Macromolecules 1987, 20, 552-557

Axial Thermal Contraction and Related Mechanical Properties of a Polymer Lattice: Proposition of a String-in-Medium Model

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ABSTRACT: In order to interpret the characteristic thermal and mechanical properties of aromatic polyamide fibers (the negative thermal expansion and the positive temperature dependence of the compliance) observed for both bulk samples and crystalline lattices along the chain direction, a theoretical treatment is made based on a "string-in-medium" model; a flexible string is embedded in a medium and fluctuates thermally in an external field of extensional stress. An expression for the strain ϵ along the chain axis is derived as a function of the stress σ and temperature T: $\epsilon(\sigma,T) = \sigma/E_0 - {}^1/_2\sum u_k/(\rho v^2 + \sigma)$, where E_0 is Young's modulus under no lateral thermal agitation, u_k is the total energy of each transverse acoustic mode, v is its phase velocity along the chain, ρ is the density, and the summation runs over all transverse modes. From this equation the thermal expansion coefficient α ($=\partial\epsilon/\partial T$), the compliance J ($=\partial\epsilon/\partial\sigma$), and its stress dependence $\partial J/\partial\sigma$ are derived. The equation for the thermal expansion coefficient is also interpreted in terms of the Grüneisen theory and corrected slightly by a positive contribution due to the thermally excited longitudinal mode. The difference in the compliance between the value obtained under isothermal conditions and that obtained under adiabatic conditions is discussed. The equations are found to reproduce quantitatively the experimental results reported previously.

I. Introduction

In principle, the thermomechanical properties of a solid are described by three variables, the pressure P, the volume V, and the temperature T, or, more generally, by the stress tensor $\bar{\sigma}$, the strain tensor $\bar{\epsilon}$, and T. The characteristic thermal and mechanical properties in a polymer system can be detected particularly in the direction of the molecular chain axis because of its unique one-dimensional nature, although, of course, effects of intermolecular interactions on these properties must not be neglected. Therefore it is considered that the stress and strain along the chain direction, σ and ϵ, are especially important. The relationship among these variables can be expressed by the generalized equation of state $\epsilon = \epsilon(\sigma,T)$. The first derivative of ϵ with respect to T gives a thermal expansion coefficient α ($=\partial\epsilon/\partial T$) and that with respect to σ gives an elastic compliance J ($=\partial\epsilon/\partial\sigma$). The inverse of J is the elastic modulus E.

In a series of our studies,[1-3] the stress and temperature dependences of the strain have been investigated for highly oriented aromatic polyamide fibers by means of thermomechanical analysis[1] and tensile testing[2] for the macroscopic bulk dimension and by means of X-ray diffraction for the microscopic lattice dimension.[3] These dependences are briefly summarized as (i) $\partial\epsilon/\partial T < 0$, (ii) $\partial^2\epsilon/\partial T\partial\sigma = \partial J/\partial T > 0$, and (iii) $\partial^3\epsilon/\partial T\partial\sigma^2 = \partial^2 J/\partial T\partial\sigma < 0$. Phenomenon (i) has been interpreted as the contraction of the chain length originating from the lateral thermal fluctuation of the fully extended molecular chains (the *negative thermal expansion*).[4-15] Moreover, we have attributed the other characteristic phenomena to this thermal fluctuation mechanism,[1-3] although no similar interpretation has yet been made for the *temperature dependence of the crystalline modulus*.[11,12,16-23]

In this paper, in order to explain these characteristic properties of aramide fibers quantitatively, an expression for the strain $\epsilon(\sigma,T)$ along the string direction is presented based on a "string-in-medium" model, in which a flexible string is embedded in a continuous medium and fluctuates thermally under the application of an extensional stress. From this equation, the temperature dependences of J and $\partial J/\partial\sigma$ are derived under the isothermal condition at the classical limit, and the difference in the compliance between the isothermal and adiabatic conditions is briefly discussed. Finally, these theoretical results are compared quantitatively with experimental results.[1-3] Before discussing our own investigations, we review previous work on the above-mentioned subjects and point out some problems involved in them.

