depolarization¹⁰, acoustic study¹¹, dielectric measurement^{12,13}, and IR spectra¹⁴.

Summarizing, copolymers of VF_2/TrFE , and VF_2/TFE exhibit ferroelectric phase transitions for VF_2 content between 60 and 80 mol%. This transition mainly occurs intramolecularly (i.e. by conformational changes leading to a nonpolar chain structure) rather than intermolecularly (i.e. by randomization of dipole vectors of polar chains).¹⁵

Brillouin scattering study of phase transitions

Brillouin scattering spectroscopy which measures the frequencies and linewidths of acoustic phonon modes provides data on the sound velocities and elasticities in the material. The basis of this method is the following. When a laser beam with frequency ω_0 passes through a medium, the illuminated parts of this medium emit or scatter their own light which includes frequency components of ω_0 and $\omega_0 \pm \omega_B$. The ω_B is called the Brillouin frequency shift which provides insight into the nature of the medium. The Brillouin frequency shift ω_B relates to the sound velocity V in the medium along a certain direction by the Brillouin equation:

$$\omega_B = \frac{2\pi V}{\lambda_0} (n_i^2 + n_s^2 - 2n_i n_s \cos \theta)^{\frac{1}{2}} \quad \text{I-1}$$

where λ_0 is the incident light wavelength, n_i and n_s are refractive indexes for incident and scattered light respectively, and θ is the angle between the incident and scattered light directions inside the medium. The sound velocity is related to the elastic constant C by:¹⁶

$$C = \rho V^2 \quad \text{I-2}$$

where ρ is the mass density of the medium. A phase transition occurring

in the amorphous or crystalline region affects the elastic properties and therefore can be investigated by Brillouin scattering. Krüger¹⁷ in 1986 presented the first results on hypersonic behavior in the phase transition for 70/30 mol% VF₂/TrFE copolymers using Brillouin scattering. This report of Brillouin scattering studies of this kind of polymer appeared later than studies by other methods partially because of difficulties in experiment and theory.⁷⁻¹⁴

Structural phase transitions

Transitions accompanied by microscopic structural change are called structural phase transitions. In particular, ferroelectric transitions are structural phase transitions. Structural phase changes in solids are quite often accompanied by observable acoustic anomalies.¹⁸ In some cases a particular elastic constant or combination of elastic constants may fall to zero at the phase transition. In many materials such anomalies are due to interaction between acoustic modes and other lattice vibrational or dielectric modes that fall in energy as the phase transition is approached from either side. Such modes are referred to as soft modes. The emphasis in light scattering of phase transitions was gradually shifted from simple soft mode analysis to aspects of spectra associated with mode coupling, polarization coupling with the phonons, and modification of the classical

soft mode behavior due to critical fluctuations. Landau made a momentous contribution to understanding of phase transitions by expanding the free energy in terms of long-range order parameters Q . On the basis of Landau's theory, Rehwal¹⁸ provided a detailed coupling theory for elastic constant behavior in structural phase transitions. Many researchers studied phase transition behaviors corresponding to various coupling modes by Brillouin scattering for some single crystals. Their experimental results can be explained by that phenomenological theory.

Phase transitions in semicrystalline materials

PVF₂ and its copolymers are semicrystalline with crystallinity of about 50% in PVF₂ and more in its copolymers. These polymers and copolymers contain crystals with different sizes embedded in an amorphous matrix. This causes difficulties in both experiment and theoretical analysis. In experiment, the samples are translucent rather than completely transparent which causes high noise level in Brillouin spectra. In theoretical analysis, the sound velocity behavior across phase transitions is totally different from the prediction of theory because crystals with different sizes or different environments have different transition temperatures. There is no theory for phase transition behavior in semicrystalline material. This may be why the first research work on phase

transitions in this kind of copolymer using Brillouin scattering appeared rather late and the first researcher presented the experimental results without theoretical explanation.

Outline of the present work

We measured the temperature dependencies of sound velocity and attenuation for 60/40, 70/30, 80/20 mol% VF_2/TrFE and 81/19 mol% VF_2/TFE copolymers. There are several aspects of this work: (1) We performed similar experiments for similar copolymers with different compositions to confirm that the transition behavior revealed in Krüger's work is common to other samples with higher or lower VF_2 content. Then we developed some physical explanations for this kind of behavior in semicrystalline materials. (2) We obtained the first attenuation data for 70/30 mol% VF_2/TrFE isotropic copolymer. (3) We reconfirmed by Brillouin scattering the well-known fact that the transition temperature in VF_2/TrFE copolymers increases with increasing VF_2 content. (4) There was an unresolved suspicion, based on Krüger's results, that the transition temperature indicated by the temperature dependence of sound velocity along the stretch direction (x axis) is significantly different from that indicated by the data for sound velocity perpendicular to the x direction. Krüger believed that such a difference does not actually exist. We confirmed

that this difference really exists and suggest a "two transition" model to explain it.

In Chapter II, we review the basic light scattering theory and the coupling theory relative to phase transitions. Chapter III describes the experimental system and how the sound velocity and attenuation were measured. Chapter IV presents the experimental data of sound velocity and attenuation. In Chapter V, we present a theoretical explanation for the phase transition behavior in semicrystalline materials, explain the "two transition" model and provide an overall discussion of our results.

CHAPTER II

THEORY OF BRILLOUIN SCATTERING IN VINYLIDENE FLUORIDE-
TRIFLUOROETHYLENE COPOLYMERSIntroduction

In this chapter we will present a description of the Brillouin spectrum of vinylidene fluoride-trifluoroethylene (VF_2/TrFE) copolymers. The material is semicrystalline with crystallinity of about 50%¹⁹ in VF_2 polymer and more in their copolymers⁹ depending on thermal history. The copolymer consists of very small-size crystals (100 to 200 Å, much less than visible light wavelength) embedded in the amorphous matrix.²⁰ The β phase is currently the most important in the PVF_2 polymers and their copolymers. The unit cell of $\beta\text{-PVF}_2$ was found by Gal'perin et al.²¹ to have space group $m2m$. Its a and b dimensions ($a = 5.58$ Å, $b = 4.91$ Å) render this cell pseudo-hexagonal (the difference from true hexagonal being less than 1%). In our calculation of stiffness constants, we will take it as a hexagonal crystal.

The complete theory of Brillouin scattering in cubic crystals has been

given by Benedek and Fritsch.²² Nobody has yet provided the theory of Brillouin scattering in semicrystalline material. We will present here the calculation of Brillouin scattering in hexagonal crystals and leave the explanation for semicrystalline material for Chapter IV.

The Spectrum of the Scattering Field

The scattered beam radiated by the oscillatory polarizations is subject to Maxwell's equations. The medium contains about 10^7 atoms in a region as small as the cube of the light wavelength. Hence for dimensions of this order a solid may be regarded as a continuum. A light wave passing through the medium produces an oscillating dipole moment per unit volume of polarization $\vec{P}$ at point $\vec{r}$ and time t which radiates or scatters electromagnetic waves in all directions. According to electromagnetic theory²³ we simply write down the electric field $d\vec{E}'$ at the field point R created by the oscillating dipole moments within a volume $|d^3r| \ll \lambda^3$

$$d\vec{E}'(\vec{R}, t) = \left[\frac{\hat{I}_{\vec{R}-\vec{r}} \times (\hat{I}_{\vec{R}-\vec{r}} \times \partial^2 \vec{P}(\vec{r}, t) / \partial t^2)}{C^2 |\vec{R}-\vec{r}|} \right]_{t'=t-|\vec{R}-\vec{r}|/C} \quad \text{II-1}$$

where the vector $\vec{R}$ is the observation point outside the medium and $\vec{r}$ is the radiating point inside the medium. The unit vectors $\hat{I}_{\vec{R}-\vec{r}}$ and $\hat{I}_k$ are

shown in Figure 1. If the incident light intensity is low the local polarization is linearly proportional to the electric field, i.e.

$$\vec{P} = \vec{\alpha} \cdot \vec{E} \quad \text{II-2}$$

where $\vec{E}$ is the electric field of the incident wave within the medium.

$$\vec{E}(\vec{r}, t) = \vec{E}_0 e^{i(\vec{k}_0 \cdot \vec{r} - \omega_0 t)} \quad \text{II-3}$$

where $k_0 = n\omega/c$ is the wave vector of the light wave and α is a tensor polarizability, while n is the refractive index. To analyze the origin of the scattering it is convenient to decompose α into its time average part $\langle \alpha \rangle$ plus the time-space fluctuations $\delta\alpha(\vec{r}, t)$ produced by the thermal fluctuations in the medium. The thermal fluctuations in a crystal cause off-diagonal components to appear in the polarizability tensor so that we regard $\delta\alpha$ as being a tensor whose elements fluctuate in time. Then we have the polarization at each point in the medium as:

$$\vec{P}(\vec{r}, t) = [\langle \vec{\alpha} \rangle + \delta\vec{\alpha}(\vec{r}, t)] \cdot \vec{E}_0 e^{i(\vec{k}_0 \cdot \vec{r} - \omega_0 t)} \quad \text{II-4}$$

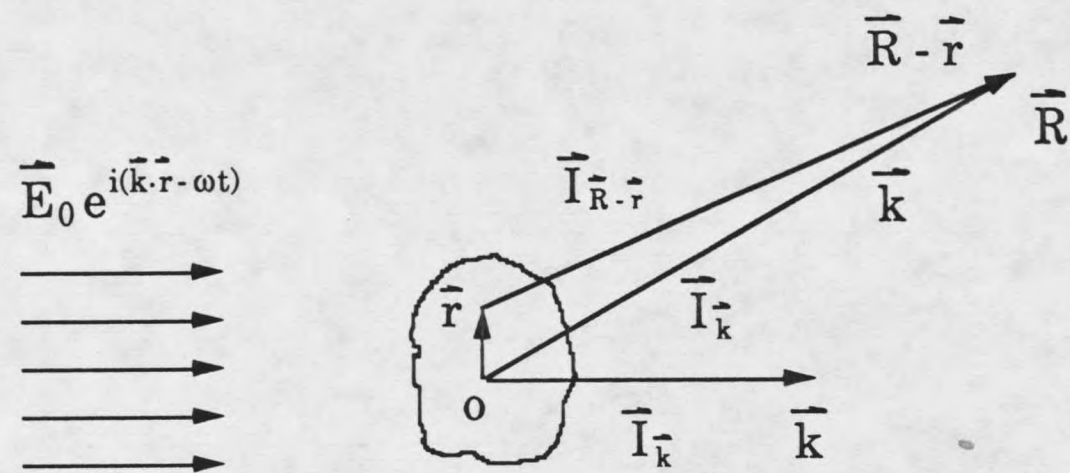


Fig. 1. Light scattering diagram

To calculate the $\partial^2 \vec{P}(\vec{r}, t) / \partial t^2$ required in (II-1) we have

$$\frac{d\vec{P}}{dt} = \left[-i\omega_0 \langle \vec{\alpha} \rangle - i\omega_0 \delta \vec{\alpha} + \frac{d(\delta \vec{\alpha})}{dt} \right] \cdot \vec{E}_0 e^{i(\vec{k}_0 \cdot \vec{r} - \omega_0 t)} \quad \text{II-5}$$

and

$$\frac{d^2 \vec{P}}{dt^2} = \left[-\omega_0^2 \langle \vec{\alpha} \rangle - \omega_0^2 \delta \vec{\alpha} - 2i\omega_0 \frac{d(\delta \vec{\alpha})}{dt} + \frac{d^2(\delta \vec{\alpha})}{dt^2} \right] \cdot \vec{E}_0 e^{i(\vec{k}_0 \cdot \vec{r} - \omega_0 t)} \quad \text{II-6}$$

Since the characteristic frequencies for thermal fluctuations are small ($\leq 10^4$ Hz) compared to the light frequency in the optical region ($\sim 5 \times 10^{14}$ Hz), we may regard $\delta \alpha$ as a very weak function of time and only keep the first two terms in II-6 to write

$$\frac{d^2 \vec{P}(\vec{r}, t)}{dt^2} = -\omega_0^2 \vec{P}(\vec{r}, t) \quad \text{II-7}$$

Substituting II-7 and II-4 into II-1 and carrying out the integration over the illuminated volume V at the retarded time t'

$$\vec{E}'(\vec{R}, t) = -\left(\frac{\omega_0}{c}\right)^2 \frac{e^{i(\vec{k}_0' \cdot \vec{R} - \omega_0 t)}}{R} \hat{I}_k \times \left[\hat{I}_k \times \int_v [\langle \vec{\alpha} \rangle + \delta \vec{\alpha}(\vec{r}, t')] \cdot \vec{E}_0 e^{i(\vec{k}_0 - \vec{k}_0') \cdot \vec{r}} d^3 \vec{r} \right]$$

-----II-8

where we have used the typical approximation that if $\vec{R} \gg \vec{r}$

$$\hat{I}_{(\vec{R}-\vec{r})} \approx \hat{I}_k, \quad |\vec{R}-\vec{r}| \approx \hat{I}_k \cdot (\vec{R}-\vec{r})$$

and

$$\vec{k}_0' = n \omega \vec{I}_k / c, \quad |\vec{R}-\vec{r}| \approx R$$

The integral in Eq. (II-8) gives the superposition of phases of waves scattered from each illuminated point in the medium. The contribution to the integral from the $\langle \vec{\alpha} \rangle$ term is zero except in the forward direction. This light oscillates at the same frequency as the incident field and contributes only to elastic scattering. Scattering out of the incident direction results entirely from fluctuations $\delta \vec{\alpha}$ in the polarizability. Decomposing the fluctuations into their spatial Fourier components,

$$\delta \tilde{\alpha}(\vec{r}, t') = \left(\frac{1}{2\pi} \right)^{3/2} \sum_{\mu} \int d^3 \vec{q} \delta \tilde{\alpha}^{\mu}(\vec{q}) e^{i[\vec{q} \cdot \vec{r} + \omega_{\mu}(\vec{q}) t']} \quad \text{II-9}$$

where $\vec{q}$ is the wavevector of the fluctuation and $\omega_{\mu}(\vec{q})$ is the frequency of the fluctuation at this wavevector. The index denotes the possibility of a number of branches in the dispersion relation connecting $\vec{q}$ and ω . In general $\omega_{\mu}(\vec{q})$ can be complex to include a description of the damping of the fluctuations. $\omega_{\mu}(\vec{q})$ is double-valued with $\pm$ to account for the degeneracy in the dispersion relation for positive and negative running waves. Substituting Eq. (II-9) into (II-8), being careful to include the effect of time retardation in $\delta \tilde{\alpha}$, we obtain

$$\begin{aligned} \vec{E}'(\vec{R}, t) = & - \left(\frac{\omega_0}{c} \right)^2 \sum_{\mu} \hat{I}_k \times \left[\hat{I} \times \int d^3 \vec{q} [\delta \tilde{\alpha}^{\mu}(\vec{q}) \cdot \vec{E}_0] \frac{e^{i[\vec{k} \cdot \vec{R} - (\omega_0 \pm \omega_{\mu}(\vec{q})) t]}}{R} \right] \\ & \times \left(\frac{1}{2\pi} \right)^{3/2} \int d^3 \vec{r} e^{i(\vec{k}_0 - \vec{k} + \vec{q}) \cdot \vec{r}} \end{aligned} \quad \text{II-10}$$

where

$$\vec{K} = \left(\frac{n}{c} \right) (\omega_0 \pm \omega_{\mu}(\vec{q})) \hat{I}_k = \vec{K}(\vec{q}) \quad \text{II-11}$$

is the scattering wavevector.

The final integral in Eq. (II-10) is a delta function provided that the illuminated region is very large compared to the wavelength of light. In this case

$$\int e^{i(\vec{k}_0 - \vec{K} + \vec{q}) \cdot \vec{r}} d^3\vec{r} = (2\pi)^3 \delta[\vec{q} - (\vec{k}(\vec{q}) - \vec{k}_0)] \quad \text{II-12}$$

Thus the wavevector of the fluctuation which produces the scattering in the direction $\hat{1}_k$ is that which satisfies the implicit equation

$$\vec{q} = \vec{k}(\vec{q}) - \vec{k}_0 = \vec{K} \quad \text{II-13}$$

We rename $\vec{q}$ in (II-13) as $\vec{K}$, the scattering vector. The vector $\vec{K}$ in this equation can be interpreted physically in two equivalent ways. In photon terminology, it represents the conservation of momentum between the incident photon $\vec{k}_0$, the scattered photon $\vec{k}$, and the scattering fluctuation $\vec{K}$. From (II-11), we notice that the wavelength of the scattered light can be different from that of the incident light because the scattering fluctuation can exchange a quantum of energy $\pm \hbar \omega_p(\vec{K})$ with the incident photon. In classical terms, we can regard this phenomena as a Doppler process of

Bragg reflection by moving sound waves. Substituting (II-12) and (II-13) into (II-10) and replacing $\delta\vec{\alpha}$ by $\delta\vec{\epsilon}/4\pi$, where $\delta\vec{\epsilon}$ is the fluctuation in the dielectric constant tensor, we relabel and $\vec{E}'(\vec{R},t)=\vec{E}'(\vec{k},t)$ and have

$$\vec{E}'(\vec{k},t) = -\left(\frac{\omega_o}{c}\right)^2 \frac{(2\pi)^{\frac{3}{2}}}{4\pi R} \sum_{\mu} e^{i\{\vec{k}\cdot\vec{R}-[\omega_o\pm\omega_{\mu}(\vec{K})]t\}} \hat{I}_k \times [\hat{I}_k \times (\delta\vec{\epsilon}^{\mu}(\vec{K}) \cdot \vec{E}_0)]$$

-----II-14

In Eq. 14, there are three $\omega_{\mu}(\vec{K})$ for the same wavevector $\vec{K}$, one longitudinal and two transverse modes. Thus in the spectrum, there would be three Brillouin scattering peaks. The $\hat{I}_k \times [\hat{I}_k \times \delta\vec{\epsilon}^{\mu}(\vec{k}) \cdot \vec{E}_0]$ term gives the polarization of the scattered radiation.

Equation (II-14) states that the scattering results from a particular Fourier component of the dielectric constant fluctuations. In the scattering process momentum and energy are conserved.

$$\vec{k} = \vec{k}_0 + \vec{K}$$

II-15

$$\omega' = \omega_0 \pm \omega_\mu(\vec{K}) \quad \text{II-16}$$

Then we can calculate the magnitude of the wavevector $\vec{K}$ of the fluctuation wave as shown in Figure 2.

$$|\vec{K}|^2 = k^2 + k_0^2 - 2kk_0\cos\theta$$

or

$$|\vec{K}|^2 = \left(\frac{n_s\omega_s}{c}\right)^2 + \left(\frac{n_i\omega_0}{c}\right)^2 - \frac{2n_in_s\omega_0\omega_s}{c^2}\cos\theta$$

Because $\omega_\mu \ll \omega$ ($\omega_\mu/\omega \sim 10^{-5}$), we have $\omega_0 \approx \omega_s$, and so

$$|\vec{K}| = \frac{\omega_0}{c} (n_i^2 + n_s^2 - 2n_in_s\cos\theta)^{\frac{1}{2}} \quad \text{II-17}$$

where n_i and n_s are refractive indices for incident and scattered light respectively. In birefringent materials like anisotropic polymers, the

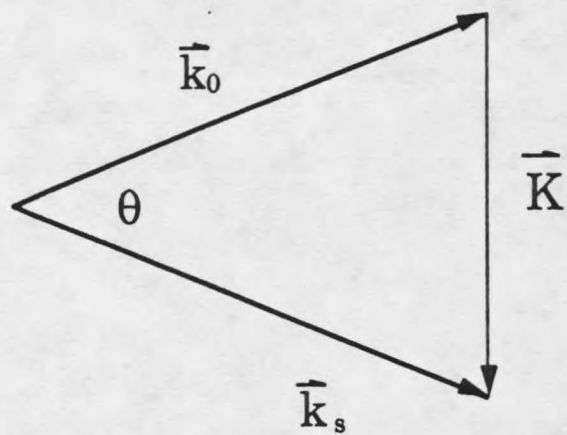


Fig. 2. Momentum conservation of photons and phonon

situation is more complicated. The general description can be found elsewhere.²⁴ Due to this birefringence each Brillouin line splits in general into four adjacent components which usually cannot be resolved by Brillouin scattering. As shown in Figure 3, the laser beam splits at the sample surface into differently polarized rays with wavevector $\vec{k}_{i1} = \hat{k}_1 k_{i0} n_{i1}$ and $\vec{k}_{i2} = \hat{k}_2 k_{i0} n_{i2}$. The direction of wave propagation ($\hat{k}_1, \hat{k}_2$) and the corresponding refractive indices (n_{i1}, n_{i2}) are obtained from the refractive indicatrix of the material. Each component of the incident light beam creates scattered light in the $\hat{k}$ direction which includes two components. We may observe four phonons following the relations

$$q_{lm} = k_{i0} (n_{il}^2 + n_{sm}^2 - 2n_{il}n_{sm}\cos\theta_{lm})^{\frac{1}{2}}$$

with $l=1,2$ and $m=1,2$. Neglecting the line splitting may result in inaccurate sound velocity and especially sound attenuation data. In our experiment the crystalline part of the copolymer has an orthorhombic ($m2m$) structure, so an unoriented sample is optically isotropic, a stretched and poled sample is optically biaxial and a stretched unpoled sample is uniaxial. The laser beam used has linear polarization parallel to the $\hat{n}_o$ or $\hat{n}_s$ direction for stretched copolymer, and the normal to the incident plane is parallel to the

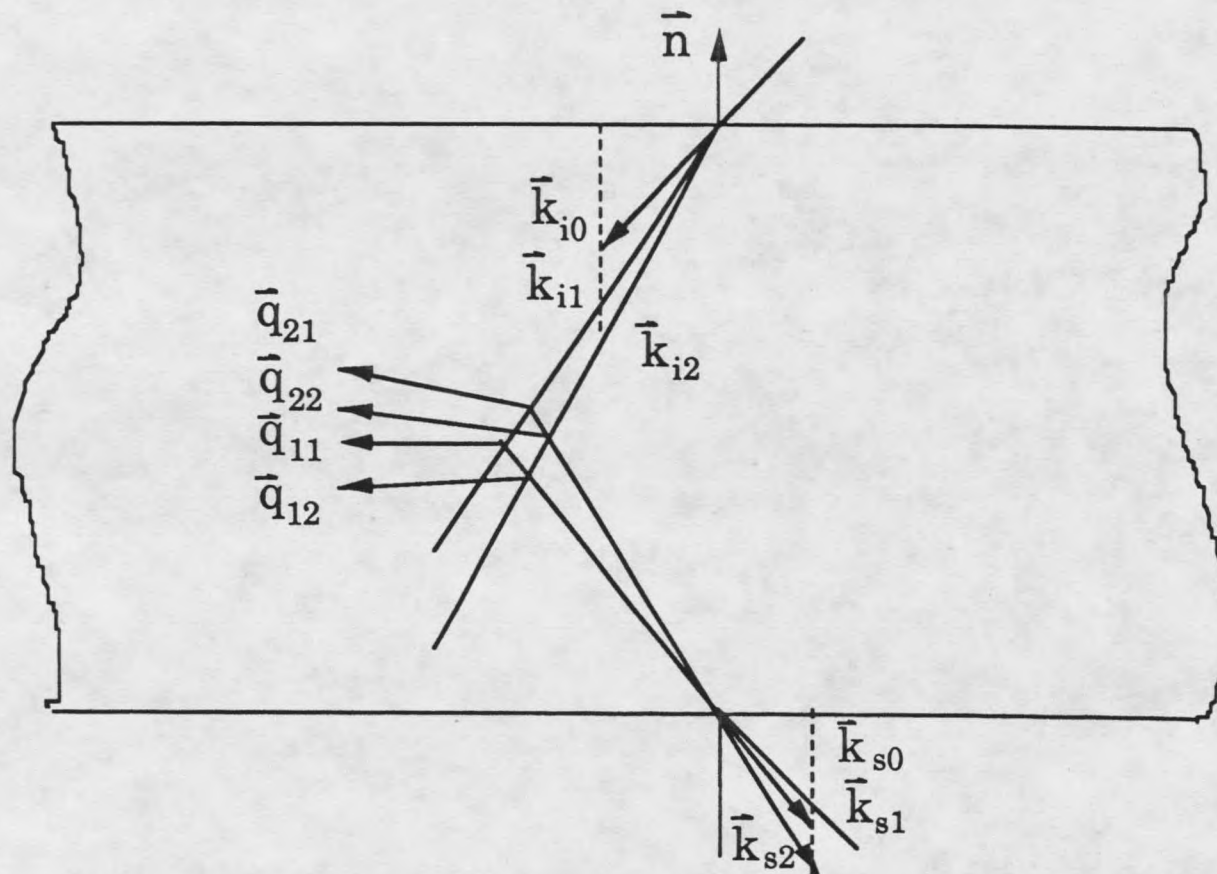


Fig. 3. Schematic drawing of the scattering situation for an optically biaxial sample using 90° scattering geometry

crystal axes. We are only interested in the longitudinal phonons, so in this case the polarization of both the incident and scattered light is the same,^{25,26} eliminating the need to deal with this birefringence splitting. If the polarization of the incident light is not parallel to either $\hat{n}_o$ or $\hat{n}_s$, the scattering light is not purely longitudinal or transverse^{22,27} (called quasi-longitudinal or quasi-transverse modes), the incident and scattered light have almost the same polarization, and the splitting caused by birefringence still can be neglected.

The relation between Brillouin frequency shift and stiffness constant

Brillouin scattering is a tool for measurement of elastic constants. We present here the basic theory of this method. Consider a distortion in which a point (x, y, z) fixed in the medium is shifted to position $(x+u_x, y+u_y, z+u_z)$. It can be shown that the equations of motion of the medium are¹⁶

$$\rho \ddot{u}_i = \frac{\partial S_{ix}}{\partial x} + \frac{\partial S_{iy}}{\partial y} + \frac{\partial S_{iz}}{\partial z} \quad \text{II-18}$$

where ρ is density of the medium and S_{ij} are components of the second-rank stress tensor. The stress components are related to components ε_{kl} of the second-rank strain tensor by

$$S_{ij} = C_{ijkl} e_{kl} \quad \text{II-19}$$

where C_{ijkl} is a component of the elastic stiffness tensor and repeated subscripts are assumed to be summed over x , y and z . The components of the strain are defined by $\epsilon_{ij} = (u_{ij} + u_{ji})$, where the displacement gradients $u_{ij} = \partial u_i / \partial x_j$. The equation of motion (II-18) becomes

$$\rho \ddot{u}_i = \frac{\partial S_{ij}}{\partial x_j} = C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l} \quad \text{II-20}$$

where we have used the invariance of the elastic stiffness tensor under interchange of its final pair of subscripts. There are three coupled equations of this form for the components of the displacement.

We seek plane-wave solutions of the equation of motion in which the displacement vector has space and time variations

$$u \sim \exp i(\vec{q} \cdot \vec{r} - \omega_q t) \quad \text{II-21}$$

leading to

$$\rho \omega_q^2 u_i = C_{ijkl} q_j q_l u_k \quad \text{II-22}$$

We define $V_q = \omega_q/q$, then

$$q V_q^2 u_i = C_{ijkl} \hat{q}_j \hat{q}_l u_k \quad \text{II-23}$$

where the $\hat{q}_i$ are the direction cosines of the sound wavevector $\vec{K}$, and the C_{ijkl} are the components of a fourth-rank tensor which is symmetric and may be written with a single suffix running from 1 to 6 using the following conversion scheme 11→1, 22→2, 33→3, 23 or 32→4, 13 or 31→5, 12 or 21→6.

A stretched but unpoled copolymer such as some of our PVF₂/TrFE copolymer samples is elastically equivalent to a hexagonal or other optically uniaxial crystal. Its elastic stiffness tensor in reduced notation is²⁷

$$\begin{array}{cccccc} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{array}$$

with $C_{11}=C_{22}$, $C_{13}=C_{23}$, $C_{44}=C_{55}$, $C_{66}=(C_{11}-C_{12})/2$. In PVF₂ polymer research, it is common to take the symmetry axis (c axis of the equivalent hexagonal crystal) as the x axis and the vector normal to the film plane pointing along the z axis⁹ so that by conversion $3 \leftrightarrow 1$, we have the same matrix of C with $C_{22}=C_{33}$, $C_{13}=C_{12}$, $C_{66}=C_{55}$, $C_{44}=(C_{33}-C_{23})/2$. Eq. II-23 leads to the eigenvalue problem

$$\begin{vmatrix} a - qV^2 & d & e \\ d & b - qV^2 & f \\ e & f & c - qV^2 \end{vmatrix} = 0 \quad \text{II-24}$$

where

$$\begin{aligned} a &= C_{11}q_1^2 + C_{66}q_2^2 + C_{55}q_3^2 \\ b &= C_{66}q_1^2 + C_{22}q_2^2 + C_{44}q_3^2 \\ c &= C_{55}q_1^2 + C_{44}q_2^2 + C_{33}q_3^2 \\ d &= (C_{12} + C_{66})q_1q_2 \\ e &= (C_{13} + C_{55})q_1q_3 \\ f &= (C_{23} + C_{44})q_2q_3 \end{aligned}$$

and

$$(a - qV^2)(b - qV^2)(c - qV^2) - d^2(c - qV^2) - e^2(a - qV^2) \quad \text{II-25}$$

$$-f^2(b - qV^2) + 2def = 0$$

A convenient way to determine all components of the elastic stiffness is to measure the eigenvalues of V_q for sound propagation direction $\vec{q}$ and to fit equation (II-25) to this data using a least squares fit.

The sound velocity along the chosen direction can be calculated from the Brillouin frequency shift $\omega_B = 2\pi f_B$ by

$$K = \frac{\omega_B}{V_q} \quad \text{II-26}$$

by (II-17)

$$V_q = f_B \lambda_0 (n_i^2 + n_s^2 - 2n_i n_s \cos\theta)^{-\frac{1}{2}} \quad \text{II-27}$$

with $\lambda_0 = c/\omega_0$, the wavelength of the incident light in vacuum. Thus we need only measure the Brillouin frequency shift of the spectrum to determine the sound velocity of thermally excited acoustic lattice vibrations. We only have interest in the longitudinal mode and we have discussed above that $n_i = n_s$.

in our case. Eq. (II-27) is reduced to

$$V_q = \frac{f_B \lambda_0}{2n \sin \frac{\theta}{2}} \quad \text{II-28}$$

When $\theta=90^\circ$, II-28 becomes²⁸

$$V_q = \frac{f_B \lambda_0}{\sqrt{2}} \quad \text{II-29}$$

and is independent of the refractive index of the material. From the v_q we can calculate the elastic stiffness constants and study the mechanical properties of the copolymer. Therefore, phase transitions occurring in the amorphous or crystalline regions in general affect the elastic properties and can be investigated by Brillouin scattering.

The VF₂-based copolymers and structural phase transitions

PVF₂ polymers and their copolymers have ferroelectric^{7,29-31} phases. Their electric and electromechanical characteristics in the ferroelectric state are a consequence of macroscopic polarization induced by the application of

a large electric field.^{32,33} PVF₂/TrFE copolymers exhibit a first order ferroelectric to paraelectric (F-P) phase transition at the Curie temperature T_c .^{7,9} Strictly speaking, this F-P transition is a structural transition of the crystalline portion of the copolymer. We now review the theory of anomalies in the sound velocity behavior near a phase transition for a single crystal. The theory for semicrystalline material will be discussed in Chapter IV.

When a crystal changes structure it transforms from a state of one symmetry to another. Such a phase change may occur discontinuously through a large-displacement rearrangement of the atoms in the crystal giving a first-order phase transition. However, the symmetry may also be changed by an arbitrarily small displacement of the atoms from their lattice points resulting in a phase transition of second order. At a first-order phase transition two different states are in equilibrium, but there is no predictable symmetry relationship between them. In contrast, for second order phase transitions the states of the two phases are the same at the transition point, and the symmetry of one phase must be higher than that of the other. In the great majority of phase transitions the more symmetric phase corresponds to higher temperature and the less symmetric phase to lower temperature. Many first order phase transitions studied show a rather small discontinuity in the order parameter versus temperature curve, so that the formalism describing continuous transitions can be used

to a reasonable accuracy also for them.¹⁸

Much has been written about acoustic anomalies and mode coupling at phase transitions.^{18,34} The following section starts with a general discussion of the interaction between strain and order parameter. Static effects will be derived that determine part of the behavior of the sound velocity. Dynamic effects, i.e. order parameter fluctuations, which are important for the ultrasonic attenuation but which can also give contributions to the sound velocity, are introduced.

1. Coupling between strain and order parameter - static effects

The order parameter characterizes the amount of change taking place during the transition. Normally it is defined on an atomistic scale, but in many cases macroscopic quantities are measurable that are directly proportional to the microscopic order parameter.

In the spirit of the Landau and Devonshire theory of phase transitions,^{35,36} we start from an expansion¹⁸ of the free energy density in powers of the order parameter components Q_i , their spatial gradients and the components ϵ_k of the strain tensor.

$$F(Q_p, \epsilon_k, T) = F_0(T) + \frac{1}{2}a_2(T)f_2(Q_i) + \frac{1}{4}a_4f_4(Q_i) + \frac{1}{6}a_6f_6(Q_i) + \dots + \frac{1}{2}b(\nabla Q)^2 + \dots + F_m(\epsilon_k) + F_c(Q_p, \epsilon_k) \quad \text{II-30}$$

In this equation the $f_n(Q_i)$ denote the n th-order invariants of the components of the order parameter, that are homogeneous functions of degree n in the components Q_i , which remain unchanged under all possible symmetry operations. The purely elastic contribution is denoted by F_m . All the coefficients are considered as weakly temperature dependent with the exception of a_2 which goes through zero like $\alpha(T-T_c)$ at the temperature T_c . The coupling term F_c describes the interaction between strain and order parameter. This term is responsible for the spontaneous strain appearing in connection with the ordering process, and also describes the effect of an external strain upon the order parameter.

The elastic constants $C_{mn} = \partial^2 F / \partial \epsilon_m \partial \epsilon_n$ are usually measured under the condition that the order parameter can change freely under the influence of the externally applied ultrasonic strain, i.e. that its conjugate force $Z_k = \partial F / \partial Q_k$ is kept zero. The elastic constants $C_{mn}^{(Q)}$ entering the expression for the purely elastic free energy F_m are those determined under the condition $Q_k = 0$. The difference $C_{mn}^{(Z)} - C_{mn}^{(Q)}$ is due to the motion of the

order parameter, driven by the external strain and its reacting stress³⁷

$$C_{mn}^{(Q)} - C_{mn}^{(Z)} = \sum_{k,l} \frac{\partial^2 F_c}{\partial \epsilon_m \partial Q_k} \chi_{kl}^{(e)} \frac{\partial^2 F_c}{\partial \epsilon_n \partial Q_l} \quad \text{II-31}$$

$$\chi_{kl}^{(e)} = \left(\frac{\partial^2 F}{\partial Q_k \partial Q_l} \right)_e^{-1} = \left(\frac{\partial Z_k}{\partial Q_l} \right)_e^{-1} = \left(\frac{\partial Z_l}{\partial Q_k} \right)_e^{-1} \quad \text{II-32}$$

The coupling free energy density is usually written in terms of increasing powers of ϵ_i and Q_k

$$F_c(\epsilon_p, Q_k) = \beta_{ij} Q_i \epsilon_j + \gamma_{ijk} Q_i Q_j \epsilon_k + \delta_{ijk} Q_i \epsilon_j \epsilon_k + \dots \quad \text{II-33}$$

Figure 4 from Rehwald gives the behaviors of the elastic moduli for the three dominating lowest order coupling terms in equation (II-33), assuming $a_4 > 0$.

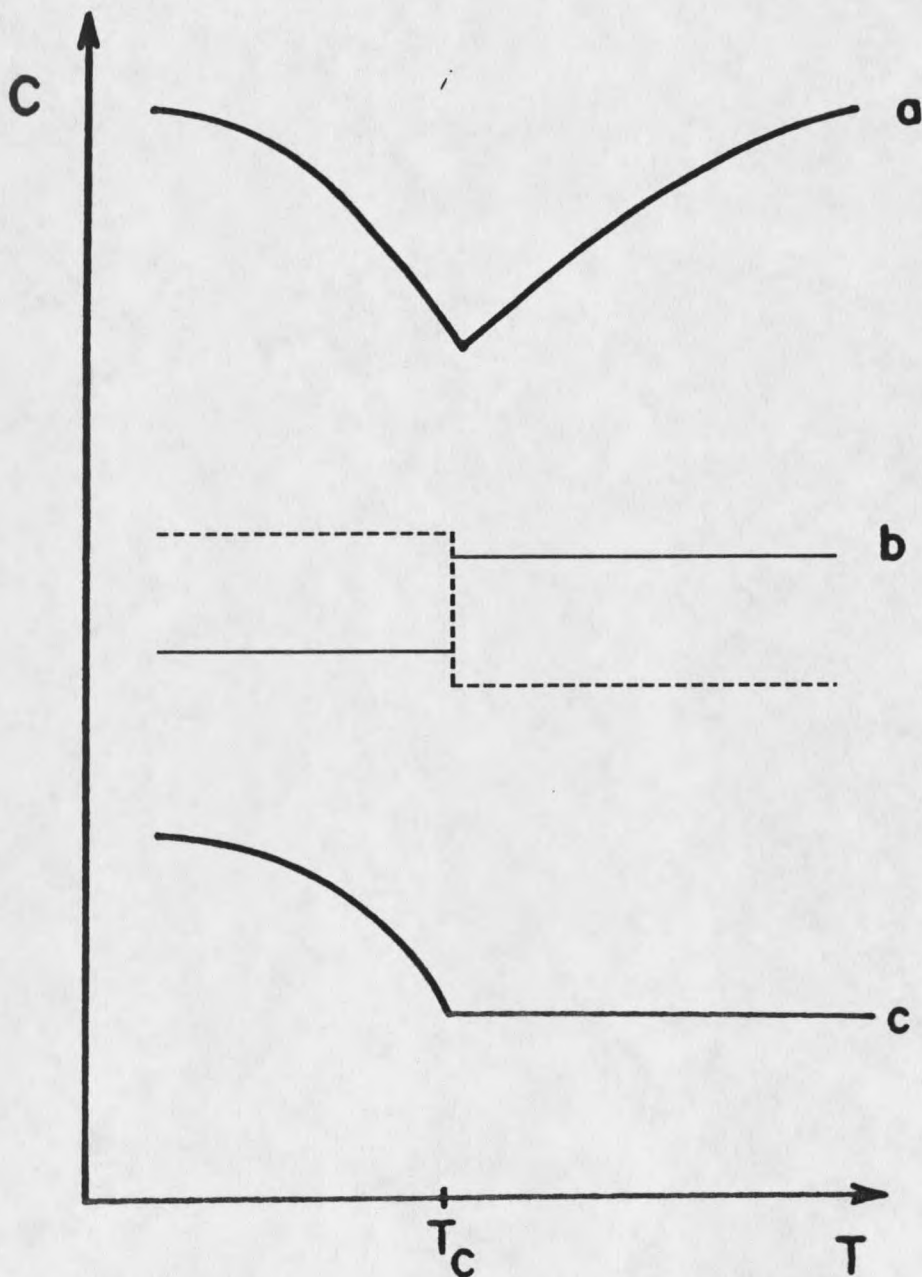


Fig. 4. Elasticity versus temperature for (a) eQ coupling, (b) eQ^2 coupling, solid line for second-order transition dotted line for first order transition, (c) e^2Q coupling

2. Dynamic effects

Brillouin scattering measures the dynamic behavior of the elasticity C at frequency ω in accordance with¹⁶

$$C(\omega) = \rho V^2(\omega) \quad \text{II-34}$$

where ρ is the crystal density and v is the sound velocity corresponding to C . The dynamic effects on the elasticity are taken into account by introducing a frequency dependent susceptibility into the elasticity equation³⁵

$$\tilde{C}(\omega) = C^{(0)} - \frac{C^{(0)} - C^{(2)}}{(1 - i\omega\tau)} \quad \text{II-35}$$

which assumes a single dynamic relaxation time τ . This equation separates into a real elasticity, measured by Brillouin scattering in accordance with equation (II-34) and an imaginary part which determines the phonon halfwidth (τ).³⁸

$$\rho V^2(\omega) = \operatorname{Re}(C) = C^{(Q)} - \frac{C^{(Q)} - C^{(Z)}}{(1 + \omega^2 \tau^2)} \quad \text{II-36}$$

and the attenuation α is

$$\alpha = \frac{\omega}{2 \rho V^3(\omega)} \operatorname{Im}(C) = \frac{\omega \tau}{2 \rho V^3(\omega)} \frac{C^{(Q)} - C^{(Z)}}{1 + (\omega \tau)^2} \quad \text{II-37}$$

In Landau-Khalatnikov theory $\tau = \tau_0 t^{-1}$, where t is the reduced temperature $(T_c - T)/T_c$ and τ_0 is the individual-dipole relaxation time. For longitudinal phonons propagating along a direction perpendicular to the polar axis, the velocity V and the attenuation α in the FE phase are given by^{39,40}

$$V^2 = V_\infty^2 - \left[\frac{V_\infty^2 - V_0^2}{1 + \omega^2 \tau_0^2 t^{-2}} \right] \quad \text{II-38}$$

$$\alpha = \left[\frac{V_\infty^2 - V_0^2}{2 V^3} \right] \left[\frac{\omega^2 \tau_0 t^{-1}}{1 + \omega^2 \tau_0^2 t^{-2}} \right] \quad \text{II-39}$$

where the velocities V_∞ and V_0 designate the high and low frequency limit

velocities, respectively. Such contributions to the attenuation anomaly causes a maximum near, but below, T_c .

The above phenomenological theory gives a general qualitative understanding of anomalies of sound velocity and attenuation. There are a large number of studies of various crystals by Brillouin scattering^{35,41,42} which revealed many kinds of anomalies corresponding to different coupling types. Among many kinds of coupling we emphasize one that gives a small dip in sound velocity at the transition and a maximum in attenuation near, but below the transition point. We believe that our experimental results result from this type of coupling.

CHAPTER III

EXPERIMENTAL PROCEDURE

Brillouin scattering provides a measure of the acoustic phonon behavior near structural phase transitions. Brillouin scattering in solids became feasible with the invention of the multi-pass Fabry-Perot interferometer in 1970.⁴³ In the present experiment a five-pass system provided adequate resolution and contrast to measure the frequencies of the acoustic phonons in vinylidene fluoride copolymers with trifluoroethylene (VF_2/TrFE) and tetrafluoroethylene (VF_2/TFE). In this chapter, the experimental equipment and procedures are discussed.

General description of equipment

The apparatus can be divided into the optical system, temperature control and measurement system, and computer control system. The optical arrangement used for Brillouin scattering in this experiment is shown schematically in Figure 5. The original three-pass system was set up by

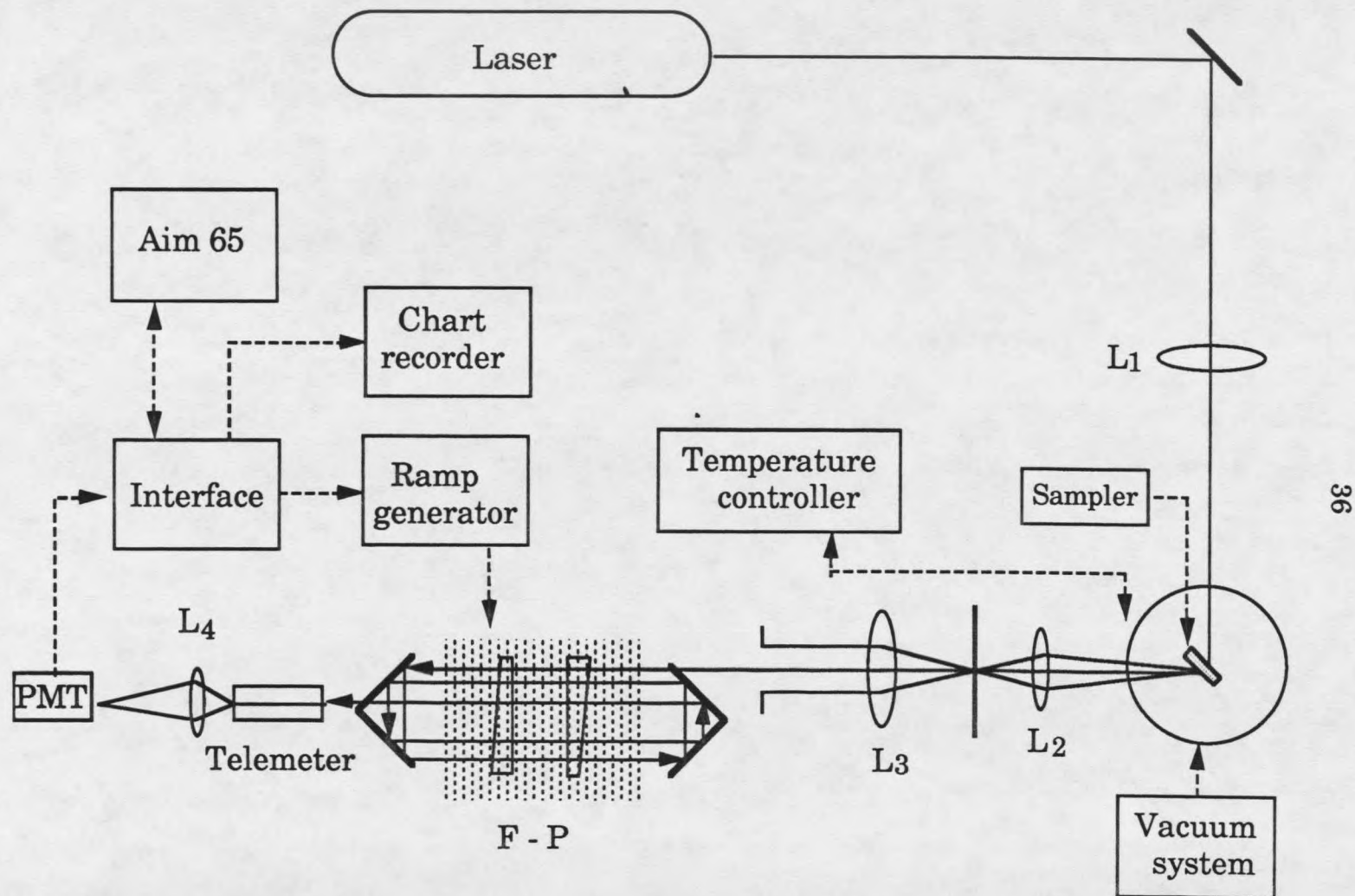


Fig. 5. Experimental set-up

Dr. M. Yamada, Dr. T. Hikita, Mr. P. Schnackenberg and Dr. J. T. Wang. We, Dr. P. Young and myself, improved it for purposes of polymer studies by converting it to a five-pass interferometer system.