Negative Thermal Expansion. Metals with a one-dimensional chain-like structure along the c axis, such as Te and Se, were found to possess negative values of the thermal expansion coefficient [$\alpha_c = -1.6 \times 10^{-6}$ K^{-1} for Te (1925,[4] 1940[5]) and $\alpha_c = -17.89 \times 10^{-6}$ K^{-1} for Se (1940[5])]. In 1960, Cole and Holmes[6] measured the linear thermal expansion along the a, b, and c axes of the orthorhombic polyethylene crystal and found a negative thermal expansion coefficient along the c axis, -2.0×10^{-5} K^{-1}. In 1962, Swan[7] also obtained a negative value, $(-3.5 \pm 5) \times 10^{-6}$ K^{-1}, but he hesitated to conclude this sign due to the experimental error. In 1970, two groups, Kobayashi and Keller[8] and Davis et al.,[9] carried out precise X-ray diffraction measurements of the thermal expansion along the c axis of the polyethylene crystal and confirmed a negative sign for α_c of about -1.2×10^{-5} K^{-1}. To date, a negative thermal expansion or thermal contraction along the chain direction in the crystalline region has been reported for many kinds of polymer materials, e.g., cotton cellulose,[10] nylon 6,[10,11] isotactic polypropylene,[12] poly(oxymethylene),[13] and so on. The mechanism of such a thermal contraction has been considered by some workers. Kobayashi and Keller (1970),[8] Davis et al. (1970),[9] and Baughman (1973)[14] ascribed the negative α_c to internal rotational motion around single C–C bonds caused by thermal agitation. Taking account of the lateral fluctuation of the chain, Chen et al. (1980)[15] carried out a lattice dynamical calculation for the planar-zigzag polyethylene molecule under no tension.

Temperature Dependence of Elastic Compliance. The elastic compliance or modulus along the chain axis of polymer crystals has been widely measured by X-ray diffraction[16] since the first report by Dulmage and Contois in 1958.[17] The modulus has been also estimated from the frequency dispersion curve of the longitudinal acoustic mode, which can be obtained from coherent inelastic neutron scattering[18] and Raman scattering[19,20] spectral data. However, most of these measurements have been made only at room temperature. To date, the temperature dependence of the crystalline modulus $E_l(T)$ has been observed only by means of X-ray diffraction. Measuring

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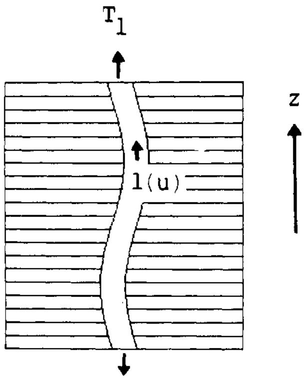

Figure 1. String-in-medium model. The string is embedded along the z axis in the medium or the surrounding strings under thermal agitation and under application of tension.

the $E_l(T)$ of polyethylene and poly(oxymethylene), Ward et al. attributed the observed temperature dependences to the change in modulus of the amorphous region or the change in the stress distribution of the sample under the assumption of constancy of the true crystalline modulus (1979,[21] 1981[22]). The temperature dependence of the crystalline modulus has been reported also for nylon 6 by Miyasaka et al.,[11] for poly(butylene terephthalate), poly(ethylene terephthalate), and polypropylene by Nakamae et al.,[12] etc. Recently, the temperature variation in the crystalline modulus of poly(p-phenyleneterephthalamide) has been reported.[23] Such a dependence, however, has been attributed to particular properties of the examined individual polymers. It might be said that a general theory for the temperature dependence of the modulus along the chain axis has not yet been presented.