The light source was a Lexel Model 95-2 argon ion laser operating at a wavelength of 5145 Å in a single mode which was achieved by a temperature-controlled etalon. Both laser frequency and power output stabilization were achieved by allowing at least a half hour warmup of the etalon and laser system prior to taking data. The laser was operated at 100 mW. The laser beam was polarized in the vertical plane. A lens L_1 focused the incident beam on the sample which was set in the cryostat which will be described later. The scattering angle in this experiment was 90°.

The collection lens L_2 focused the scattered light from the sample through a 100 µm pinhole, and this transmitted light was collimated by L_3 . The collimated beam was then passed through a five-pass Fabry-Perot interferometer. The light from the Fabry-Perot was focused by a telescope lens onto the exit pinhole of the lens housing. The lens L_4 imaged the light from the pinhole on a Model R464 head-on photomultiplier tube (PMT). Just in front of the PMT there was a D1-515 color filter with center wavelength 514.5 nm and band width (FWHM) 1.0 ± 0.2 nm which was a key element in obtaining satisfactory Brillouin peaks from copolymers. There was a computer-controlled partially-blocking shutter between the

lens and the exit pinhole of the telemeter. The shutter was closed in the Rayleigh spectrum range and greatly attenuated the Rayleigh scattered light but was open in the Brillouin spectrum range. A home-made high voltage power supply provided high voltage (1450 V) for the cathode of the PMT. The output current from the anode of the PMT was the input of a pulse amplifier. The analog output of the amplifier was fed into a home-made counter and the digital number was stored in a AIM-65 computer and then the signal was displayed on an oscilloscope or chart recorder.

The light gathering and focusing optics and the alignment techniques had been described in detail elsewhere.^{25,44}

Characteristics of the Fabry-Perot

The Fabry-Perot interferometer played a key role in determining Brillouin frequency shift. We briefly review its characteristics to provide a better understanding of how that frequency shift was measured.

The condition for constructive interference for a transmitted wavefront is

$$2nd\cos\theta = m\lambda$$

where n is the refractive index of the medium between the two reflecting mirror surfaces, d is the mirror spacing, θ is inclination of the normal of the mirrors to the wavefront direction, in our case $\theta=0$, m is the order of interference, and λ is the wavelength. Then (III-1) becomes

$$nd = \frac{m\lambda}{2} \quad \text{III-2}$$

If d decreases by $\lambda/2$, a wave with the same wavelength is still able to pass this interferometer but the order of the interference lowers by one. There will be another wave with different wavelength which may pass this interferometer but with the m th order interference. Hence we have

$$nd = (m-1)\frac{\lambda_1}{2} = m\frac{\lambda_2}{2} \quad \text{III-3}$$

and

$$\delta\lambda = \lambda_1 - \lambda_2 = \frac{\lambda_1^2}{2dn} \quad \text{III-4}$$

$\delta\lambda$ is called the Free Spectral Range (FSR) which is usually expressed in frequency $\delta\nu=c/2nd$, where c is the speed of light.

Assuming the optical length nd changes by $\lambda_1/2\mu$, where μ is not an integer, the wavefront of wavelength λ_3 is allowed to pass this interferometer if the following formula is satisfied:

$$nd - \frac{\lambda_1}{2\mu} = (m - i) \frac{\lambda_3}{2} \quad \text{III-5}$$

where m, i are integers. Then

$$\lambda_3 = \frac{2(nd - \lambda_1/2\mu)}{2nd/\lambda_1 - i} \quad \text{III-6}$$

Finally we have

$$\lambda_3 - \lambda_1 = \frac{\lambda_1^2(i - 1/\mu)}{2nd(1 - i\lambda_1/2nd)} \approx \frac{\lambda_1^2(i - 1/\mu)}{2nd} \left[1 + \frac{i\lambda_1}{2nd} \right] \quad \text{III-7}$$

Normally $m \gg i$, i.e. $2nd \gg i\lambda$

$$\Delta\lambda = \lambda_3 - \lambda_1 \approx \frac{\lambda_1^2(i - 1/\mu)}{2nd} = (i - 1/\mu)FSR \quad \text{III-8}$$

or

$$\Delta\nu = (i - 1/\mu)FSR \quad \text{III-9}$$

Here, $\delta\nu$ is the frequency shift from the original wave (Rayleigh in our case) and i is the shift order which is different from the order of interference.

The Fabry-Perot interferometer (FP) is a Burleigh Instruments Model RC-140. It uses matched sets of piezoelectric PZT transducers constructed from interferometrically matched PZT discs. This PZT material offers the best linearity and hysteresis characteristics with better than 1% and 0.5% respectively. The RC-42 Ramp Generator drives the FP interferometer. The ramp generator controls the PZT to provide two basic functions, scanning and alignment, with two independent circuits.

The finesse is the key measure of the interferometer's ability to resolve closely spaced lines (close frequencies). Typical finesse for this system was about 40.⁴⁴ The finesse F_p in a multi-pass system is⁴⁴

$$F_p = \frac{F_1}{(2^{1/p} - 1)^{1/2}} \quad \text{III-10}$$

where p is the number of passes, and F_1 is the finesse for a single pass. In our case of five passes, the finesse is about 104. The contrast in a multi-pass system is also improved significantly⁴⁴; the contrast $C_1 = 4F_1^2/\pi^2$, while C_p is C_1^p .

Computer control system

This system consists of the AIM-65 computer, interface and software. The AIM-65 was used to define functions to interface with user provided peripherals, such as the ramp generator and photomultiplier, etc. The BASIC language was used for programming.

The diagram for interfacing the computer to the ramp generator is shown in Figure 6. The Fabry-Perot interferometer is scanned by applying a high voltage ramp to three piezoelectric stacks. This voltage ramp is controlled either by the front control panel knobs on the Burleigh RC-42 ramp generator or alternatively by the computer.

Acquisition of spectra is accomplished under computer control, thereby allowing the computer to make multiple scans of the spectrum. By adding these scans together it provides necessary signal averaging while eliminating the effects of spectrometer drift during the course of measurement. Each scan should be roughly 1.25 free spectral ranges in width and should provide two elastic (Rayleigh) peaks in each scan. The computer also provides a signal to toggle a relay on and off which operates a partial shutter on and off before and after the scan through each elastic peak. Provision is also made for changing the scan rate through the elastic peaks from that of the remainder of the scan.

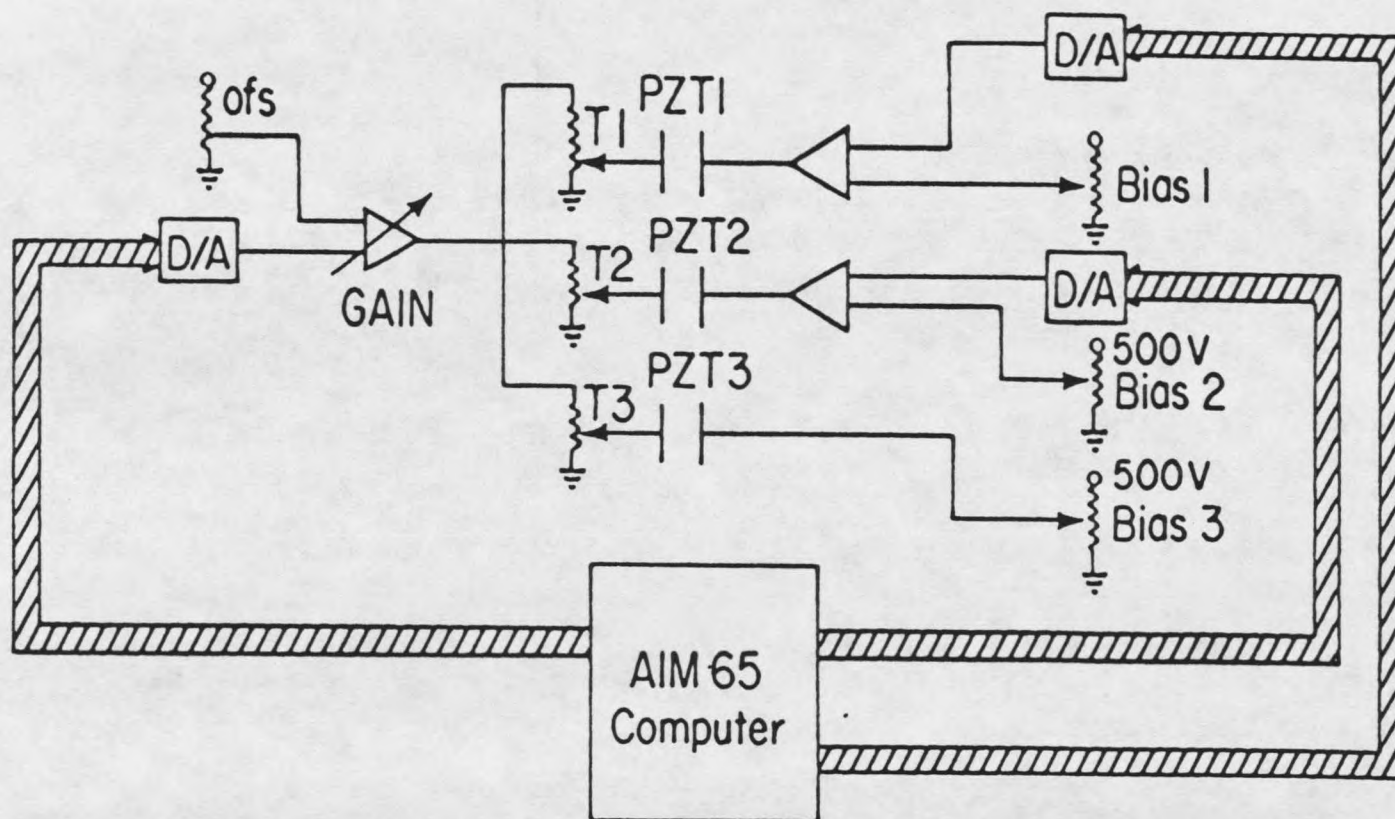


Fig. 6. Computer operation of the Fabry-Perot

Each scan is divided into 256 channels in which the computer looks for the channel containing the maximum number of counts in the first 128 channels of the scan. This channel is assumed to be the elastic peak location and is used to generate the offset necessary to align the new scan data with the accumulated scan data before adding it into the accumulated data. In this manner the drift in the offset of the Fabry-Perot is compensated. This same offset is used to calculate a new ramp "start" position to keep the channel number of the first elastic peak in each scan constant. If this offset is found to be more than four channels, the scan is ignored and the computer assumes that a "glitch" was observed in the first 128 channels of the scan.

The Fabry-Perot controller program written in BASIC and machine language has several functions such as initializing the ramp generator, optimizing the Fabry-Perot, scanning and accumulating data, display, and recording data on disc.

Temperature control and measurement

The sample was mounted in an optical cell which was described elsewhere.⁴⁵ Its structure is shown in Figure 7. The cell with four optical windows is surrounded by a copper radiation shield can and copper outer can which is connected to the liquid nitrogen tank. This tank acts as a

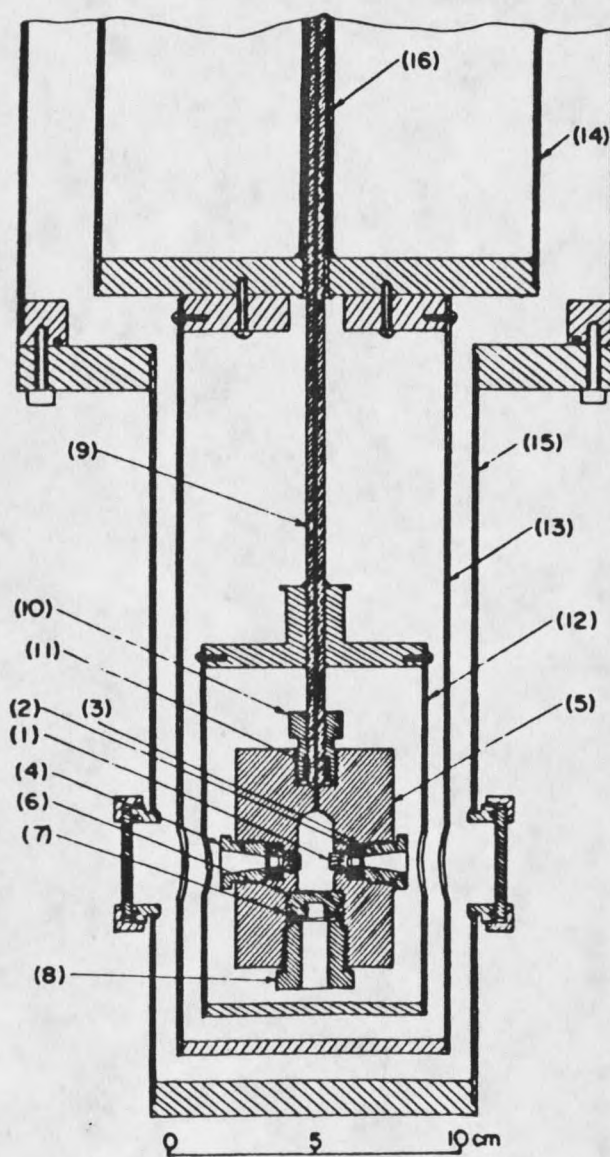


Fig. 7. Cryostat

constant-temperature heat sink. The space inside of the dewar is evacuated to 10^{-5} torr to minimize the heat losses. The temperature of the cell and inner copper shield are controlled by a Scientific Instruments, Inc. Model 3610A and Cole-Parmer Model BA 2155-54 cryogenic temperature controller respectively. In our experiment, the temperature of the inner shield should be about 10 K lower than that of the cell. The control accuracy is $\pm 0.1^\circ$ K. Both controllers also measure the temperatures of cell and shield. To determine the heating effect of the laser beam on the sample, the actual temperature of the sample was measured independently. An Omega Engineering, Inc. Model F3105 platinum RTD sensor was stuck on the sample very close to the laser spot using highly thermal conductive cement. The tolerance of this sensor is $\pm 0.2^\circ$ below 100° C and $\pm 0.3^\circ$ above 100° C. It was found that when the laser light struck on the sample the temperature rose by about 2.5° and then stabilized.

PVF₂ and its copolymers have ferroelectric phases. The speed and procedures of heating and cooling may influence their behaviors of sound velocity and attenuation. In our experiment we used the following procedures in heating and cooling samples. The samples were first cooled to about -70° C, then we made frequency shift measurements while heating it from -70 to about $+130^\circ$ C to finish the heating run. Then we kept the sample at the highest temperature for about 20 minutes, after which we

reduced the temperature to about 0° C to finish the cooling run. The temperature steps varied between 1.5° C and 2.5° C, with each step lasting about 20 minutes.

Sample preparation

The PVF₂/TrFE copolymers were bought from Pennwalt Company in pellet form for 60/40 mol% VF₂/TrFE and in powder form for 80/20, and 70/30 mol% VF₂/TrFE and 81/19 mol% VF₂/TFE. Dr. J. F. Legrand kindly supplied us an 80/20 VF₂/TrFE stretched film and we prepared the isotropic films. There are two ways to prepare powder or pellet copolymer into transparent films, the melting and dissolving method. The melting method was used in preparing 70/30 VF₂/TrFE and 81/19 VF₂/TFE copolymers and the dissolving method was used for 60/40 copolymer. The melting method used the following procedure:⁴⁶ (1) We put the 70/30 mol% VF₂/TrFE or 81/19 mol% VF₂/TFE copolymer powder in a milled-out cavity in one of two parallel copper plates, with special thin plastic films of melting point near 400° C between the copper plates and the powder. Use of these films provides copolymer samples with good surfaces. These pieces of copper were compressed together by a strong spring so that upon heating and melting the powder, the air was driven out, the plates touched, and bubble-free liquid polymer remained in the cavity. (2) We heated the sample up to

200° C for about 10 minutes, then quenched it in water at room temperature. (3) The film was then annealed above 120° C for 3 hours. The film thus obtained has very good optical surface properties so that no index matching liquid is necessary to perform Brillouin scattering experiments.

In the dissolving technique, we simply dissolved the 60/40 and 80/20 mol% VF₂/TrFE powder in 50% acetone and 50% tetrahydrofurane, 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.

To prepare the oriented samples, films obtained by the above processes 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.

CHAPTER IV

EXPERIMENTAL RESULTS

Brillouin scattering measurements were performed on the two longitudinal acoustic phonon modes propagating along the stretch direction (x axis) and the direction perpendicular to x in the film plane (y axis). The stretching makes most of the polymer chains take the same direction. The x direction phonon corresponds to the stiffness constant C_{11} and describes stiffness along the chain direction. The y axis phonon corresponds to the stiffness constant C_{22} ($C_{22}=C_{33}$) and describes stiffness along the interchain direction. These copolymers are semicrystalline materials with fair transparency only for thin films. These two modes are the only ones observable by Brillouin scattering to study anomalous behavior near the structural phase transition because the shear mode is invisible to Brillouin scattering for m2m symmetry.⁴⁷ Poling does not observably affect the measured stiffness constants¹⁷ so we only studied the oriented and isotropic but unpoled samples.

We measured the temperature dependence of sound velocity and attenuation of phonons for 70/30 mol% VF₂/TrFE isotropic copolymer, sound velocity along x and y axes for 80/20, and 60/40 mol% VF₂/TrFE oriented and isotropic samples. To eliminate suspicion that the TrFE plays a special role in the phase transition behavior, we performed similar experiments for VF₂/TFE copolymers.

Data Analysis

The sound velocity is calculated from the experimentally measured Brillouin longitudinal mode frequency shifts by the Brillouin formula

$$\frac{\delta v}{v_0} = \frac{v}{c} (n_i^2 + n_s^2 - 2n_i n_s \cos \theta)^{\frac{1}{2}} \quad \text{IV-1}$$

As discussed in Chapter II, in our case the incident and scattered light has the same polarizations, $n_i = n_s$, and the frequency shift will be independent of refractive index n_i for 90° scattering (see Chapter II). However the actual inside scattering angle is not 90° but greater than 90° as shown in Figure 8. For our copolymers, $n \approx 1.4$, the angle between the incident light and the normal of film surface is 45°, and ϕ is about 30° ($\sin 45^\circ = 1.4 \sin \phi$). The actual

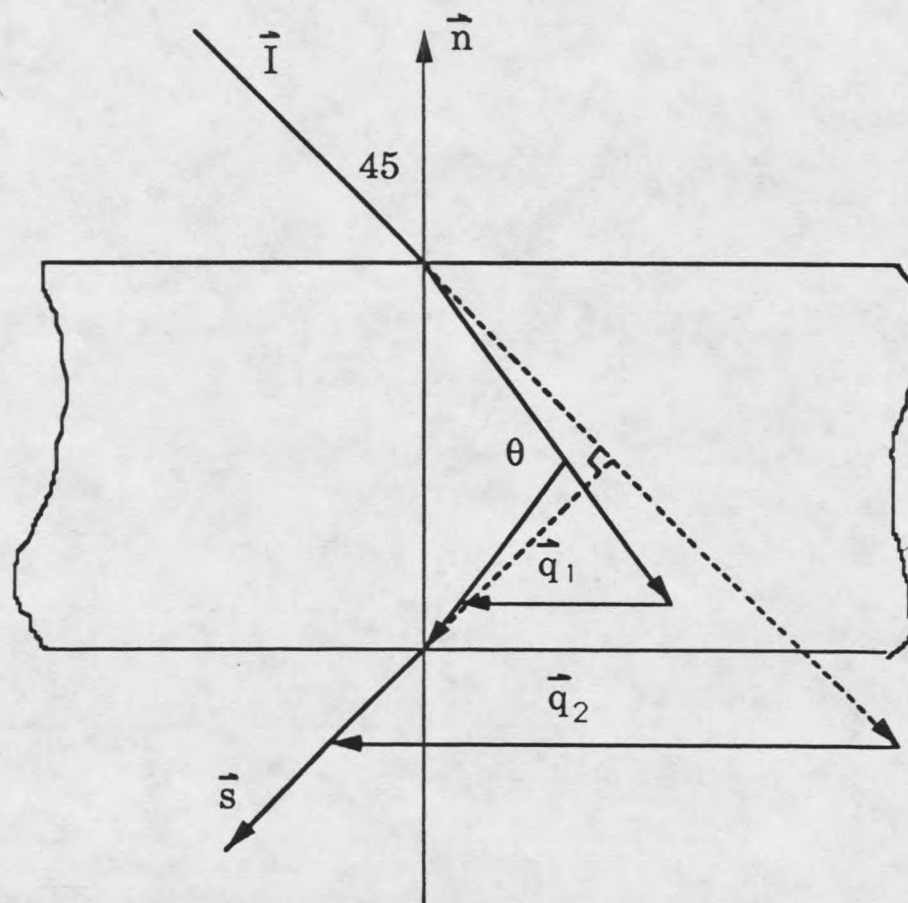


Fig. 8. The actual Brillouin scattering angle inside the sample

scattering angle will be 120° . The sound wave direction determined in this geometry is the same as that in the absence of this refractive problem. So the sound velocity data provides information on stiffness behavior in the same direction but at a different K-v dispersion point. This might be why former researchers did not discuss this scattering angle problem.

In some cases, the reflection of incident light on the second surface of the film creates its own Brillouin scattering signals.^{28,48} These signals are also longitudinal but much weaker than the major one. They used to be confused sometimes with the transverse mode from the original incident light. Figure 9 shows how they are created. We observed them in several experiments. They were distinguished from possible transverse modes by two facts. 1). A longitudinal mode has the same polarization as the incident light, while the polarization of a possible transverse mode is perpendicular to the incident light. We can easily tell one from another by using an analyzer. 2). The frequency of a transverse mode is lower than that of a longitudinal one and should appear near the Rayleigh peak in the Brillouin spectrum. Normally the Brillouin frequency shift created by reflection is larger than the original one. Figure 10 shows the reflection peaks in the spectrum.

As indicated in Chapter II, three modes appear in the spectrum simultaneously, one longitudinal and two transverse. We can set an

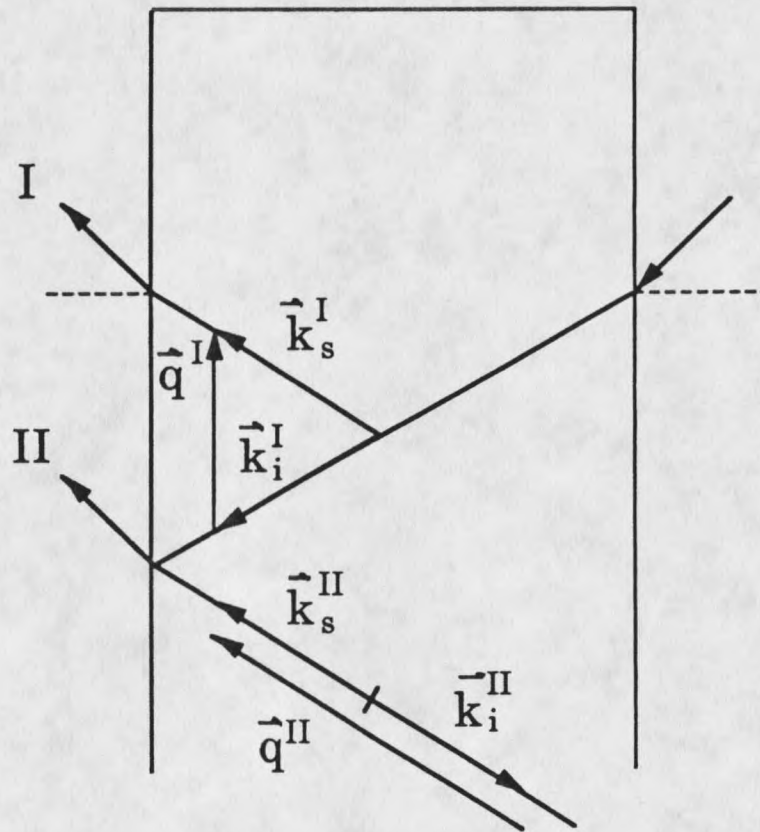


Fig. 9. Light scattering from reflected beams

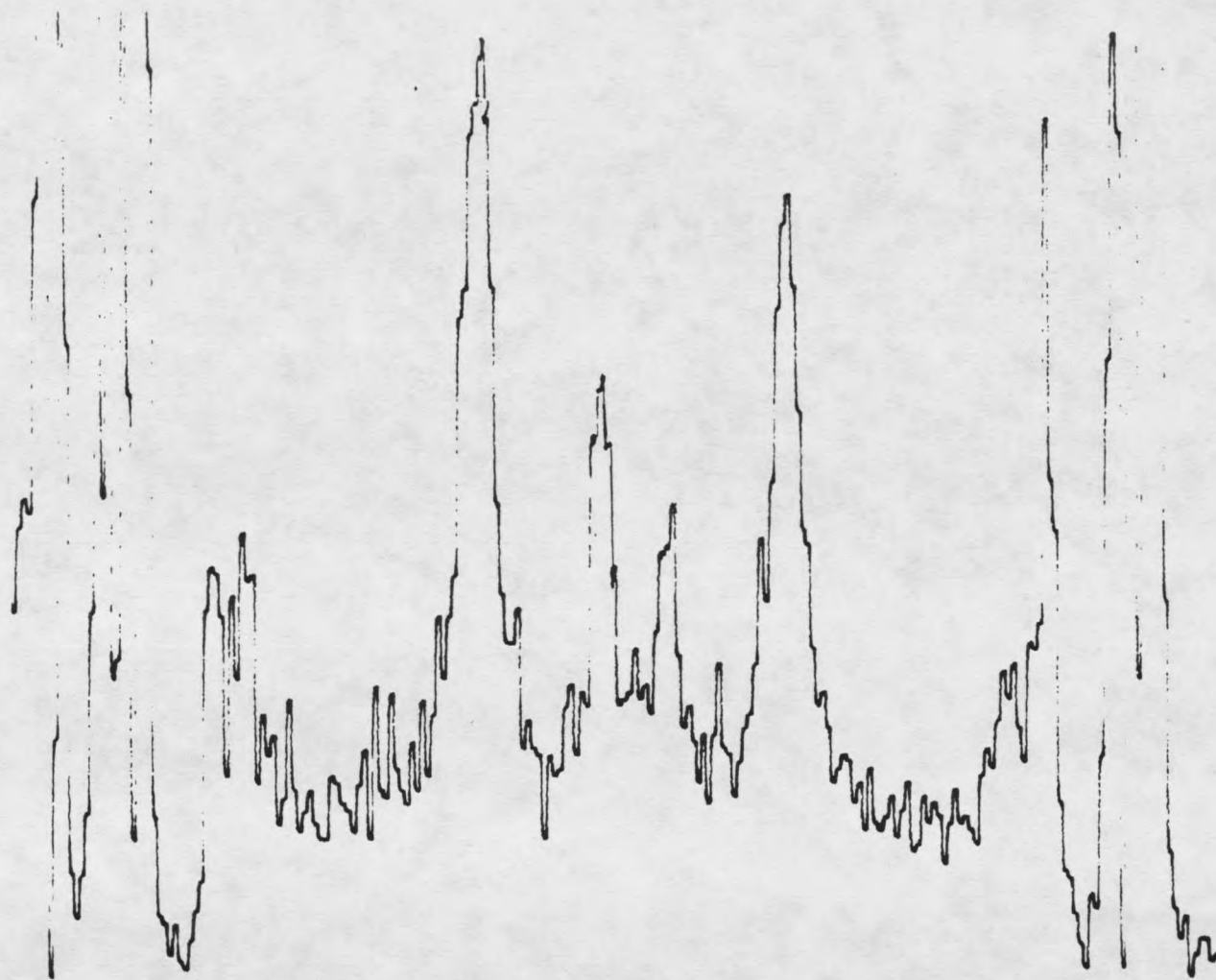


Fig. 10. Brillouin spectrum with reflection peaks

analyzer vertically in front of the pinhole to eliminate interference from the transverse modes. In our experiments, the transverse modes did not show up, probably because they are too weak to be above the noise.

The Brillouin spectrum

Typical traces of the spectrum are shown in Figure 11. The two side maxima are Rayleigh peaks and the two peaks between them are Brillouin scattering peaks. The original measurements are the Brillouin peak shifts from the Rayleigh peak, and the line width. For a certain phonon the positions of Brillouin peaks in the spectrum can be chosen by selecting suitable FSR, i.e. suitable Fabry-Perot spacing d . One should avoid having the two Brillouin peaks too close to each other so that they overlap, or separated too much so they move into the "skirts" of the Rayleigh peaks. After the spectrum was observed we found the frequency shift from

$$\delta v = \frac{L}{m} FSR \quad \text{IV-2}$$

where L is the channel in which the Brillouin peak is located and m is the total channel number change from the first to second Rayleigh peaks. The scan is divided into 256 channels so the resolution of this system is about

FSR/250. The typical FSR in the experiment is 12 GHz, so by the equation $v = \lambda f_p / \sqrt{2}$, the resolution in velocity is about 17 m/s.

The observed line width consists of three contributions: (1) The intrinsic instrumental broadening W_{inst} which includes the effect of the Fabry-Perot characteristics and the laser line broadening due to the jittering claimed by the manufacturer to be about 10 MHz. From the definition of finesse $F = FSR / W_{fp}$, where W_{fp} is the line width from the Fabry-Perot, $W_{fp} = FSR / F$. In our case the finesse is about 100, FSR is about 14 GHz, and $W_{fp} \approx 140$ MHz which is much wider than the laser line broadening of 10 MHz. Accordingly, $W_{inst} \approx W_{fp} = 0.01$ FSR. (2) The collection angle broadening W_{ang} which is determined by²⁵

$$W_{ang} = \frac{1}{2} \cot\left(\frac{\theta}{2}\right) \theta_c \delta v$$

where θ is scattering angle, and θ_c is collection angle calculated from collection optics, in our case about 4° . The W_{ang} is about $0.03\delta v$. (3) the natural phonon line width (FWHM) W_{ph} that we have interest in. For calculating W_{ph} , the natural phonon spectrum and the instrumental function were assumed to have Lorentzian distribution, and the broadening due to collection optics was assumed to have rectangular distribution. In

this case, the W_{ph} is given by⁴¹

$$W_{ph} = (W_{obs}^2 - W_{ang}^2)^{\frac{1}{2}} - W_{inst} \quad \text{IV-3}$$

The relation between the phonon decay rate Γ or the natural phonon line width $\Gamma/\pi = W_{ph}$ and the attenuation coefficient α is given by^{41,49} $\Gamma/\pi = \alpha v/\pi$.

Data presentation

In the following discussion, we denote measured data and various transition temperatures for oriented samples by the sound propagation direction index x or y and denote data for isotropic samples by index i, for example v_x , T_{cy} and T_{gi} .

Figures 12, and 13 show the temperature dependence of the sound velocity for 70/30 mol% VF₂/TrFE isotropic copolymers for heating and cooling runs. The temperature dependence of sound velocity appears quite clearly. The first kink in the v-T curve represents the glass transition T_g at about -23° C which was determined by fitting sound velocity data in temperature range -70° to 25° C to the following equation⁵⁰

$$V(T) = a_1 - a_2 T - a_3 [\text{abs}(T - T_g)] \quad \text{IV-4}$$

where a_1 , a_2 , a_3 are fitting parameters which describe the slope of the T-v curve. The ferroelectric to paraelectric (FP) transition is found to be about $T_c=100^\circ \text{ C}$ by a method¹⁷ which will be discussed in detail in Chapter V. A broad hysteresis appears clearly in comparing the heating and the cooling runs. Figures 14, and 15 show the phonon attenuation in heating and cooling runs. No anomaly was observed in the heating run. In the cooling run, near but below the paraelectric to ferroelectric (PF) transition point there is an obvious maximum. We also observed the Brillouin peak splitting in this region. Figures 16, and 17 compare normal Brillouin peaks to split peaks. The reason for splitting will be discussed in Chapter V.

Figures 18-21 show the temperature dependence of sound velocity for 80/20 mol% VF₂/TrFE copolymers. Figure 18 shows v_x , v_y and v_i vs. temperature in the -70° to 25° C range. They have almost the same T_g . Figures 19-21 shows v_i , v_y , and v_x vs. T for heating and cooling runs. The v_y and v_i vs. T curves show FP and PF phase transitions and clear hysteresis. Their T_c is higher than T_{ci} for 70/30 mol% copolymer. The phase transition did not appear in the v_x vs. T curve.

Figures 22-25 show similar results of v_i , v_y and v_x vs. temperature for

60/40 mol% VF₂/TrFE copolymers. All T_c values for these samples are lower than for their partners from 80/20 and 70/30 mol% samples. Figures 26-29 show similar results for VF₂/TFE 81/19 mol% copolymers. No phase transitions were observed in the data.

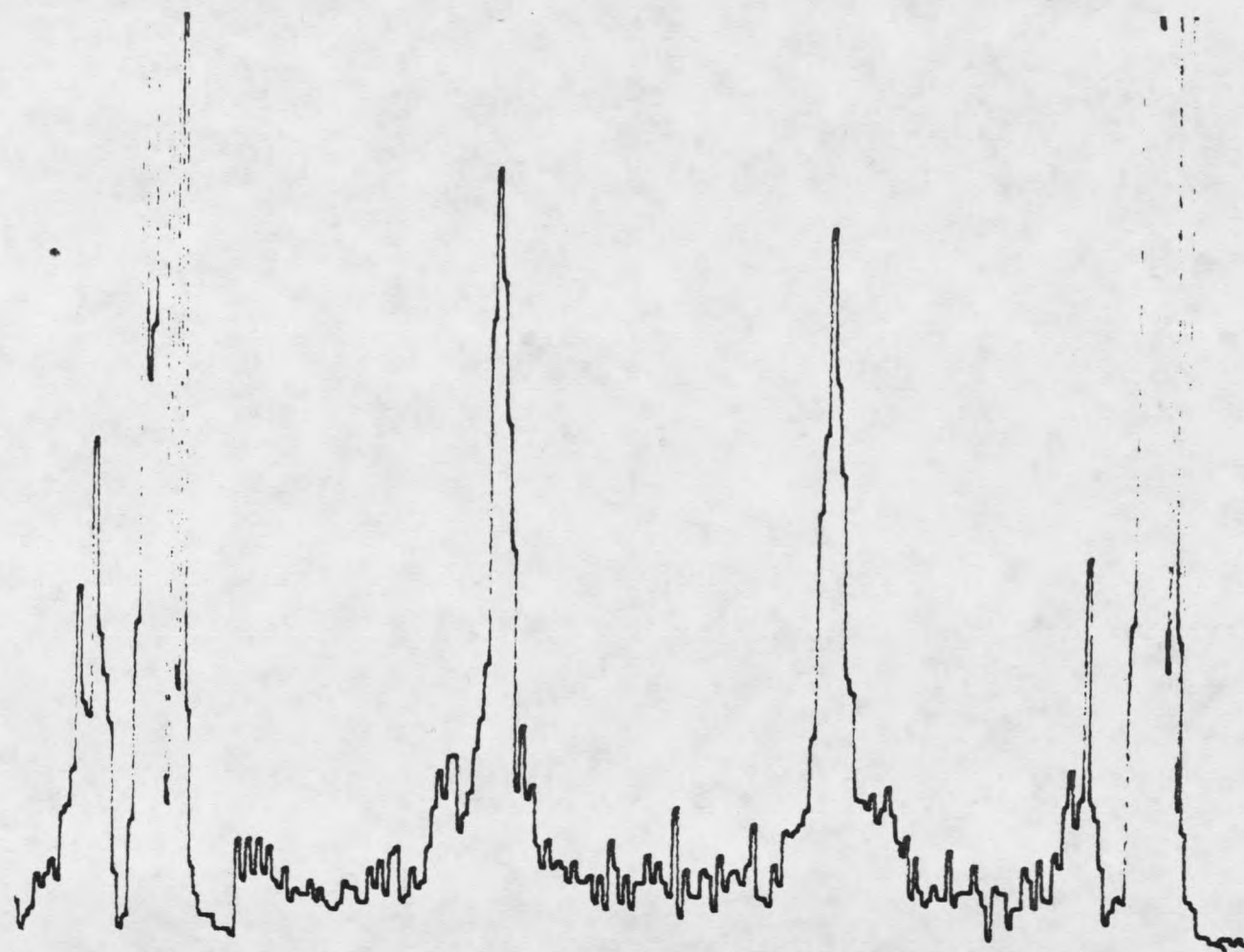


Fig. 11. Typical traces of the Brillouin spectrum

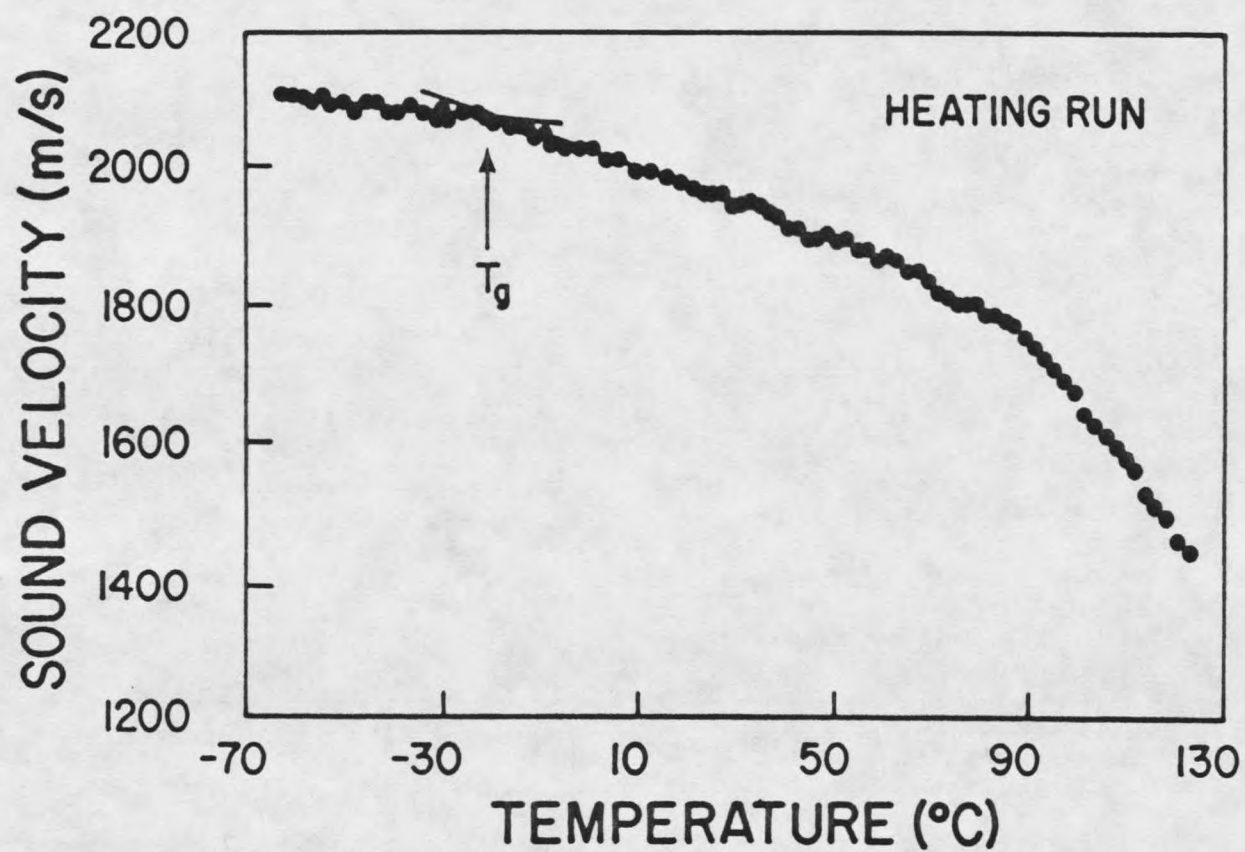


Fig. 12. Sound velocity vs. temperature curve with fitting lines from heating run for 70/30 mol% VF₂/TrFE isotropic copolymer

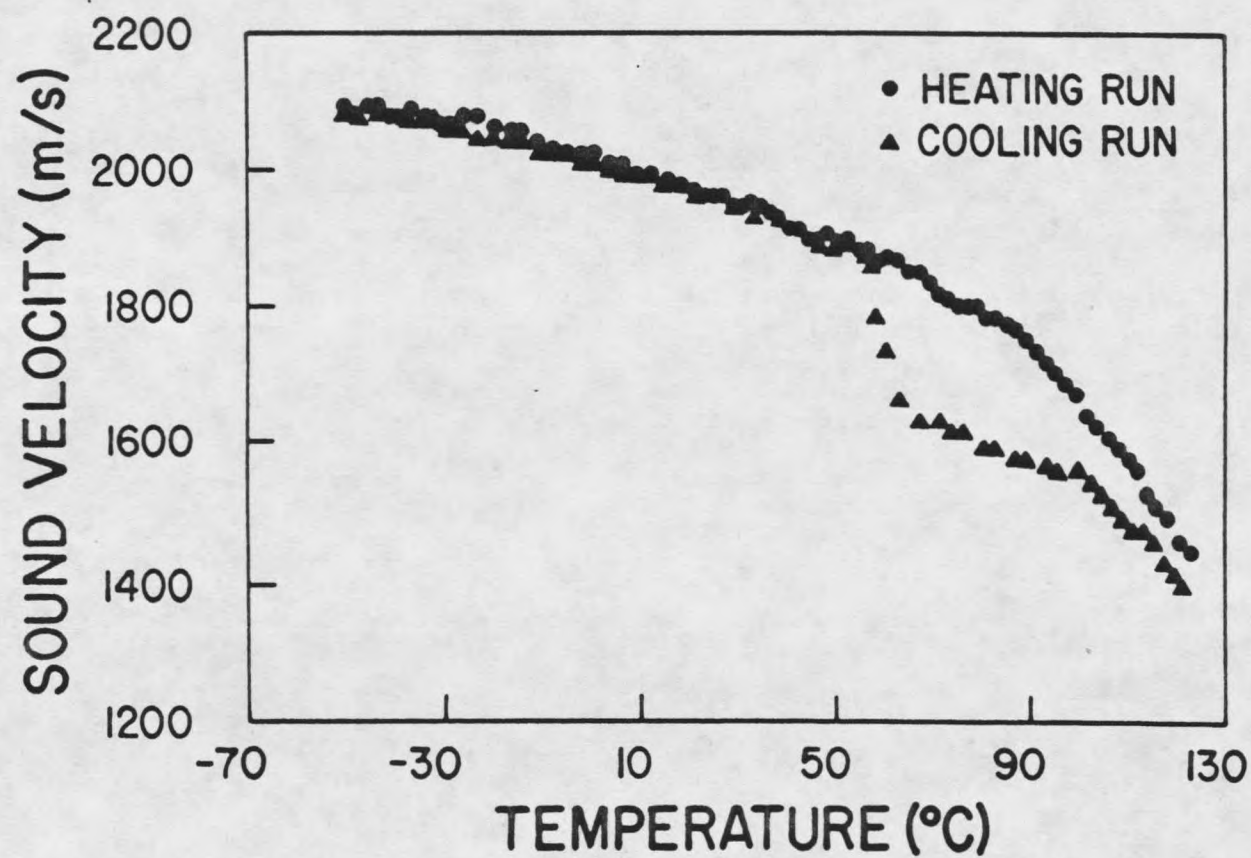


Fig. 13. Sound velocity vs. temperature curves from both heating and cooling runs for 70/30 mol% VF₂/TrFE copolymers