II. String-in-Medium Model

Expression of Strain. Figure 1 depicts the string-in-medium model. Here the string that simulates the behavior of a molecular chain is positioned along the z axis. The internal coordinate along the string is denoted by u, and the path length along this string is defined by $l(u)$. The string is assumed to be embedded in a continuous medium, which reacts with the string through the following two types of interaction: (i) the time-averaged potential field, which holds the string at the equilibrium position and (ii) the thermal agitation, which causes the string to fluctuate in the x–y plane. Table I lists the physical definitions of the main variables.

The dimensional element dl of the string is related to the Cartesian coordinate elements dx, dy, and dz by

$$\mathrm{d}l^2 = \mathrm{d}x^2 + \mathrm{d}y^2 + \mathrm{d}z^2 \tag{1}$$

and the expansion of the element is given by

$$\frac{\mathrm{d}l}{\mathrm{d}u} = 1 + \frac{T_l}{E_0 S} \tag{2}$$

Here we utilize T_l for the tensile force along the string of cross-sectional area S by assuming that the direction of the string does not deviate much from the z axis and thus the direction cosine is almost equal to unity. E_0 is Young's modulus under no lateral thermal agitation. The strain ϵ along the z axis is given by

$$\epsilon = \overline{(\mathrm{d}z/\mathrm{d}u)} - 1 \tag{3}$$

The overbar denotes the time-averaged value. Considering that $\mathrm{d}z/\mathrm{d}u \simeq 1$, $|\mathrm{d}x/\mathrm{d}u| \ll 1$, and $|\mathrm{d}y/\mathrm{d}u| \ll 1$, eq 3 is rewritten as follows by using eq 1 and 2.

$$\epsilon = \frac{T_l}{E_0 S} - \frac{1}{2}\overline{\left[\left(\frac{\mathrm{d}x}{\mathrm{d}u}\right)^2 + \left(\frac{\mathrm{d}y}{\mathrm{d}u}\right)^2\right]} \tag{4}$$

Table I
List of Main Symbols Used in This Paper

u: internal coordinate of the string
$l(u)$: distance along the string
$[x(u), y(u), z(u)]$: locus of the string in Cartesian coordinates
ϵ: elongation along the x axis
ρ_l: linear density of the string
T_l: tension applied to the string
X_s, X_m: restoring forces respectively originating from the string itself and the surrounding medium
S: cross-sectional area of the string
E_0: Young's modulus of the string under no lateral thermal agitation per unit area
$\rho = \rho_l/S$: density per unit volume
$\sigma = \sigma_l/S$: external tensile stress per unit area
J: compliance
E $(=1/J)$: Young's modulus of the string per unit area
α: thermal expansion coefficient along the z axis
k: wave vector of the transverse mode along the z axis
u_k: time-averaged energy of each transverse mode
A_k: amplitude of transverse mode
T: absolute temperature
$\mathrm{k_B}$: Boltzmann constant
v: phase velocity of transverse mode along the z axis under no tension
C: heat capacity of all transverse modes per unit volume
C_p/V: heat capacity of the system (this notation is used only in section III)
γ: Brüneisen parameter

Here we will consider the lateral motion of the string at a finite temperature under the application of a tensile force T_l along the z axis. The equation of motion for the string under the tension is given by[24]

$$\rho_l \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -X_s - X_m - T_l \frac{\mathrm{d}^2 x}{\mathrm{d}u^2} \tag{5}$$

$$\rho_l \frac{\mathrm{d}^2 y}{\mathrm{d}t^2} = -Y_s - Y_m - T_l \frac{\mathrm{d}^2 y}{\mathrm{d}u^2} \tag{6}$$

where ρ_l is the linear density of the string and t is time. On the right-hand side of eq 5 and 6, the first and second terms represent the restoring forces due to the string itself and the surrounding medium, respectively, and the third term originates from the external tension. Hereafter we deal mainly with eq 5 because eq 5 and 6 are of the same form. If the variable x, the coordinate of the string element displaced normally from the z axis, is represented by a Fourier series expansion of the type