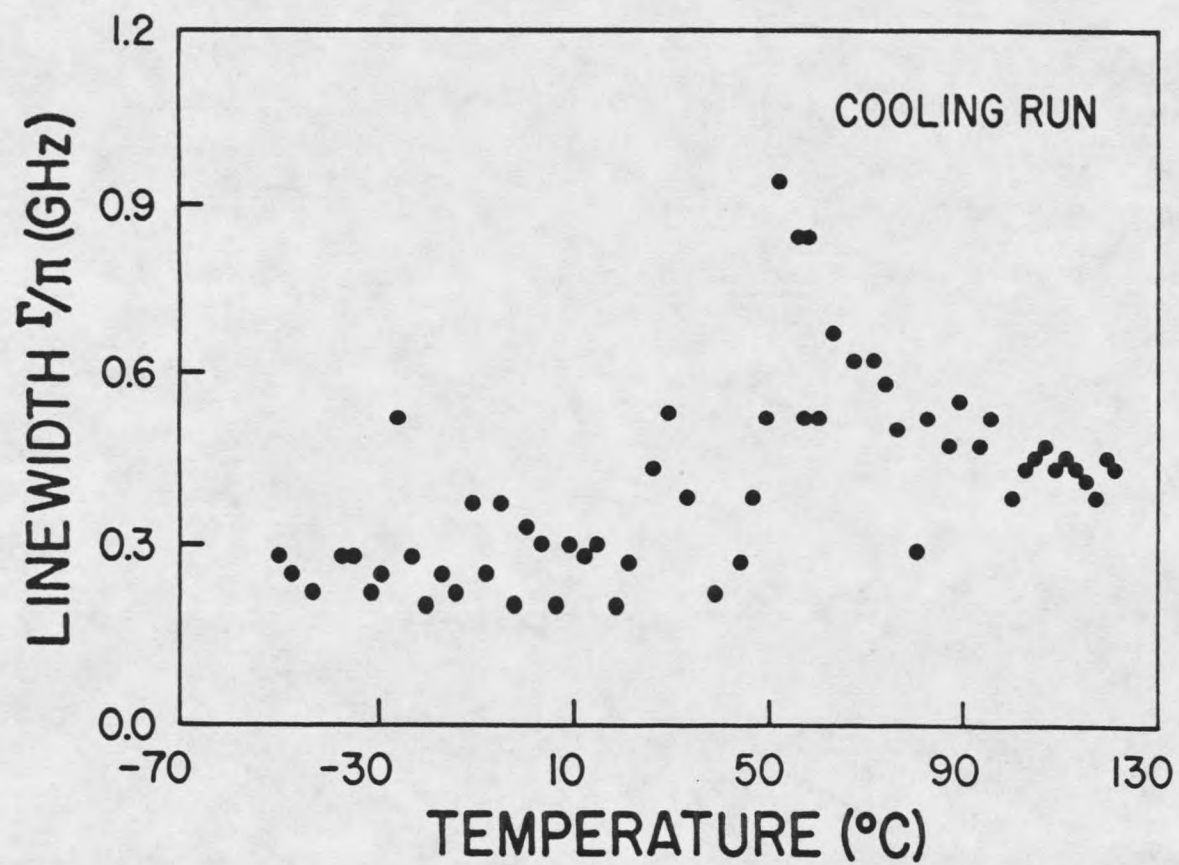


Fig. 14. Sound attenuation vs. temperature from cooling run for 70/30 mol% VF₂/TrFE copolymer

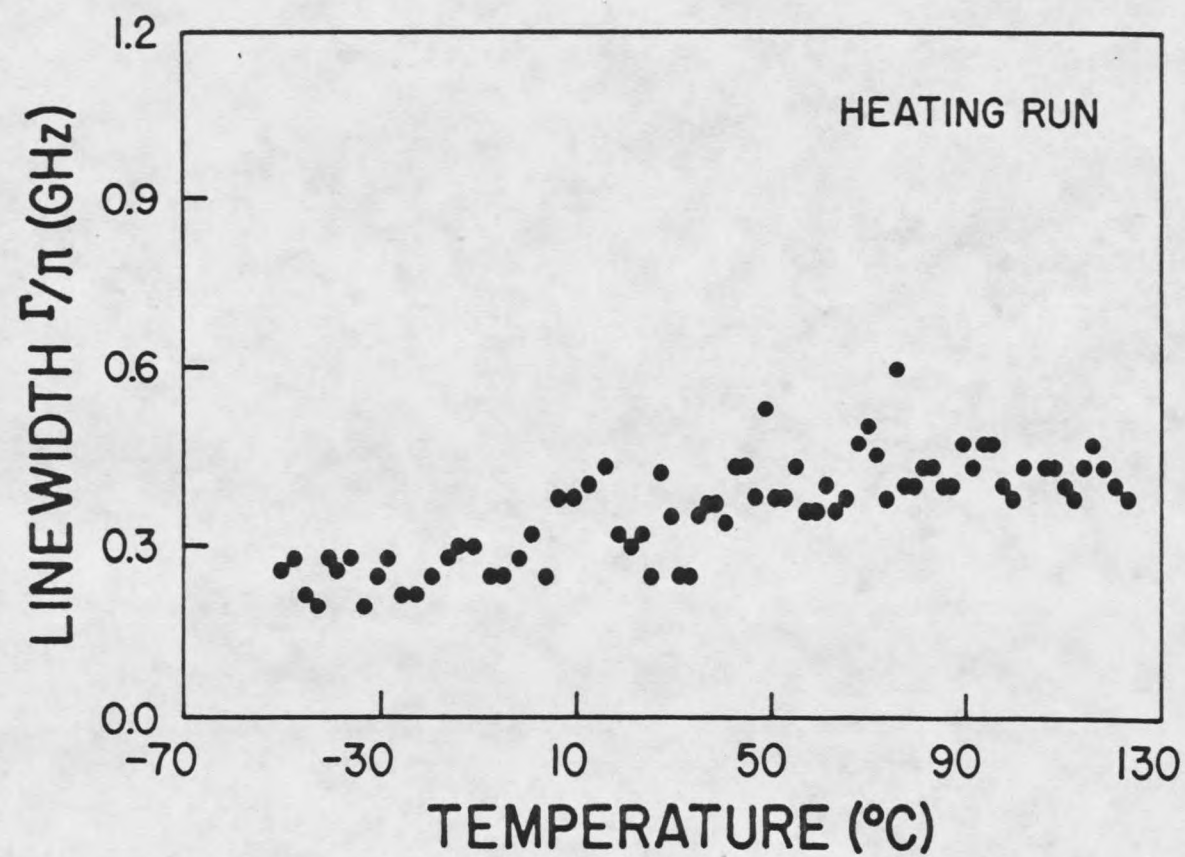


Fig. 15. Sound attenuation vs. temperature from heating run for 70/30 mol% VF₂/TrFE copolymer

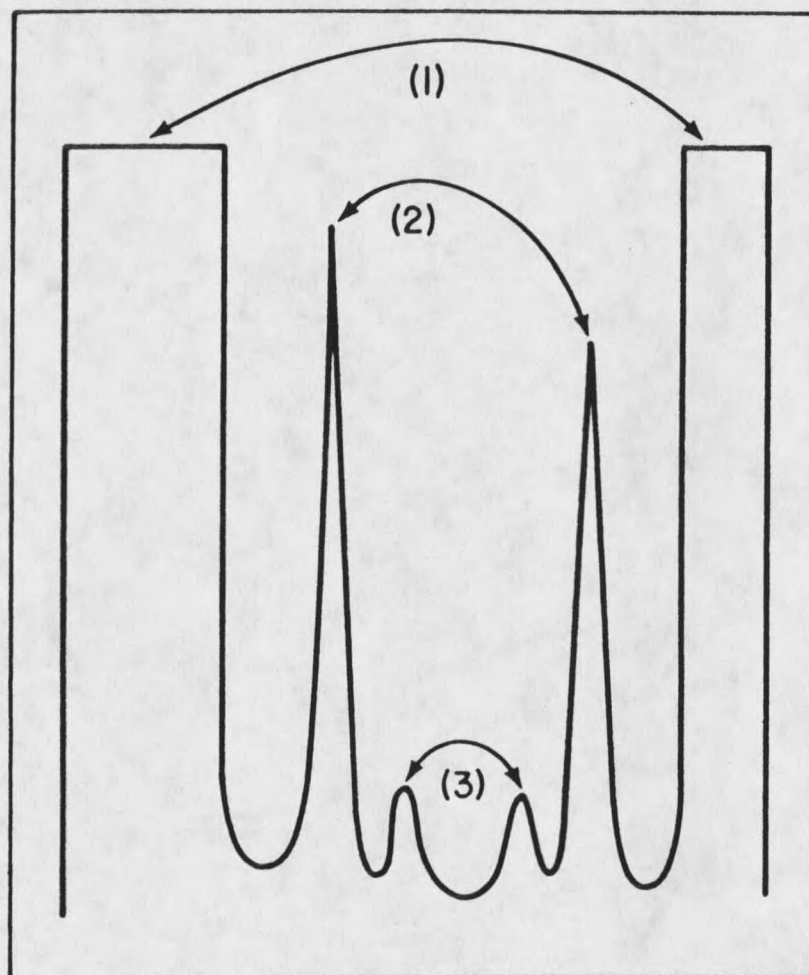


Fig. 16. Normal Brillouin peaks at $T=45^{\circ}\text{C}$ for 70/30 mol% copolymer. Peak types (1-3) are identified in text. All Brillouin peaks belong to their nearest Rayleigh peaks

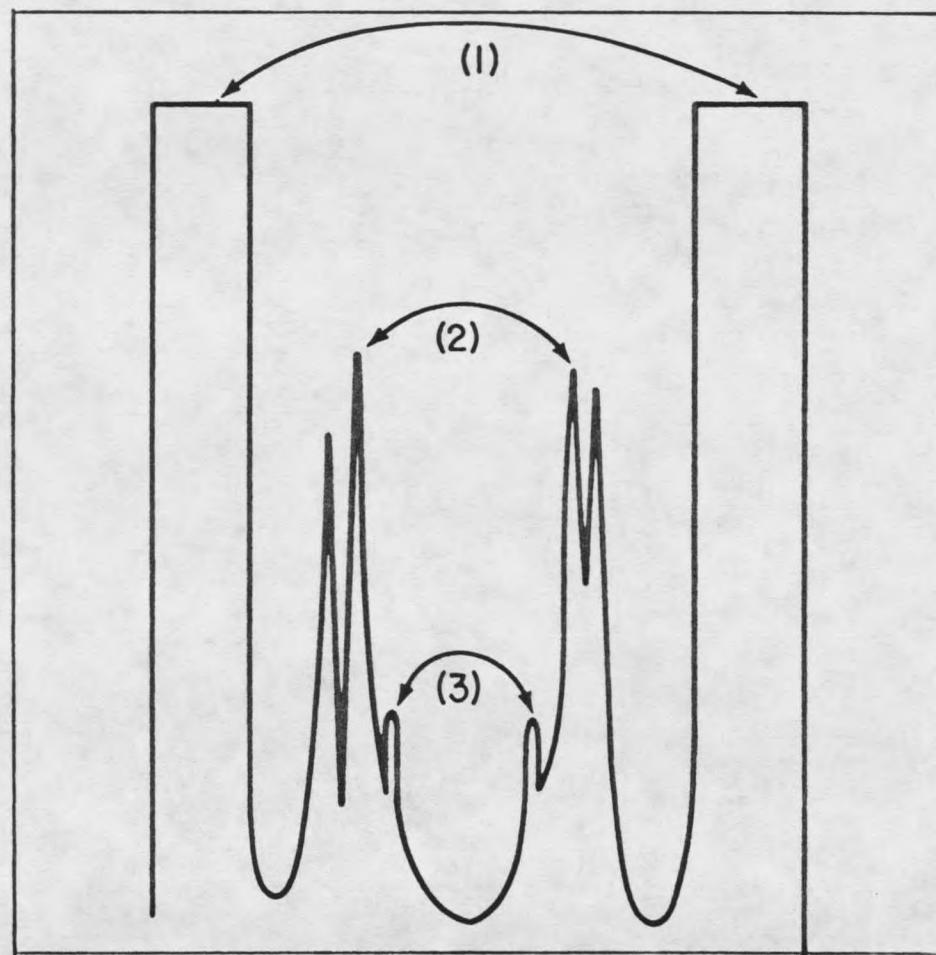


Fig. 17. Split Brillouin peaks at $T=57.6^{\circ}\text{C}$ for 70/30 mol% copolymer

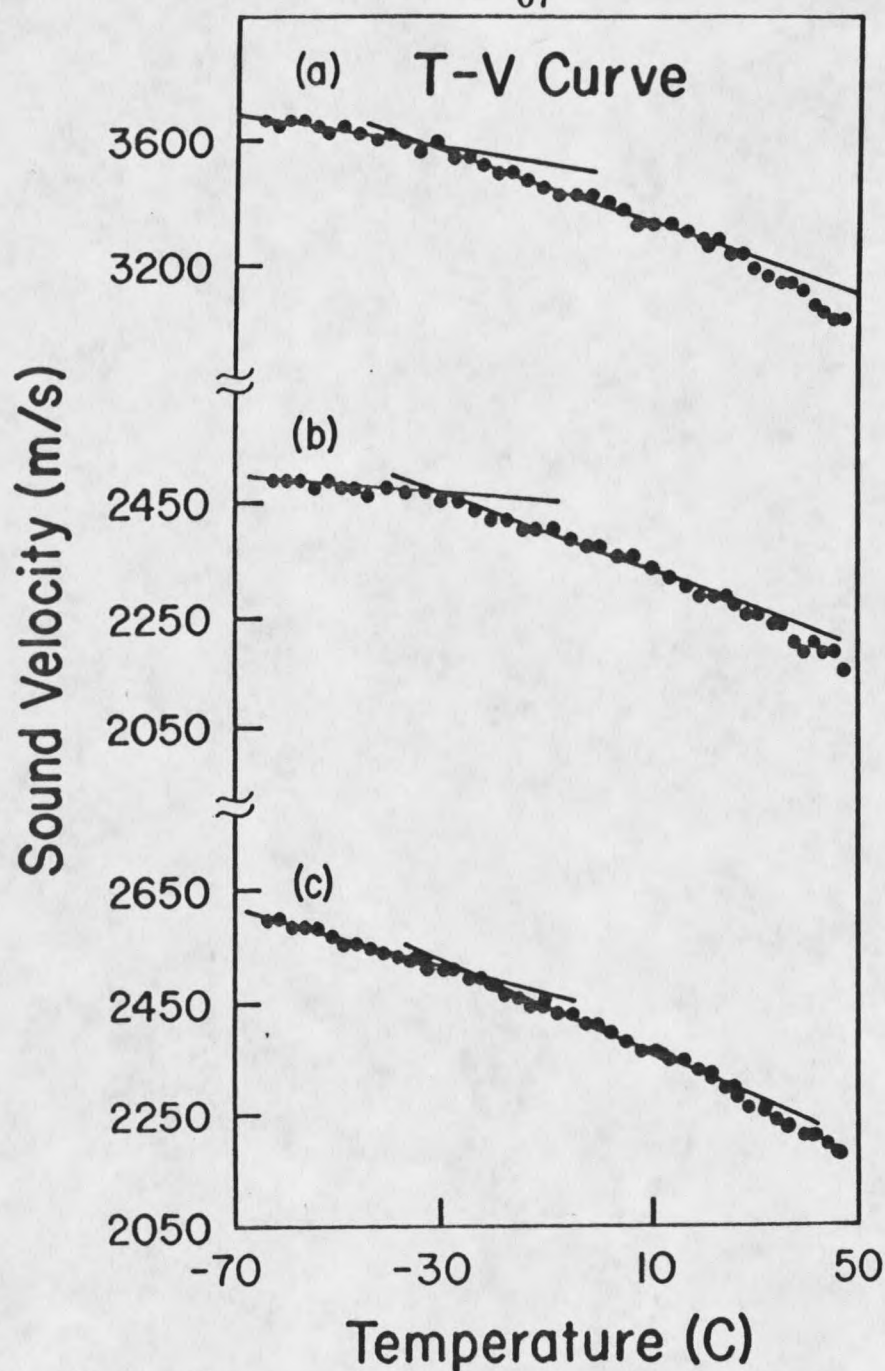


Fig. 18. Temperature dependence of sound velocity for 80/20 mol% VF₂/TrFE copolymers in temperature range of -70 to 25° C. (a) stretched sample for sound propagation along x axis, (b) stretched sample for sound propagation along y axis, (c) isotropic sample

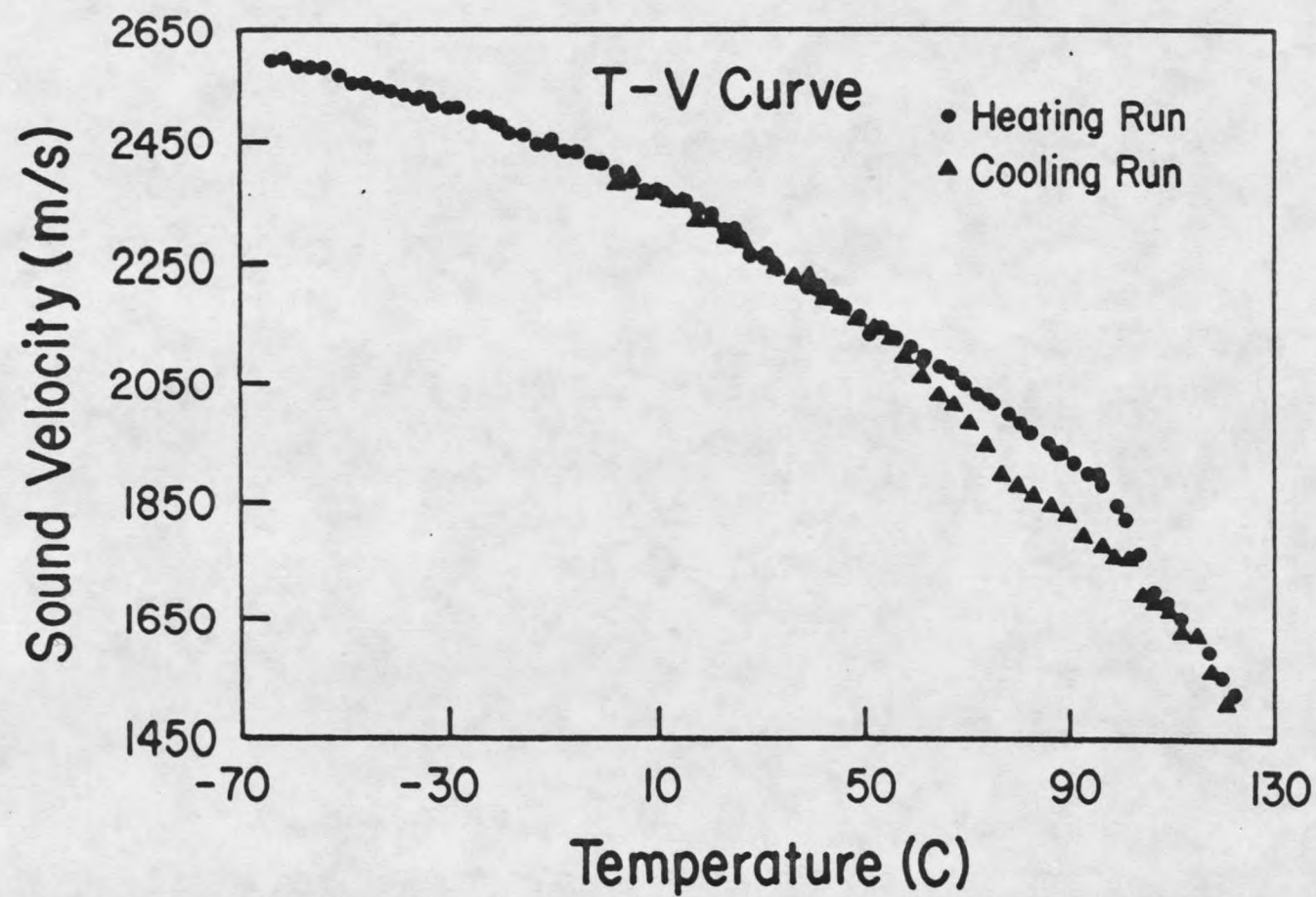


Fig. 19. Sound velocity vs. temperature for isotropic 80/20 mol% VF_2/TrFE sample, o: heating run, Δ : cooling run

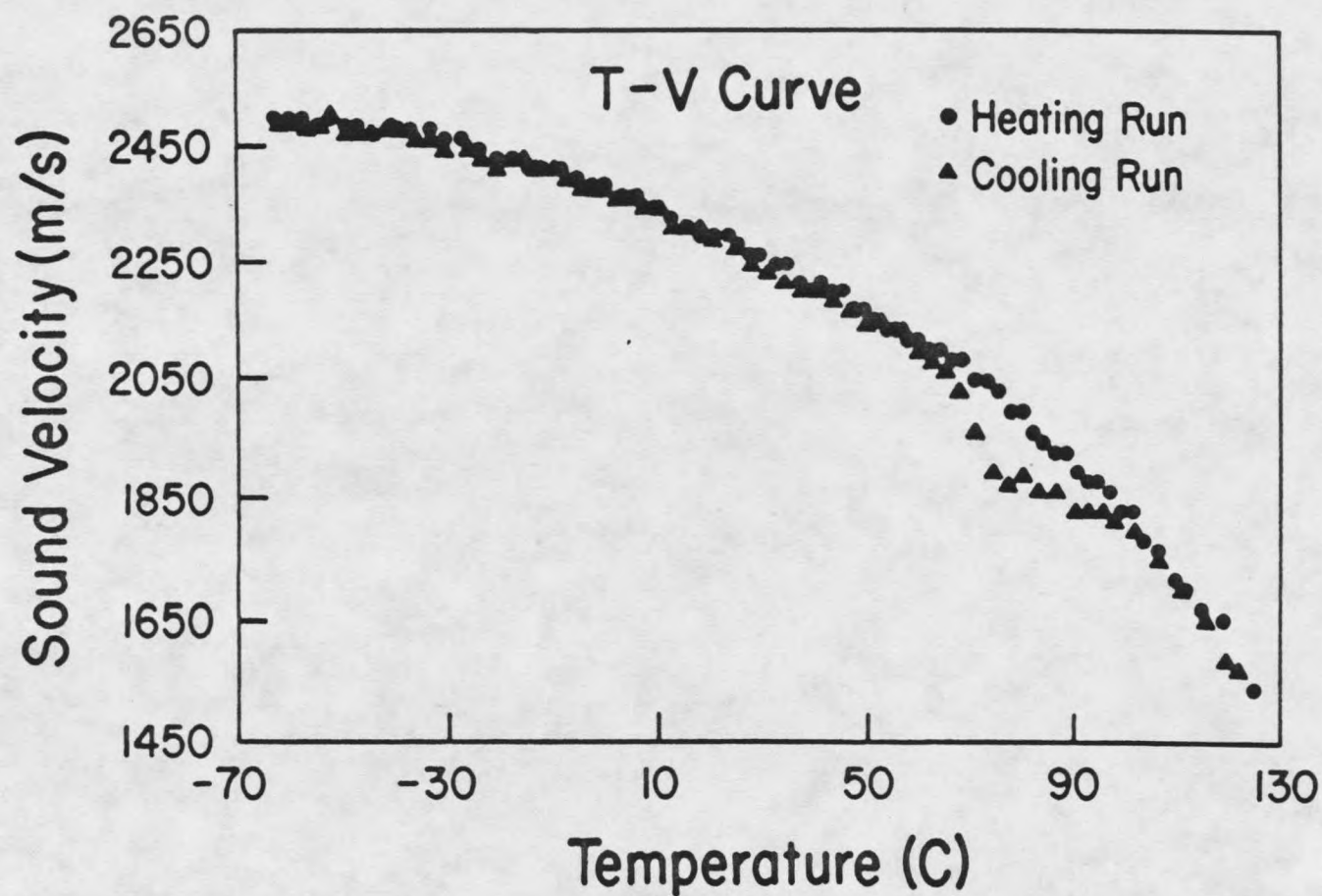


Fig. 20. Sound velocity vs. temperature for stretched 80/20 mol% VF₂/TrFE sample for sound propagation along y axis, o: heating run, Δ: cooling run