$$x = \sum_k A_{xk} \exp(iku - i\omega t) \tag{7}$$

eq 5 is transformed as

$$\rho_l \omega^2 = \chi(k) + T_l k^2 \tag{8}$$

where we assume that X_s and X_m are linear functionals of $x(u)$, or $X_s(e^{iku}) + X_m(e^{iku}) = \chi(k)e^{iku}$. In eq 7 and 8, k and A_{xk} denote the wave vector along the z axis and the amplitude of the Fourier component, respectively. Hereafter A_k will be employed for the representation of A_{xk} or A_{yk}. Equation 8 is just the dispersion relation of the transverse mode of the vibration. ω is the frequency of the transverse mode.

Referring to eq 7, the time-averaged square of the amplitude A_k of the mode k is related to its total energy u_k by

$$\overline{A_k^2} = u_k/\rho_l \omega^2 \tag{9}$$

where the equality between the potential and kinetic energies in the harmonic motion (PE = KE = $(1/2)\rho_1\omega^2\overline{A_k^2}$) is used. The value of u_k is given by Bose–Einstein statistics as

$$u_k = \frac{\hbar\omega}{\exp(\hbar\omega/\mathbf{k}_B T) - 1} \tag{10}$$

where the zero-point vibrational energy is neglected. Using eq 4, 7, and 9, we write the strain ϵ as

$$\epsilon = \frac{T_l}{E_0 S} - \frac{1}{2}\sum k^2 \overline{A_k^2}\ \cdot \tag{11}$$

$$\epsilon = \frac{T_l}{E_0 S} - \frac{1}{2}\sum \frac{k^2 u_k}{\rho_l \omega^2} \tag{12}$$

where the summation runs over k of the string in the vibrational directions of the x and y axes. Using the relations $\rho_l = \rho S$ and $T_l = \sigma S$ (see Table I), we write eq 12 as

$$\epsilon = \frac{\sigma}{E_0} - \frac{1}{2}\sum \frac{k^2 u_k}{\rho \omega^2} \tag{13}$$

where the summation is made over k corresponding to the unit volume of the system.

From eq 8 the frequency of the mode under the free tension ($T_l = 0$) is given by

$$\rho_l \omega_0^2 = \chi(k) \tag{14}$$

It is considered that eq 14 gives, inversely, the physical meaning of $\chi(k)$, and then those of $X_s(x)$ and $X_m(x)$. We define here the phase velocity along the string under no tension as

$$v = \omega_0/k \tag{15}$$

Therefore the dispersion relation of the transverse mode under the tension is rewritten as

$$\rho\omega^2 = \rho v^2 k^2 + \sigma k^2 \tag{16}$$

Using eq 16, we rewrite eq 13 as

$$\epsilon = \frac{\sigma}{E_0} - \frac{1}{2}\sum \frac{u_k}{\rho v^2 + \sigma} \tag{17}$$

This equation is convenient to consider the complex effect of the external force and thermal agitation. In the following several sections we discuss some characteristic features derived from this basically important equation.

Here we discuss the magnitude of $1/\rho v^2$ and its physical meaning. It should be noticed that the $\chi(k)$ in the above equations must be, strictly speaking, redefined as $\chi(k_x,k_y,k_z)$. We recall that the equation of motion for the elastic solid is given by the so-called Christoffel equation[25]

$$\rho\omega^2 e_i = \sum\sum\sum c_{ijkl} k_j k_l e_k \tag{18}$$

where c_{ijkl} is a component of the elastic constant tensor and i, j, k, and l are x, y, or z. Equation 18 gives three sets of the eigenvalue $\rho\omega^2$ and eigenvector (e_x, e_y, e_z) as a function of the wave vector (k_x, k_y, k_z), and each corresponds to the frequency and vibrational direction of the one longitudinal mode and two transverse modes. In particular, the eigenfrequency of the transverse mode is preferably determined by the shear components of the elastic constant tensor. Since, in general, the elastic constant of a shear component is much smaller than that of the tensile or compressive components,[26] the range of possible values of ρv^2 ($=\rho\omega^2/k_z^2$) may be restricted approximately to the range such that