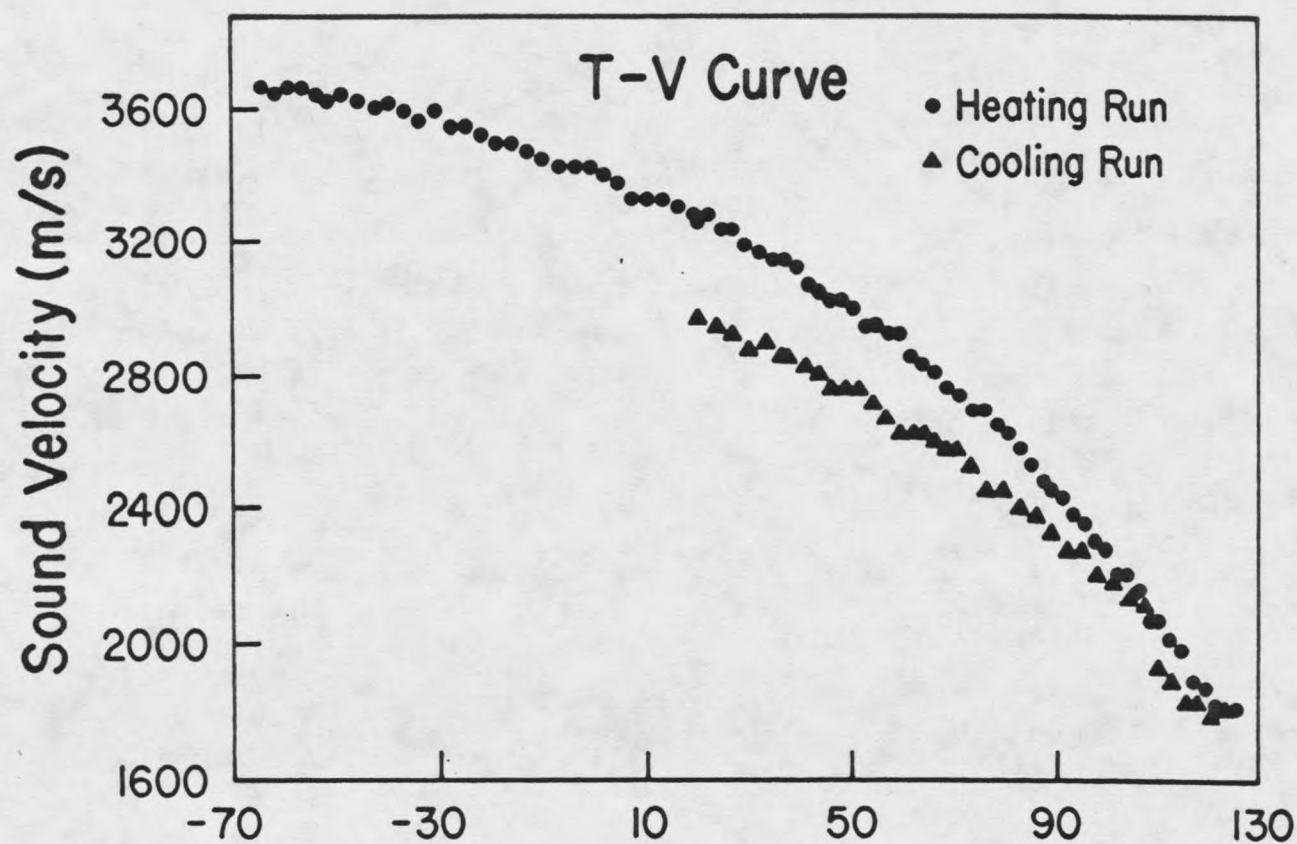


Fig. 21. Sound velocity vs. temperature for stretched 80/20 mol% VF_2/TrFE sample for sound propagation along x axis, o: heating run, Δ : cooling run

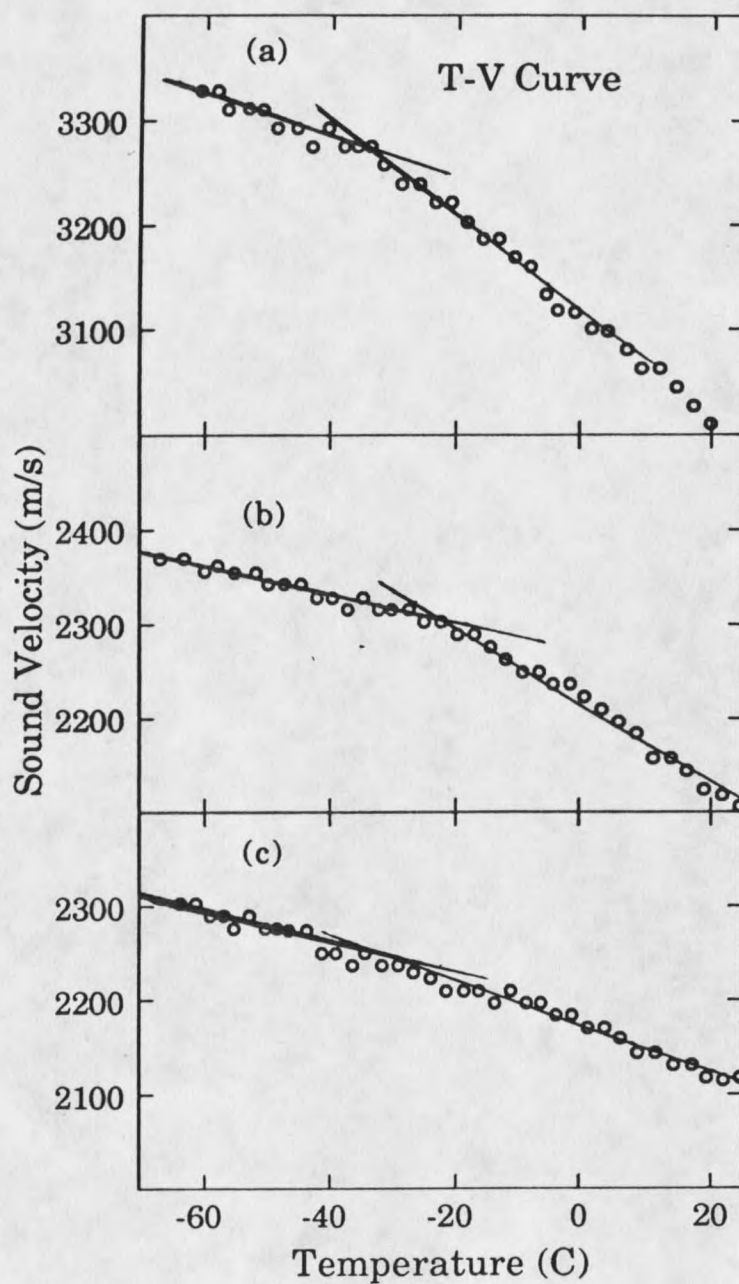


Fig. 22. Temperature dependence of sound velocity for 60/40 mol% VF₂/TrFE copolymers in temperature range of -70 to 25° C. (a) stretched sample for sound propagation along x axis, (b) stretched sample for sound propagation along y axis, (c) isotropic sample

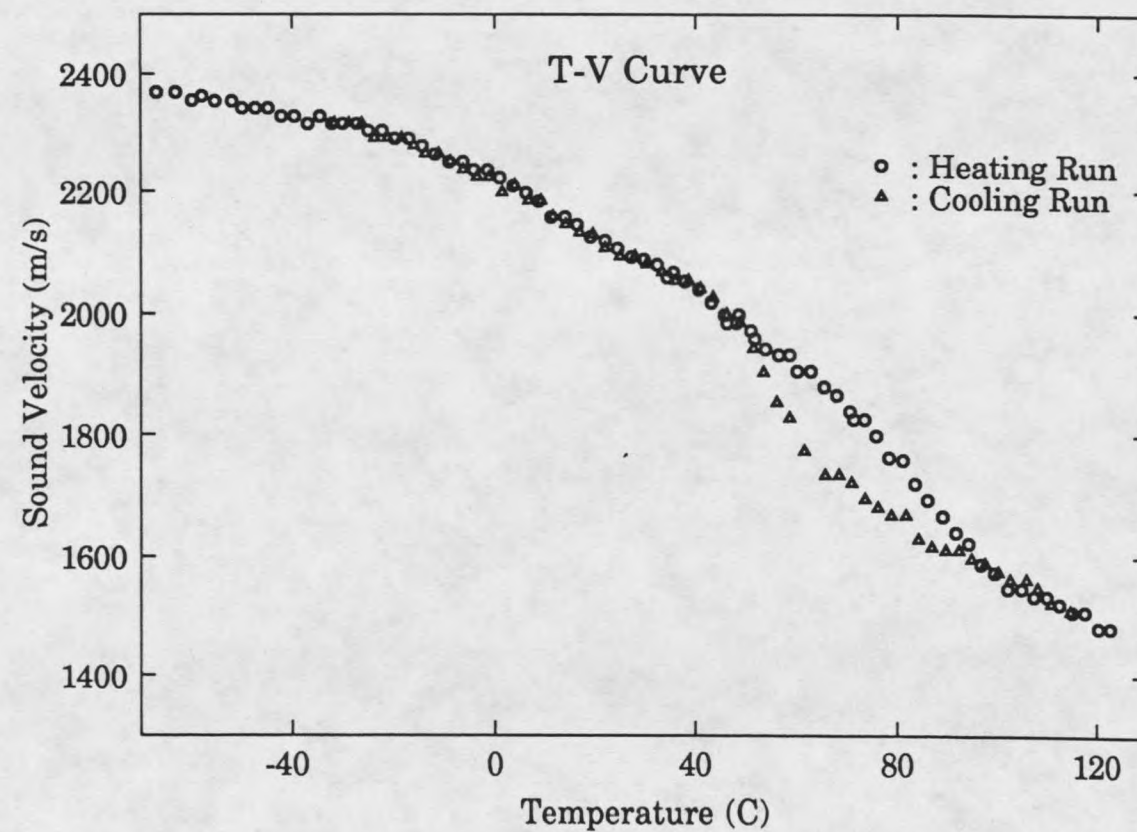


Fig. 23. Sound velocity vs. temperature for isotropic 60/40 mol% VF_2/TrFE sample, o: heating run, Δ: cooling run

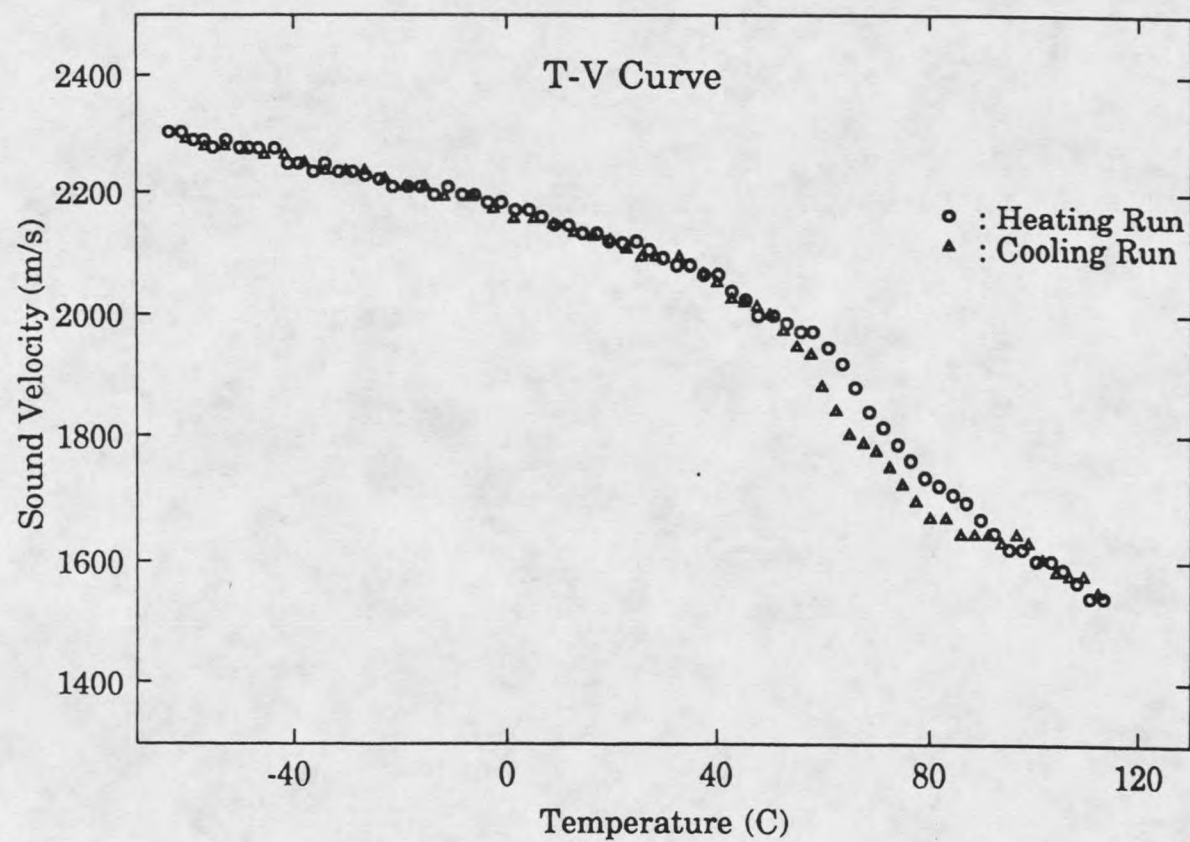


Fig. 24. Sound velocity vs. temperature for stretched 60/40 mol% VF_2/TrFE sample for sound propagation along y axis, ○: heating run, △: cooling run

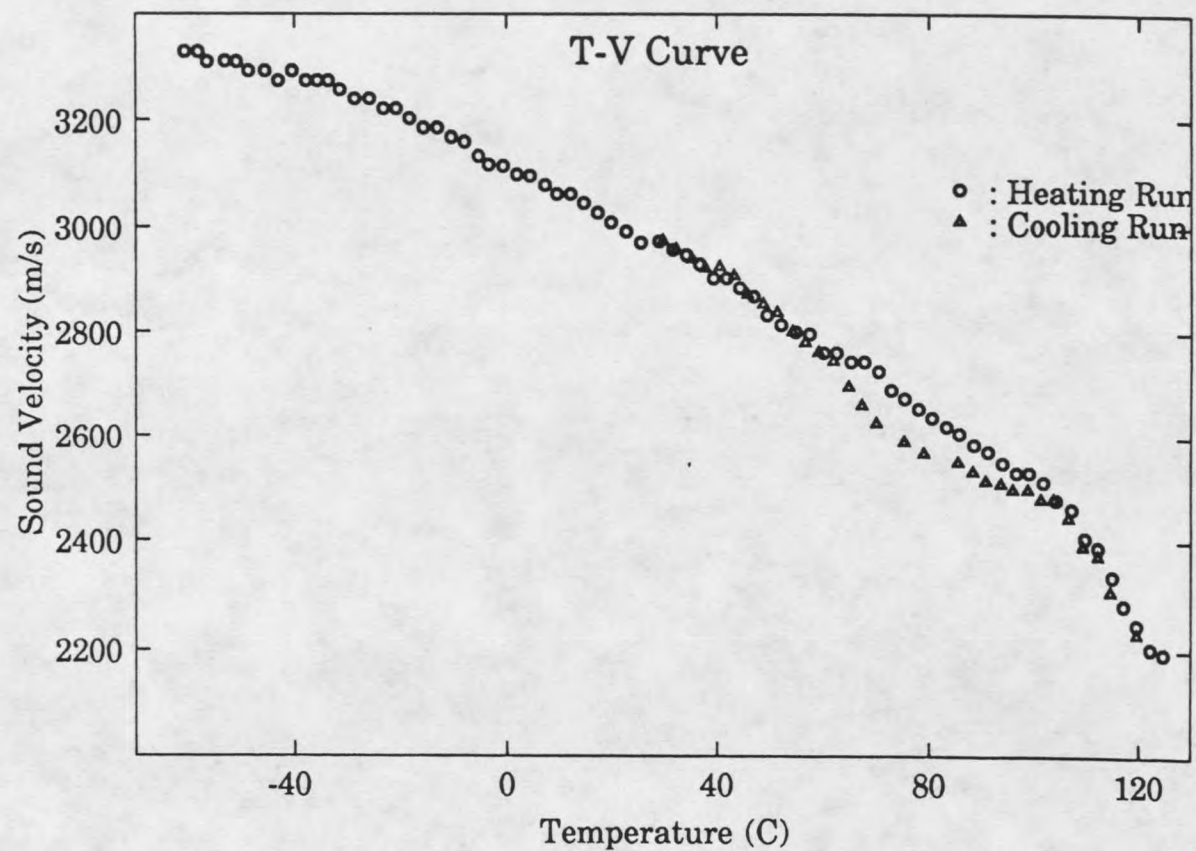


Fig. 25. Sound velocity vs. temperature for stretched 60/40 mol% VF₂/TrFE sample for sound propagation along x axis, o: heating run, Δ: cooling run

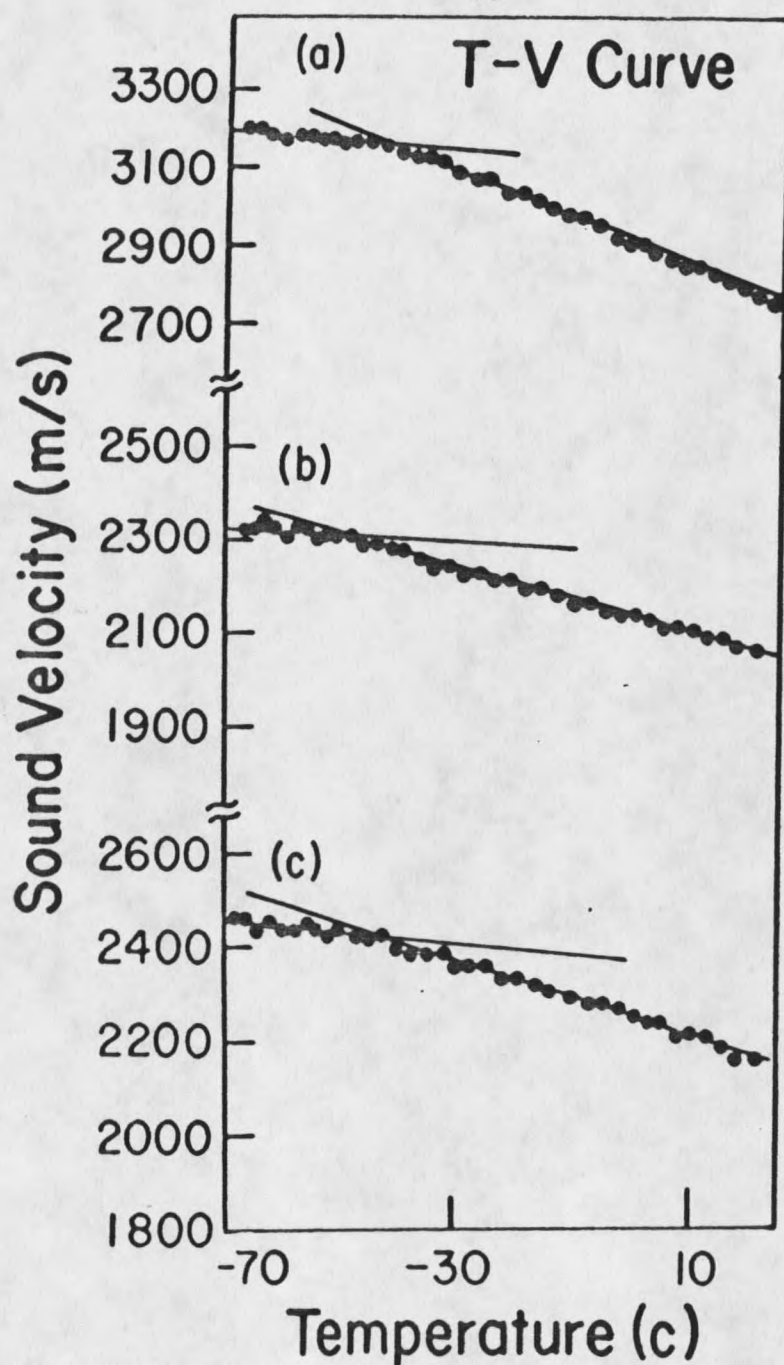


Fig. 26.

Temperature dependence of sound velocity for 81/19 mol% VF_2/TFE copolymers in temperature range of -70 to 25°C .
 (a) stretched sample for sound propagation along x axis,
 (b) stretched sample for sound propagation along y axis,
 (c) isotropic sample

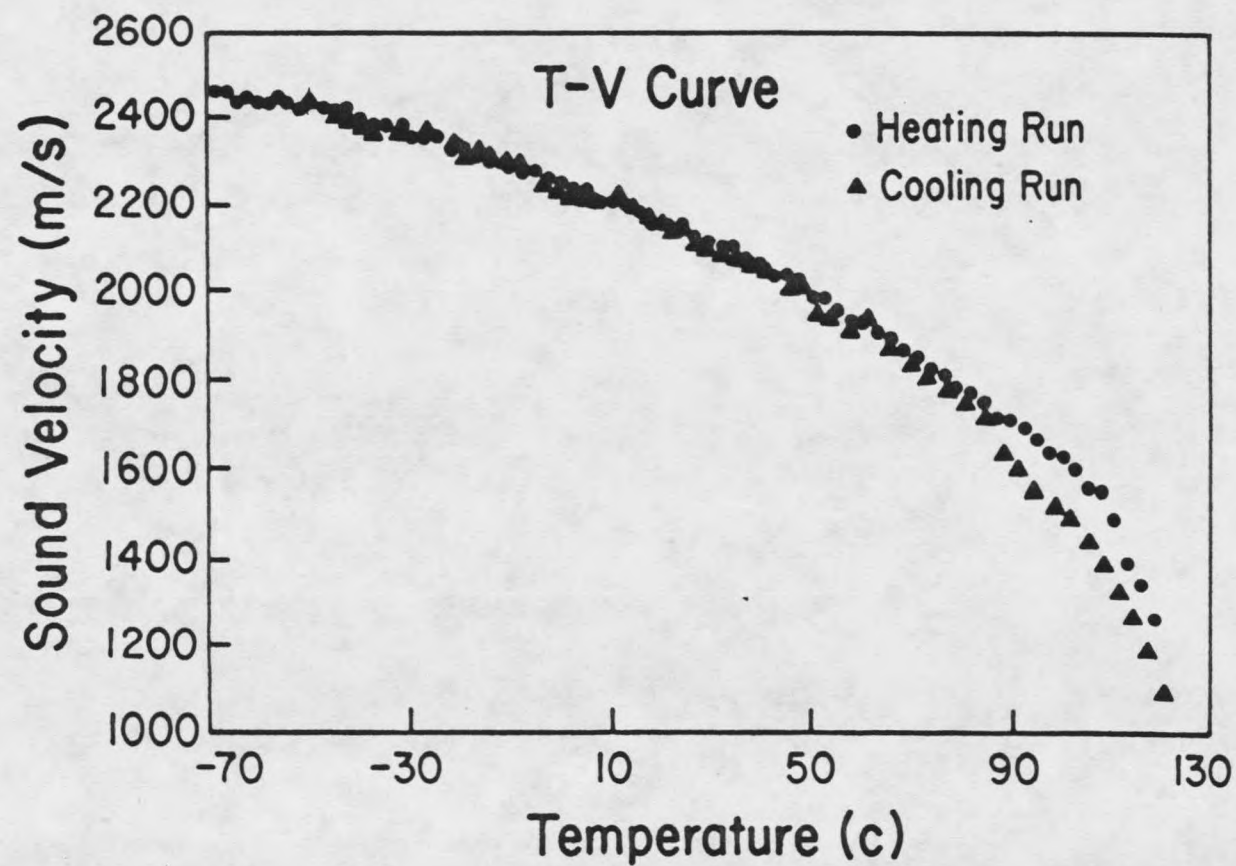


Fig. 27. Sound velocity vs. temperature for isotropic 81/19 mol% VF_2/TFE sample, o: heating run, Δ : cooling run

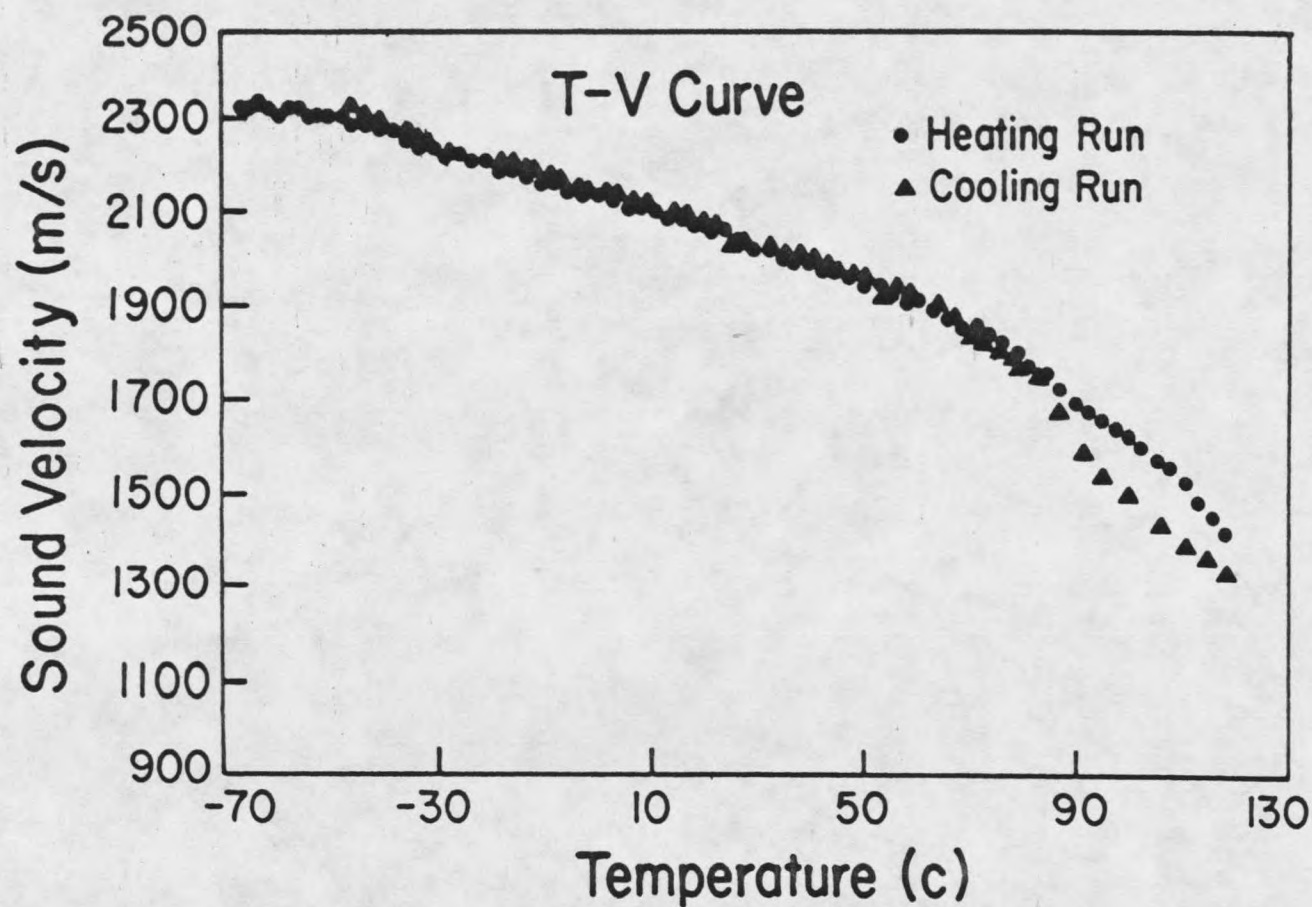


Fig. 28. Sound velocity vs. temperature for stretched 81/19 mol% VF₂/TFE sample for sound propagation along y axis, o: heating run, Δ: cooling run

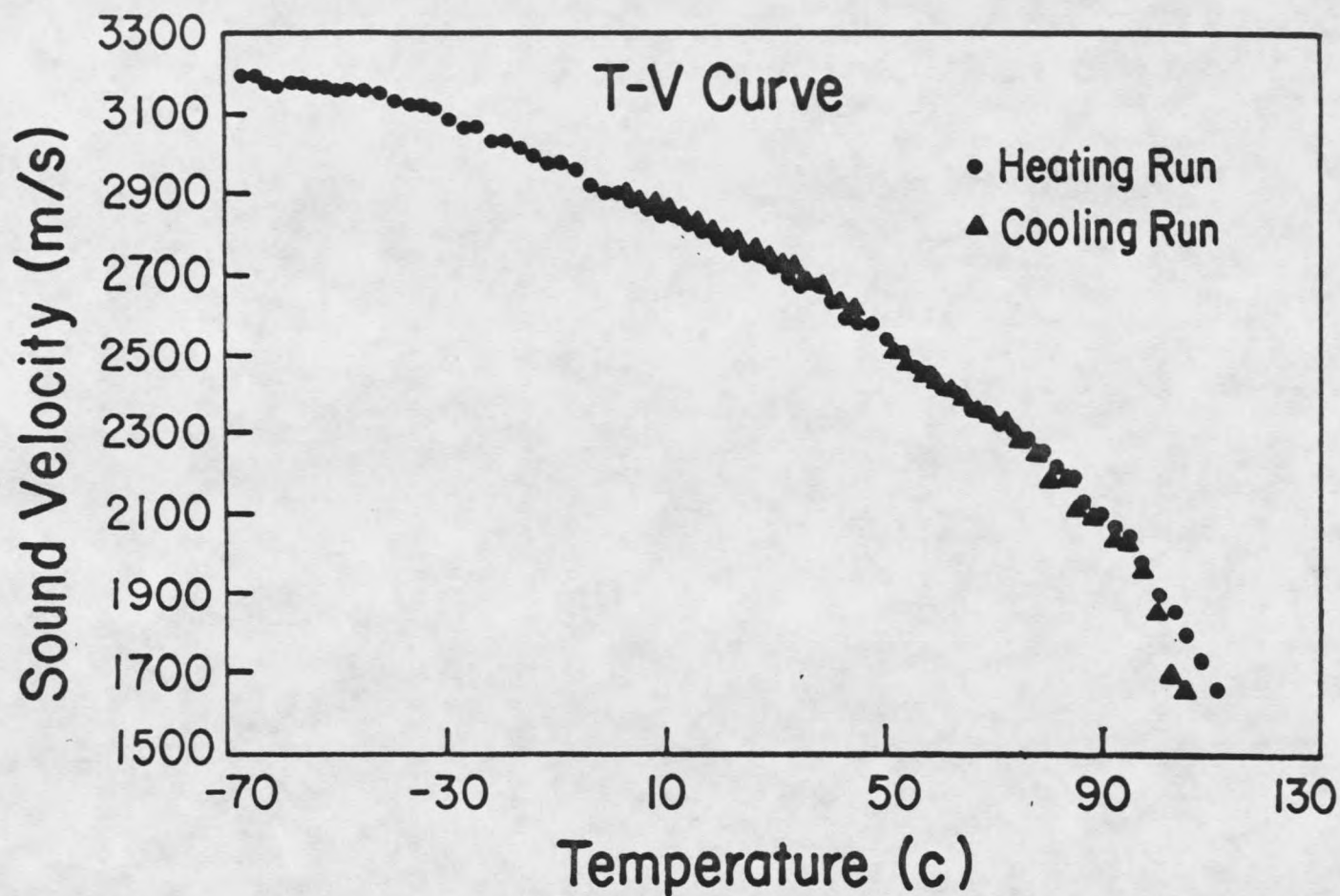


Fig. 29. Sound velocity vs. temperature for stretched 81/19 mol% VF_2/TFE sample for sound propagation along x axis, o: heating run, Δ : cooling run

CHAPTER V

DISCUSSION

The molecular and crystal structure of VF₂-based copolymers

In order to understand the mechanism of the phase transitions of PVF₂ and its copolymers, it will be helpful to look at their molecular and crystal structures. PVF₂, formula (CH₂-CF₂)_n, has a chain-like structure in its carbon bonds. The C-C bonds have three possible conformations which determine the different phases. Figure 30 (a) shows these three bond conformations. If all carbon bonds lie on the same plane, these bonds are called TT. If the bonds tilt in or out of the plane (2 or 3 direction shown in the figure) these bonds are called G or $\bar{G}$. If all the polymer chains are TT, the conformation is called all-trans which corresponds to the ferroelectric (β) phase of polymer; see Fig. 30 (b). Chains with an irregular TGT $\bar{G}$ conformation have the disordered helical conformation which corresponds to the paraelectric (α) phase; see Fig. 30 (c). The TT chain has a dipole moment caused by CF₂ and CH₂ dipoles all with the same direction, but in TGT $\bar{G}$ dipoles are in all directions and cancel each other. The PVF₂

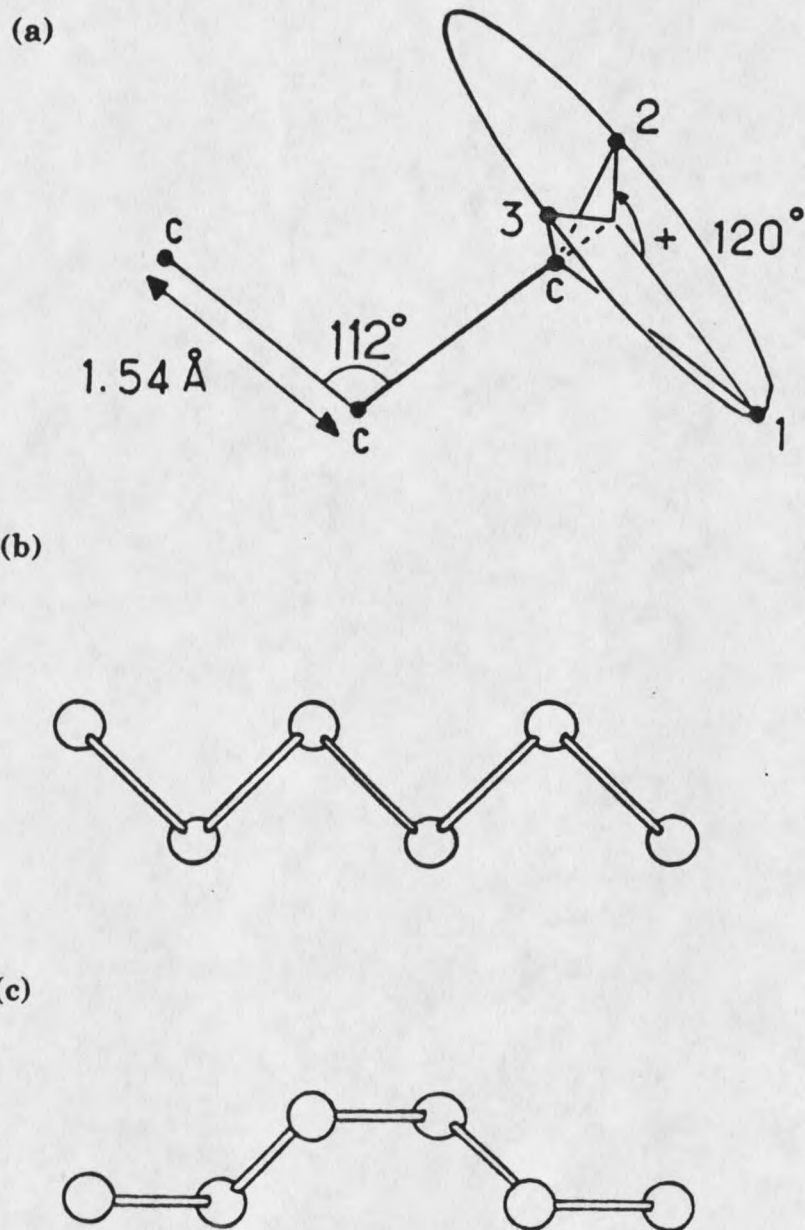


Fig. 30. (a) Three possible C-C bonds in T, G, and $\bar{G}$ directions
 (b) TT conformation (zigzag planar)
 (c) TGT $\bar{G}$ conformation (non-planar)

polymers in the TGT $\bar{G}$ conformation can be transformed to the TT conformation by electrical or mechanical methods. As indicated in Chapter I, a thermally caused transformation has never been seen.

However if CF₂-CHF (trifluoroethylene) or CF₂-CF₂ (tetrafluoroethylene) species are randomly inserted into VF₂ polymer chains in sufficient concentrations, the copolymer chains order in the all-trans conformation automatically, i.e. in the β phase. Reasons for this lie in steric effects associated with the Van der Waals radii of fluorine and hydrogen.⁵¹ The copolymers of VF₂/TrFE and VF₂/TFE with VF₂ content from 40 to 80 mol% are ferroelectric and have all-trans conformation at room temperature. But each TT chain can take any direction around its chain axis, so the above copolymers are not necessarily piezoelectric. They can be made piezoelectric by high-electric field poling.

PVF₂-based copolymers are semicrystalline. Small crystalline lamella are embedded in an amorphous matrix as shown in Figure 31 from Broadhurst. The chains in the isotropic copolymer take all directions. Since the molecular lengths are of the order of 100 times the lamellae thickness, each molecule may pass many crystal layers.⁵² In the stretched (oriented) copolymers, most chain axes take the stretch direction (x axis in following discussion). The gaps between the crystalline units are smaller in the transverse direction than in the stretch direction.⁵³

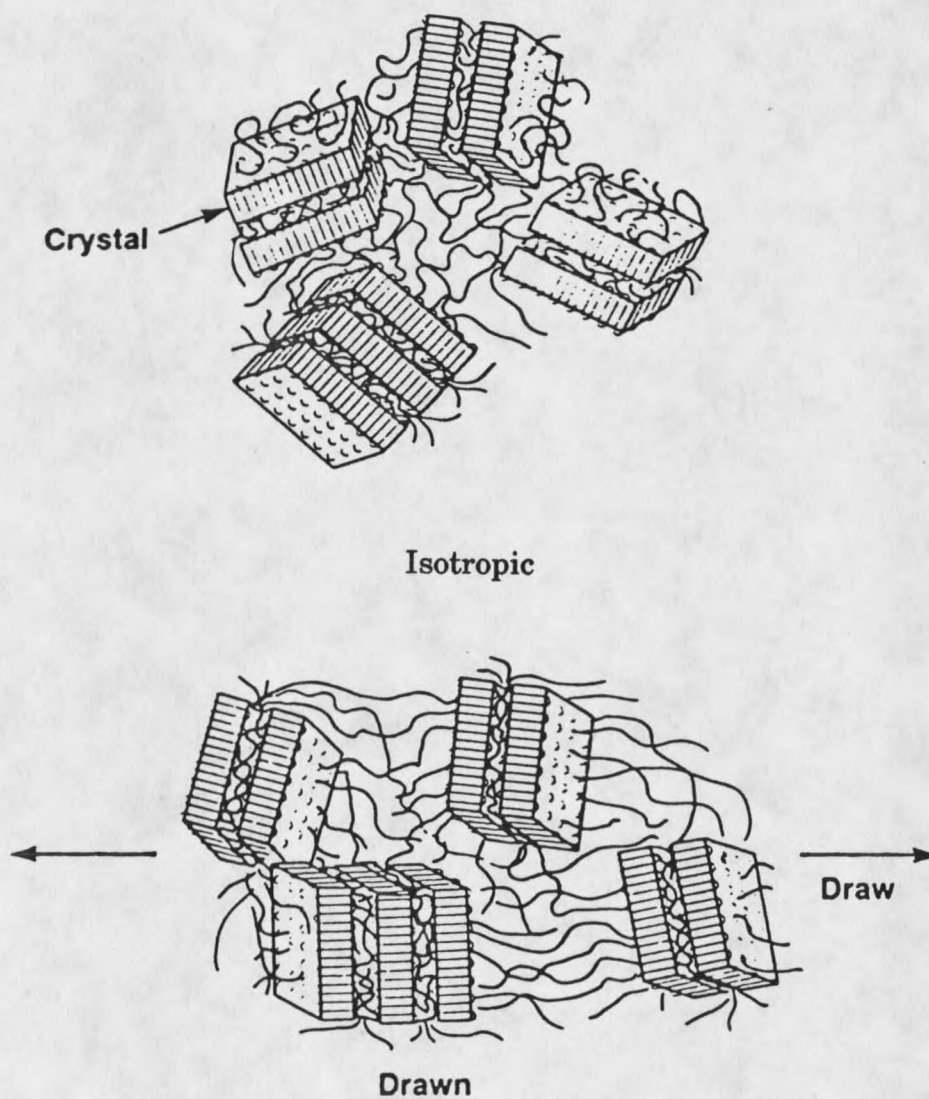


Fig. 31. Schematic picture showing random stacks of crystal lamellae in a sample of VF_2 and their orientation after the film is stretched to several times original length.

Figure 32 shows the crystal structure of the copolymer in the β phase. The space group is orthorhombic $m2m$, but its a and b dimensions ($a=8.58 \text{ \AA}$, $b=4.91 \text{ \AA}$) render this cell pseudo-hexagonal with deviation less than 1% from true hexagonal.⁵⁴

Interpretation of temperature dependence of sound velocity

Light scattering spectroscopy offers experimental evidence for the structural phase transition. The theory as reviewed in Chapter II has been performed in the framework of a phenomenological approach. A quantitative explanation of experimental results is not available now. Even on the basis of phenomenological theory, it is still difficult to understand the experimental data for this kind of semicrystalline material. Krüger's results for temperature dependence of sound velocity for 70/30 mol% PVF₂/TrFE were similar to ours shown in Fig. 13. He determined the phase transition points by kinks on the curves. From our results, the sound velocity vs. temperature curve can roughly be divided into three linear parts and one curved transition part. From low temperature (about -70° C) to the kink point identified as the glass transition point T_g and from T_g to about 25° C, the curves are basically linear with different slopes. The glass transition at T_g concerns freezing out of motions in the amorphous part of the copolymer. In this part, the temperature dependence of sound velocity

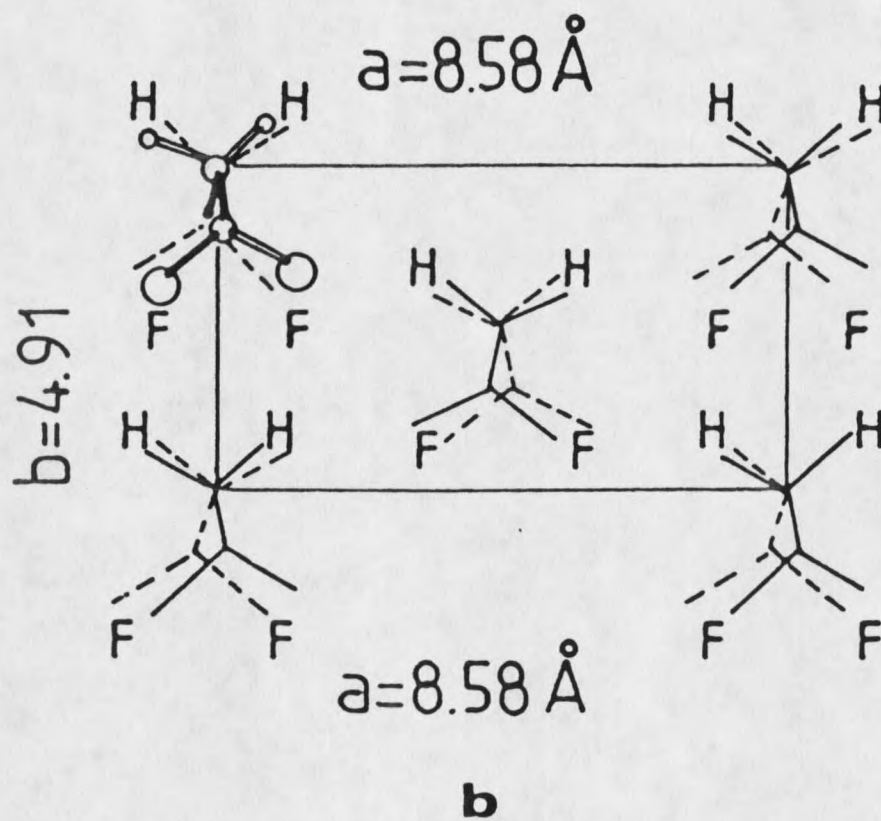


Fig. 32. Unit cell of PVF_2 β phase

is small and related to the thermal expansion below T_g , but becomes much larger above T_g . It can be reasonably assumed that the thermal dependences are linear and have different rates in different phases. The crossing of these two linear parts then corresponds to the glass transition. We determined the glass transition by fitting data to a kink linear equation as indicated in Chapter IV. Above about 25° C the curve becomes obviously nonlinear and becomes linear again at about 100° C. It is believed that the ferroelectric to paraelectric (F-P) transition occurs in the curved area because beside the thermal expansion there is some coupling between polarization and strain due to the sudden structure change. The linear part at the end of the curve is believed to be in the paraelectric phase and the temperature dependence to be only from the thermal expansion. The above argument appears quite plausible even though nobody presented it before. But some unclear points still exist as to what kind of coupling occurs and why the curve looks like it does.