$$0 < 1/(\rho v^2) \lesssim 1/G \tag{19}$$

where G represents the typical magnitude of the shear elastic constants. In order to gain more physical insight into the case of a polymer crystal, it would be better to return to the string-in-medium model in Figure 1. As stated above, the fluctuation of the string propagates along the z axis. If the medium is replaced with an assembly of strings moving with the same phase as the original string, such a movement of the strings corresponds to the transverse mode with the wave vector (0, 0, k_z). Then the movement with the wave vector (k_x, k_y, k_z) in the region where $|k_x|$, $|k_y| \ll |k_z|$ is considered to have a frequency determined mainly by the shear deformation between strings; $\rho\omega^2 \simeq Gk_z^2$. On the contrary, if the surrounding strings vibrate with a phase largely different from that of the original string, such a vibration is considered to have a higher frequency because of the compressive deformation between the strings. Therefore, in the summation of eq 17, etc., the transverse mode that propagates nearly along the z axis is considered to contribute an appreciably large weight. We call such a transverse mode a flexural mode. The ratio of the flexural modes to all the transverse modes is estimated in section IV based on the experimental results for PBA.

High-Temperature Limit and Isothermal Compliance. It should be noted that in the summation of eq 17, u_k depends on the stress σ because ω depends on σ according to eq 16. However, u_k approaches $\mathbf{k}_B T$ and becomes independent of σ at a sufficiently high temperature. In this case the right-hand side of eq 17 can be expanded in a power series of σ as

$$\epsilon = -\frac{1}{2}\sum \frac{\mathbf{k}_B T}{\rho v^2} + \left[\frac{1}{E_0} + \frac{1}{2}\sum \frac{\mathbf{k}_B T}{\rho^2 v^4}\right]\sigma - \left[\frac{1}{2}\sum \frac{\mathbf{k}_B T}{\rho^3 v^6}\right]\sigma^2 + \ldots \tag{20}$$

where the first term is negative and implies chain contraction due to the thermally excited transverse modes. Differentiating eq 20 with respect to σ, we get the expression for the (isothermal) compliance

$$J = \frac{1}{E_0} + \frac{1}{2}\sum \frac{\mathbf{k}_B T}{\rho^2 v^4} - \left[\sum \frac{\mathbf{k}_B T}{\rho^3 v^6}\right]\sigma + \ldots \tag{21}$$

where the first term is the compliance under no lateral thermal agitation. The second term is the compliance accompanied with the contraction at a finite temperature. As the tension increases, the thermal contraction decreases, resulting in a decrement of the compliance. The third term corresponds to this negative stress dependence of the compliance, which is given by

$$\partial J/\partial\sigma = -\sum \frac{\mathbf{k}_B T}{\rho^3 v^6} + \ldots \tag{22}$$

It should be noted that the specific heat C of the transverse wave per unit volume is given in the classical limit by

$$C = \sum \mathbf{k}_B \tag{23}$$

Defining the average over the mode k and the x and y directions as

$$\left\langle \frac{1}{\rho^n v^{2n}} \right\rangle = \sum \frac{1}{\rho^n v^{2n}} \Big/ \sum 1 \tag{24}$$

and differentiating eq 20–22 with respect to T, we have

$$\frac{\partial\epsilon}{\partial T} \simeq -\frac{C}{2}\left\langle \frac{1}{\rho v^2} \right\rangle - \frac{CT}{2}\frac{\partial}{\partial T}\left\langle \frac{1}{\rho v^2} \right\rangle \tag{25}$$

$$\frac{\partial J}{\partial T} \simeq \frac{C}{2}\left\langle \frac{1}{\rho^2 v^4} \right\rangle + \frac{CT}{2}\frac{\partial}{\partial T}\left\langle \frac{1}{\rho^2 v^4} \right\rangle \tag{26}$$

$$\frac{\partial^2 J}{\partial T\,\partial\sigma} \simeq -C\left\langle \frac{1}{\rho^3 v^6} \right\rangle - CT\frac{\partial}{\partial T}\left\langle \frac{1}{\rho^3 v^6} \right\rangle \tag{27}$$

From these equations we can understand how the heat capacity and the frequency of the transverse modes relate to the negative thermal expansion and so on.

Adiabatic Compliance. Here we consider the case when the system behaves adiabatically under the application of ultrasonic tension (megahertz frequency). The classical adiabatic condition of the harmonic oscillator is given by the constancy of the integral $\int p\,dq$ in the phase space under the application of external force, where p and q denote the conjugated momentum and position, respectively. In our system, p and q correspond to $i\omega\rho A_k$ and A_k, respectively, and such an adiabatic condition is written as

$$\frac{\partial}{\partial\sigma}(\overline{A_k^2\omega}) = 0 \tag{28}$$

Using the dispersion relation of eq 16, we rewrite eq 28 as

$$\frac{\partial}{\partial\sigma}(\overline{A_k^2}) = -\frac{k^2}{2\rho\omega^2}\overline{A_k^2} \tag{29}$$

Differentiating eq 11 under the adiabatic condition and using eq 29 and 9, we finally obtain the adiabatic compliance J_a as

$$J_a = \left(\frac{\partial\epsilon}{\partial\sigma}\right)_S = \frac{1}{E_0} + f\sum\frac{k^4 u_k}{(\rho\omega^2)^2} \tag{30}$$

where the subscript S means the condition of constancy of the entropy and the factor f of the second term is $^1/_4$. This equation is rewritten in the case of the classical limit ($u_k = \mathbf{k}_B T$) as

$$J_a = \frac{1}{E_0} + f\sum\frac{\mathbf{k}_B T}{\rho^2 v^4} - 2f\left[\sum\frac{\mathbf{k}_B T}{\rho^3 v^6}\right]\sigma + \ldots \tag{31}$$

The factor f ($=^1/_4$) of the second term should be compared with that of the second term in eq 21, where the corresponding factor is $^1/_2$ and originates from the following isothermal condition:

$$\partial(\overline{A_k^2\omega^2})/\partial\sigma = 0 \tag{32}$$

The temperature of the transverse mode is increased under the adiabatic application of tension according to eq 28. At high temperature, however, we must take into account that many other modes, including optical modes, can be thermally excited and behave like an internal heat bath for the transverse modes of which temperature is adiabatically increased by the extension of the chain. As a consequence, it is considered that the suitable value of the factor f is between $^1/_2$ and $^1/_4$ instead of $^1/_4$ in eq 30 and 31 for the adiabatic case. The difference in the factors in eq 21 and 31 between the isothermal and adiabatic compliances might explain the experimental difference in the slope of J_t vs. T and that of J_s vs. T in the lower temperature range (the subscripts t and s imply "tensile" and "sonic").[2]

III. Contribution of Longitudinal Mode to Thermal Expansion and Relation to Grüneisen Parameter γ

In the preceding section we discussed the role of the transverse mode on the temperature dependences of ϵ, J, and $\partial J/\partial\sigma$ along the chain direction. Here we generalize the expression of thermal expansion (eq 25) by considering the contribution of both the transverse and longitudinal modes based on the theory of Grüneisen and Goens.[27] For simplicity, the system of cylindrical or hexagonal symmetry will be dealt with as an example. The c axis is taken as the unique axis. The a and b axes are equivalent. According to the Grüneisen–Goens theory, the thermal expansion coefficient along the chain axis α_3 is given by[27,28]