Anomalies of sound velocity involved in that curved phase transition region are of course not as clear for this copolymer as for a single crystal. We believe that the broad curved region results from a statistical mixture contributed by crystals with different sizes and environments, such a large region of coexistence of ferroelectric and paraelectric phases was widely observed.⁵⁵ In the following part we study the coupling theory for one

crystal of PVF₂-based copolymer and expand it to the semicrystalline material. Equation II-33 and Figure 4 show the three dominating coupling terms and their behavior in the transition region. Obviously, no model in Fig. 4 matches our results. The coupling terms are linear coupling $\beta_{ij}Q_i\epsilon_j$, and nonlinear couplings $\gamma_{ijk}Q_iQ_j\epsilon_k$, $\delta_{ijk}Q_i\epsilon_j\epsilon_k$. Which coupling terms are not zero is determined by the symmetry of the crystal. Our copolymer β phase crystals have space group $m2m$, the terms $\beta_{ij}Q_i\epsilon_j$ and $\gamma_{ijk}Q_iQ_j\epsilon_k$ are nonzero^{18,56} for stretched and poled samples. For stretched but unpoled samples like some of ours the linear coupling term vanishes. So the anomalies in our sound velocity in the transition range come from the coupling term $\gamma_{ijk}Q_iQ_j\epsilon_k$. We have defined the sound wave direction, so in the following calculations we omit the subscripts for convenience. Rehwald calculated the stiffness behavior in the transition region for the above three coupling terms for a second-order transition.¹⁸ The F-P transition in PVF₂-based copolymers is first order. We present a similar calculation of transition behavior for a first order transition using Landau's theory.

In Landau's expansion of free energy in Eq. II-30, a second order transition takes place if $a_4 > 0$, and in this case the sixth-order term is usually omitted. On the other hand, $a_4 < 0$ is characteristic of a first order transition, and the sixth-order term has to be kept. The situation is quite different from second order transition. We rewrite Eq. II-30 as

$$F(Q_p \epsilon_k T) = F_0(T) + \frac{1}{2} a_2(T) f_2(Q_l) + \frac{1}{4} a_4 f_4(Q_l) + \frac{1}{6} a_6 f_6(Q_l) + \dots + \frac{1}{2} b (\nabla Q)^2 + \dots + F_m(\epsilon_k) + F_c(Q_p \epsilon_k) \quad \text{V-1}$$

with

$$F_m(\epsilon) = \frac{1}{2} b_2 \epsilon^2 + \frac{1}{4} b_4 \epsilon^4 + \dots + \dots \quad \text{V-2}$$

and

$$F_c(Q, \epsilon) = \beta Q \epsilon + \gamma Q^2 \epsilon + \delta Q \epsilon^2 \quad \text{V-3}$$

We need to calculate Eq. (II-31) to find $\Delta C = C^{(Q)} - C^{(Z)}$. Their physical definitions were given in the text of Chapter II. Substituting Eq. (II-30) into Eq. (II-31), ΔC is given by

$$\Delta C = C^{(Q)} - C^{(Z)} = \gamma^2 \chi Q_s^2 \quad \text{V-4}$$

where Q_s is the spontaneous polarization at the transition, determined by $F=0$ and $\partial F/\partial Q=0$. In the absence of coupling to the strain, we would have

$$\frac{1}{2}a_2 + \frac{1}{4}a_4Q^2 + \frac{1}{6}a_6Q^4 = 0 \quad \text{V-5}$$

$$a_2 + a_4Q^2 + a_6Q^4 = 0 \quad \text{V-6}$$

We solve V-4 and V-5 to obtain

$$Q_s^2 = -\frac{4a_2}{a_4} \quad \text{V-7}$$

By Eq. (II-32), we find χ :

$$\chi = \left[\frac{\partial^2 F}{\partial Q^2} \right]_{Q=Q_s}^{-1} = (a_2 + 3a_4Q_s^2 + 5a_6Q_s^4)^{-1} \quad \text{V-8}$$

By (V-4) and (V-5) we find

$$\chi = (-4a_2 - 2a_4Q^2)^{-1} = (4a_2)^{-1} \quad \text{V-9}$$

just below the transition. Then we obtain

$$\Delta C = C^{(Q)} - C^{(Z)} = -\frac{\gamma^2}{a_4} > 0 \quad \text{V-10}$$

If this result were for a second order (continuous) transition, $C^{(Q)}$ just below the transition temperature T_c would be equal to $C^{(Q)}$ just above T_c . The $C^{(Z)}$ we measured by sound velocity would equal to $C^{(Q)}$ minus a positive $(-\gamma^2/a_4)$. The behavior of $C^{(Z)}$ would be a step-like decrease from high temperature to low temperature as shown in Fig. 4 (solid line), which is opposite to our experimental results. However, the F-P transition in PVF₂-based copolymer is first order, so $C^{(Q)}$ is not continuous across the transition. We have to calculate a jump of $C^{(Q)}$. At the transition, from (II-30), we have

$$\left(\frac{\partial F}{\partial \epsilon}\right)_Q = 0 = b_2 \epsilon + b_4 \epsilon^3 + \gamma Q^2 \quad \text{V-11}$$

$$\left(\frac{\partial F}{\partial Q}\right)_\epsilon = 0 = a_2 Q + a_4 Q^3 + a_6 Q^5 + 2\gamma Q \epsilon \quad \text{V-12}$$

Solving Eqs. (V-11) and (V-12) simultaneously, for the high-T phase we must substitute $Q=0$ so that $\epsilon_0=0$. In the low-T phase we have $Q \neq 0$ so we get a nonzero root ϵ_1 . The $C^{(Q)}$ slightly below T_c is

$$C^{(Q)} = \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_Q = b_2 + 3b_4 \epsilon^2 \quad \text{V-13}$$

so $C^{(Q)}$ jumps from b_2 in the high-T phase to $b_2 + 3b_4 \epsilon_1^2$ in the low-T phase.

From Eq. V-10, the measured $C^{(Z)}$ is

$$C^{(Z)} = C_L^{(Q)} - \Delta C = b_2 + (3b_4 \epsilon_1^2 - \Delta C) \quad \text{V-14}$$

The $C^{(Z)}$ could be step-like up or down across the transition region as shown in Fig. 4 (dotted line), determined by which term is bigger in the parenthesis of Eq. (V-14).

The sound velocity in our results decreases continuously with increasing temperature and still does not match the step-down behavior. It is well known that, besides depending on material properties and thermal history, the transition temperature of a crystal is also dependent on its size. In theories of phase transitions, the size of a single crystal is often considered as infinite, but crystal lamellae in semicrystalline material have finite size. The limiting transition temperature T_c considering size effects only is given by

$$\lim_{L \rightarrow \infty} T_c(L) = T_c \quad \text{V-15}$$

and generally

$$\frac{dT_c(L)}{dL} < 0 \quad \text{V-16}$$

The size of crystals in our copolymer is about 100 to 200 Å.⁵⁷ One can reasonably assume the size distribution in copolymers is Gaussian,

$$P(L) = \frac{e^{-\frac{(L-L_0)^2}{2\Delta^2}}}{(2\pi)^{\frac{1}{2}} \Delta} \quad \text{V-17}$$

where L_0 is the average crystal size, 150 Å, and Δ is the average rms size deviation. The temperature dependence of stiffness constant for a crystal is shown as in Fig. 4, a step function $\theta[T_c(L)-T]$. For practical experimental results contributed by a large number of crystals with different sizes, the stiffness constant ($\sim V^2$, see Eq. I-2) vs. temperature is

$$\langle C \rangle = C_0 \int_0^{\infty} \theta [T_c(L) - T] \frac{e^{-\frac{(L-L_0)^2}{2\Delta^2}}}{\sqrt{2\pi}\Delta} dL \quad \text{V-18}$$

Expanding $T_c(L)$ in a power series,

$$T_c(L) = T_c(L_0) + A(L_0 - L) + \frac{1}{2}B(L_0 - L)^2 + \dots \quad \text{V-19}$$

and taking the first-order approximation,

$$\langle C \rangle = C_0 \int_0^{\infty} \theta [T_c(L_0) - A(L_0 - L) - T] \frac{e^{-\frac{(L-L_0)^2}{2\Delta^2}}}{\sqrt{2\pi}\Delta} dL \quad \text{V-20}$$

The key factors in this equation are the quantity A and Δ which define a temperature interval over which the change in C occurs. We have no information about either A or Δ , so a numerical fit would lack significance. Instead we simply point out that the qualitative analysis in equations V-17 through V-20 provides a more solid base for Krüger's method. So we believe

that the first kink made by the first two linear parts corresponds to the glass transition and the second kink made by the curved part and the last linear part corresponds to the F-P transition.

Transition characteristics in PVF₂-based copolymers

We first indicate some obvious facts about the experimental results. For each sample (1) The sound velocity along the x axis (related to C_{11}) is much higher than that along the y axis (related to C_{22} or C_{33}). The values from the isotropic sample are between those for x and y axes (see Figs. 18-21, 22-25, 26-29). This is because the intramolecular C-C bonds are stronger than the intermolecular bonds. 2) The degree of hysteresis decreases with increasing TrFE content as observed by another method⁵⁶ (see Figs. 19-21 and 23-25). This fact was attributed to the transition of copolymers with higher VF₂ content having more first-order character.⁵⁶ 3) Table 1 gives the T_c for all copolymers we studied and Krüger's results for stretched 70/30 mol% VF₂/TrFE samples. The T_c decreases with increase in TrFE content as reported by other authors.^{56,57} This can be explained briefly by noting that as more CH₂ units are replaced by CHF with increasing TrFE content, the added larger fluoride ions reduce the tendency to form the orthorhombic structure (β phase). In the copolymers, the lattice spacing increases with TrFE content, which makes rotation of dipoles or

Table 1. Transition points for copolymers in °C

Compositions	T _g	T _{cx}	T _{cy}	T _{ci}
60/40 mol% VF ₂ /TrFE	-30	104	91	97
70/30 mol% VF ₂ /TrFE	-20	117*	97*	100
80/20 mol% VF ₂ /TrFE	-25	---	102	107
81/19 mol% VF ₂ /TFE	-40	---	---	---

*Krüger's results¹⁷

---see text

conformational change easier in the copolymer with higher TrFE content. The absence of the Curie point in β phase PVF₂ below the melting point⁵⁸ can be explained by this packing effect. The conformational change is not allowed in β phase PVF₂ in the crystalline lattice because of the tight packing of chains and the resulting strong dipolar and van der Waals interaction. Tighter packing caused by higher VF₂ content brings T_c higher.

4) For the same samples, the T_{cx} and T_{cy} have significant differences. Krüger first found this difference of about 20° C in his Brillouin scattering studies for 70/30 mol% PVF₂/TrFE copolymers. He identified both of them as the same F-P transition point 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. We now discuss this difference in more detail.

The difference between T_{cx} and T_{cy}

We first discuss the transition behavior for 80/20 mol% VF₂/TrFE sample shown in Fig. 19-21. 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 (see Figs. 19 and 20). Fig. 21 shows the

temperature dependence of sound velocity along the x axis. No obvious F-P transition point appears, 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 sample⁵⁹, 138° C by x-ray diffraction and infrared spectroscopy,⁸ and 138° C according to manufacturer's product data.⁶⁰ Apparently, T_c is above 125° C for 80/20 copolymers, so we can reach this temperature but cannot 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.¹⁷ 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. 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 . We used similar samples (cut from one piece) to make several measurements in the following ways: 1) Heated sample up to 125° C directly during 2.5 hours

without stopping, to minimize the effect of heating time, then started the cooling run measurement. 2) Heated the sample up to 110° and to 100° C respectively to see the effect of premelting on cooling behavior. All three cooling curves have similar behavior. 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 transition¹⁷. 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?

Fig. 23-25 show the similar behavior in T_{cx} and T_{cy} more clearly because 60/40 mol% VF₂/TrFE copolymers have much lower F-P transition temperatures. As shown in Table 1, T_{cy} =91° C, T_{cx} =104° C, and T_{ci} =97° C. The difference between T_{cx} and T_{cy} is smaller but still obvious. This difference is common behavior for all samples with various compositions. There must be some physical reason causing this difference, or else T_{cx} and T_{cy} correspond to different transition processes.

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 samples¹⁷ yielded T_{cx} =117° C

and $T_{cy}=97^{\circ}\text{C}$ while our result for an isotropic sample⁶¹ is $T_c=100^{\circ}\text{C}$. Dielectric constant measurement⁹ indicated $T_c=99^{\circ}\text{C}$ while other methods gave $T_c=105^{\circ}\text{C}$. Faria and Latour¹⁰ 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. Delzenne⁶² reported that the ferro-paraelectric transition takes place in two stages, or that perhaps there are two transitions. Moreira⁵⁵ and colleagues found two peaks in the DSC experiment for an isotropic 70/30 mol% copolymer and discussed a hypothesis of an intermediate phase and existence of two type of regions. From these results, we conclude that the process of transition from ferro to paraelectric phase is unclear. When we analyze this phenomenon it should be kept in mind that the F-P phase transition in polymers may be different from those in typical ferroelectric crystals in the following points: (1) Crystal units in polymers are not simple atom groups but are long chains which strongly connect to units in other crystal cells. (2) A conformational

transition is involved in the F-P transition in a chain. (3) Polymeric crystals are stabilized by energetic balance among conformational energy, van der Waals interaction, and electric dipolar interaction.

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 happen 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. Above this transition point, the sound velocity temperature dependence has a different slope. As indicated in Faria's work¹⁰, in this temperature range the copolymer is ferroelectric and keeps the all-trans conformation. This structural transition is denoted as F-F transition. When temperature increases further and reaches the transition point at which the all-trans conformation becomes disordered helical, the change in chain conformation forces another structural transition in the crystal. This transition is the ferroelectric to paraelectric Curie point. According to the theoretical

analysis in the second part of this chapter, the coupling effect caused by the F-F transition should be observed in anomalies of sound wave propagating along both x and y directions. One should observe two transitions in the curves of temperature dependence of sound velocity both along x and y. In the x direction curve some anomalies should be seen at the F-F transition temperature. We didn't see that because the expected anomalies occur just in the broad transition range caused by the semicrystalline property of the copolymers. The reasons that we didn't see the F-P transition anomalies in the y direction sound velocity may be (1) The structural transition caused by change in chain conformation is weak in interchain coupling energy. (2) The anomaly we saw in the x direction sound velocity curve is not caused by interchain coupling but by a sudden change in chain conformation. The sound waves propagating along y will not see this change. Accordingly we identify T_{cy} to be a structural transition point which has totally different physical significance from T_{cx} . We believe that T_{cx} , which corresponds to a transition from all trans to disordered helical conformation, is the traditional T_c .

Transition study on 81/19 mol% VF₂/TFE sample

A ferroelectric to paraelectric phase transition was never observed in PVF₂ because it may have been obscured by the melting process, which

caused an argument concerning whether PVF_2 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. Copolymers of TFE are of particular interest because they do not introduce this new chemical species -CHF- or tacticity defects as does TrFE, yet their F-P phase transitions have been detected.⁶³ They can be viewed simply as VF_2 containing an increased number of head-to-head ($\text{CF}_2\text{-CF}_2\text{-}$) defects.⁶⁴ Lovinger⁶⁵ indicated that the F-P transition point is so close to melting point that no transition can be observed for 81/19 mol% VF_2/TFE copolymer. Later, Lovinger *et al.* detected the Curie transition beginning at about 122° C in a differently prepared copolymer of the same composition.⁶³

Figs. 26-29 show temperature dependence of sound velocity up to about 120° C for isotropic samples and stretched sample for sound wave propagating along x and y axes. Determining the F-P 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 $T_m=126^\circ\text{C}$.⁶³ 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 Fig. 28, the temperature dependences of sound velocity along y show a clear tendency toward finishing the transitions, which appear likely to be completed not very far above the temperature where we stopped. In Fig. 29 showing the velocity of sound propagating along x, we could not see any tendency toward completing the F-P transition near our highest temperature. Comparing Fig. 28 with Fig. 29, 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 accurately. We believe the difference between T_{cx} and T_{cy} is caused by the above-discussed reasons. Our results for VF_2/TFE allow generalization of our conclusions about two transitions obtained from the copolymers of VF_2/TrFE and exclude any possible effect of the atomic group CHF found only in VF_2/TrFE copolymers. Because VF_2/TFE copolymer is equivalent to VF_2 containing a higher percentage of head-to-head defects, it is a reasonable inference that two-transition behavior should be possible in PVF_2 homopolymer, to the extent that it is not obscured by melting.

Sound attenuation in 70/30 mol% VF_2/TrFE sample

Fig. 14 shows the temperature dependence of the Brillouin linewidth (FWHM) Γ/π for the cooling run. The relation between Γ/π and the attenuation coefficient α is⁴¹ $\Gamma/\pi = \alpha V/\pi$. A sound attenuation anomaly occurs

in the transition range near 55° C. The heating run attenuation shown in Fig. 15 has no clear anomaly. The reason may be that the anomaly is associated with those crystallites which are part ferroelectric and part paraelectric. On cooling, the transition is sharp and many crystallites may be in that class, while on heating the transition is diffuse and few crystallites may be in that class at any given temperature.

At temperatures 58.5, 57.6 and 52.2° C for the cooling run we found that the Brillouin spectrum exhibits a multipeak structure. At these points we took the center position of the whole envelope as the Brillouin peak location to calculate the sound velocity and sound attenuation. A possible explanation for the multiple peaks is that crystallites in some regions of the sample are still in the paraelectric phase while in the remaining regions they have transformed to the ferroelectric phase. If these regions are large compared to the wavelength λ , multiple peaks should appear even though the crystallite size is expected to be small (100 Å to 200 Å) compared to λ . The origin of the regions could be nonuniform heating of the sample by the laser beam or (more interestingly) an elastic interaction between crystallites which is transmitted by intervening amorphous material. We believe nonuniform heating can be ruled out for the following reason. In Fig. 13 the sharp corner of the cooling run at 55° C extends only over about 3° C, so this is the upper limit for the temperature variation across the

active sample volume. However, the steep part of the cooling curve attributed to phase coexistence extends over 8° C, from 55 to 63° C, so a 3° C temperature spread cannot account for the simultaneous appearance, described below, of spectral peaks from both phases.

Figs. 16 and 17 show typical normal and split Brillouin peaks. The truncated outer peaks (1) are the Rayleigh peaks, (2) are the Brillouin peaks and (3) were identified as reflection peaks.²⁸ A statistical mixture of crystallites of two phases in their amorphous matrix would result in apparent line broadening in the transition regime, but not in the observed multippeak structure. Accordingly we attribute the coexistence of spectra of both phases to long-range elastic interactions between crystallites which cooperatively inhibit or promote their transition to the ferroelectric phase. We could observe such multiple peaks because our cooling run curve is much steeper in the transition regime than curves observed previously,¹⁷ perhaps because of smaller local strains giving a narrower local distribution of transition temperatures. A broad distribution would obscure the multippeak structure.

Except for the above anomaly, the sound attenuation behaviors are similar for heating and cooling runs. The natural linewidth Γ/π increases with increasing temperature. Above room temperature, we present the first results of natural linewidth because of the problems in sample surface

properties in Krüger's experiment. This linewidth includes contributions from two origins. One has dynamic origin (phonon decay) which is usually the major factor. The other has static origin, either two types of crystallite groups with different sound velocities or temperature distribution ΔT over the laser spot area. We believe the ΔT effect is not important for the following reason. If the linewidth Δv or corresponding sound velocity spread ΔV has mostly static origin (ΔT), generally there should be a direct relation between Δv and ΔT , most likely $\Delta v \propto |dV/dT|$. From Figs. 14 and 15, we see the linewidth has some correlation with T , but does not vary as $|dV/dT|$. Another estimate of the effect of ΔT comes from calculating the linewidth resulting from ΔT alone on the steepest part of the cooling curve where its effect is greatest. There, as T drops from 63 to 55° C, V increases from 1635 to 1860 m/s. For ΔT of 3° C discussed above, the corresponding ΔV is 85 m/s. The corresponding linewidth (FWHM) is 0.23 GHz. This is considerably less than the actual linewidth in that temperature range shown in Fig. 15. At low temperature the linewidth approaches that value, but there dV/dT is much smaller, so again ΔT has little effect on the linewidth. We see that the natural linewidth has mainly dynamic origin and governs the sound attenuation α over the whole temperature range except in the paraelectric-ferroelectric transition range on the cooling run. In this range, due to the above-mentioned multipeak structure, we can hardly say that

the linewidth anomaly in Fig. 15 has a dynamic origin (phonon decay) because this effect appears to be submerged by a static effect. Accordingly we have not analyzed the attenuation behavior of the sound velocity in detail.

Conclusions

From these experimental results and their theoretical analysis, some conclusions can be drawn. (1) We observed obvious anomalies in temperature dependence of sound velocity along the x and y directions. Based on our theoretical analysis, these anomalies result from a coupling free energy linear in the strain but quadratic in the order parameter, $F_c = \gamma Q^2 \epsilon$. Brillouin scattering studies on semicrystalline polymers is a young field, but our work shows that it is a productive method to study phase transitions in copolymers. (2) The phase transition behavior revealed from the temperature dependence of sound velocity along the x axis is very different from that revealed from y axis data. T_{cx} and T_{cy} have significant differences in all samples studied. These differences indicate that T_{cx} and T_{cy} correspond to different structural transition processes, i.e. there are two transitions in the whole transition process from ferroelectric to paraelectric phase. The first one, represented by T_{cy} , which normally occurs at lower temperature, is a structural transition but it does not change the

ferroelectric characteristics of the copolymer. The second one, represented by T_{cx} , is a structural transition caused by a change in polymer chain conformation which transforms the copolymer from the ferroelectric phase to the paraelectric phase. (3) The similar transition behavior in VF_2/TFE copolymers allows us to generalize our conclusion obtained from the copolymers of $VF_2/TrFE$ to PVF_2 monopolymer, and excludes any possible effect of the atomic group CHF found only in $VF_2/TrFE$ copolymers, because VF_2/TFE copolymer is equivalent to VF_2 containing a higher percentage of head-to-head defects. (4) Study of sound attenuation by Brillouin scattering is difficult but possible. We observed a maximum in sound attenuation for 70/30 mol% $VF_2/TrFE$ copolymer. Because of the complication of semicrystallinity, quantitative analysis of this attenuation is not possible now.

Suggestion for further work

(1) Since ferroelectric phase transitions in polymers are different from those in typical ferroelectric crystals it is important to clarify the unique characteristics of phase transition in polymers. It may soon be possible to form a single crystal of PVF_2 .⁵⁶ A Brillouin scattering study on a single crystal of a copolymer composition exhibiting a ferroelectric transition may clarify our analysis of the phase transition and reveal its

unique characteristics. (2) The two transition hypothesis is of great importance in understanding phase transition mechanics in VF_2 -based copolymers. Even though there are several pieces of evidence for two transitions, their interpretation is not very clear and further studies are needed. To confirm the two transition hypothesis, 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. These measurements should resolve the question concerning the existence of two transitions. (3) The computer data acquisition system should be improved to raise efficiency in dealing with data.

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