$$\alpha_3 = 2s_{13}q_1 + s_{33}q_3 \tag{33}$$

where s_{ij} denotes the elastic compliance tensor component. q_1 and q_3 imply "thermal pressure"[28] and are given by

$$q_1 = \gamma_1 C_p/V \tag{34}$$

$$q_3 = \gamma_3 C_p/V \tag{35}$$

where γ_1 and γ_3 are Grüneisen parameters. C_p/V denotes the specific heat per volume. In the quasi-harmonic approximation,[29] the Grüneisen parameter of the mode r is given by

$$\gamma_1^{(r)} = -\frac{\partial(\log\omega_r)}{\partial(\log a)} \tag{36}$$

$$\gamma_3^{(r)} = -\frac{\partial(\log\omega_r)}{\partial(\Delta\epsilon)} \tag{37}$$

where ω_r denotes the frequency of the mode r, and $\log a$ and $\Delta\epsilon$ are the mechanical strains perpendicular and parallel to the chain, respectively. The partial differentiation is made under the constancy of another variable $\log a$ or $\Delta\epsilon$. The Grüneisen parameter of the total modes is given by

$$\gamma_3 = [\gamma_3^{(l)}C_p^{(l)} + \gamma_3^{(t)}C_p^{(t)}]/[C_p^{(l)} + C_p^{(t)}] \tag{38}$$

where only the acoustic modes are taken into account and the superscripts (l) and (t) denote the longitudinal and transverse modes, respectively. The dispersion relation of eq 16 is rewritten approximately as

$$\rho\omega^2 = (\rho v^2 + E\Delta\epsilon)k^2 \tag{39}$$

where $\Delta\epsilon = \epsilon(\sigma,T) - \epsilon(0,T)$ and $E = \sigma/\Delta\epsilon$. For a small tension, $\rho v^2 \gg E\Delta\epsilon$. This equation expresses quantitatively the positive extension dependence of the frequency of the transverse mode as pointed out by Barron[29] and Gibbons.[30] Differentiating the logarithm of eq 39 with respect to $\Delta\epsilon$ and using eq 37, the Grüneisen parameter corresponding to all the transverse modes $\gamma_3^{(t)}$ is obtained after averaging over k as

$$\gamma_3^{(t)} = -\frac{1}{2}\left\langle \frac{E}{\rho v^2} \right\rangle \tag{40}$$

Substituting eq 40 into eq 38, eq 38 into eq 35, and eq 34 and 35 into eq 33, we obtain the expression for the expansibility α_3

$$\alpha_3 = 2s_{13}\gamma_1 C_p/V + s_{33}\gamma_3^{(l)}C_p^{(l)}/V - \frac{1}{2}\left\langle \frac{1}{\rho v^2} \right\rangle C_p^{(t)}/V \tag{41}$$

where we have used the identity $E = 1/s_{33}$. The third term of eq 41 is essentially the same as the first term in eq 25, $-(C/2)\langle 1/\rho v^2\rangle$. In the first term, the factor γ_1 is the Grüneisen parameter in the lateral direction, which is mainly related to the intermolecular potential and is assumed to have a value with an ordinary order of the Grüneisen parameter: 1–5. In general, $s_{13} < 0$. The first term is considered as s_{13} times the positive thermal pressure $2\gamma_1 C_p/V$ in the lateral directions. This term is called

Table II
Estimations of Modulus G_n and Specific Heat C_n

	units	PBA (PRD 49)	PPTA (Kevlar 49)
Averaged Slopes Obtained from the Tensile Experiments[2] between 300 and 600 K			
$\partial\epsilon/\partial T$	K^{-1}	-7.3×10^{-6}	-5.6×10^{-6}
$\partial J/\partial T$	(K GPA)$^{-1}$	7.6×10^{-6}	9.4×10^{-6}
$\partial^2 J/\partial T\, \partial\sigma$	K^{-1} GPa^{-2}	-10.5×10^{-6}	$-27. \times 10^{-6}$
G_1	GPa	1.0	0.60
C_1	J m^{-3} K^{-1}	14×10^3	6.7×10^3
G_2	GPa	1.4	0.70
C_2	J m^{-3} K^{-1}	32×10^3	9.1×10^3

the "Poisson contraction"[28] and contributes also to the thermal contraction along the chain. If the thermal pressure is not present, the first term becomes 0. In eq 25, if the temperature dependence of ρv^2 is not present under the hypothetical absence of lateral thermal expansion, the second term $-(1/2)CT(\partial\langle 1/\rho v^2\rangle/\partial T)$ is 0. These two conditions will be satisfied if the lateral or intermolecular potential is perfectly harmonic. In such a sense, the physical meanings of the first term of eq 41 and the second term of eq 25 are similar to one another. It is noteworthy that the second term of eq 25 has a subsidiary role in the contraction. Recently, the negative Grüneisen parameter along the chain axis has been obtained by White et al.[31,32] This fact suggests an importance of the third term in eq 41.

The second term in eq 41 represents a small thermal expansion due to the unharmonic intramolecular potential, as discussed below. The factor $C_p^{(l)}/V$ is the heat capacity of the longitudinal mode and is approximately proportional to the absolute temperature in the region below the Debye characteristic temperature of the longitudinal mode.[33] Then we can express the factor of the second term of eq 41, as a rough estimation, by

$$s_{33}\gamma_3^{(l)}C_p^{(l)}/V \simeq AT \tag{42}$$

where A is a constant and AT corresponds to the thermal expansion coefficient due to the longitudinal mode. Such a contribution of the longitudinal mode will be taken into account in the next section.

IV. Comparison with Experimental Results

For comparison of the theoretical results in the previous sections with the experimental results, we introduce the following parameters.

$$G_1 = -\frac{\partial\epsilon/\partial T}{\partial J/\partial T} \tag{43}$$

$$C_1 = \frac{2(\partial\epsilon/\partial T)^2}{\partial J/\partial T} \tag{44}$$

$$G_2 = -\frac{2(\partial J/\partial T)}{\partial^2 J/\partial T\, \partial\sigma} \tag{45}$$

$$C_2 = \frac{8(\partial J/\partial T)^3}{(\partial^2 J/\partial T\, \partial\sigma)^2} \tag{46}$$

G_n and C_n ($n = 1, 2$) have the dimensions of modulus and heat capacity per volume, respectively. Table II lists the average slopes of ϵ, J, and $\partial J/\partial\sigma$ vs. T obtained from tensile testing for highly oriented PBA and PPTA fibers[2] and the evaluated values of G_n and C_n. Alternatively, we can obtain the following theoretical estimations for G_n and C_n from eq 25–27 if the temperature dependence of ρv^2 is neglected.

$$G_n = \left\langle \frac{1}{\rho^n v^{2n}} \right\rangle \Big/ \left\langle \frac{1}{\rho^{n+1} v^{2n+2}} \right\rangle \tag{47}$$

$$C_n = C\left\langle \frac{1}{\rho^n v^{2n}} \right\rangle^{n+1} \Big/ \left\langle \frac{1}{\rho^{n+1} v^{2n+2}} \right\rangle^{n} \tag{48}$$

where ρv^2 is considered to be related intimately to the shear modulus between molecules and C is the heat capacity due to the transverse modes (refer to eq 19 and 23). Equations 47 and 48 suggest the physical meanings of G_n and C_n listed in Table II. It should be remarked that the following inequalities are derived based on eq 47 and 48.

$$G_n \geq G_{n+1} \tag{49}$$

$$C \geq C_n \geq C_{n+1} \tag{50}$$

where the sign holds only when ρv^2 = constant, irrespective of k and the direction of the transverse modes. It is recognized that the inequalities in eq 49 and 50 are contradictory with the experimental results listed in Table II. Even if we take into account the temperature dependence of ρv^2 such that $\rho v^2 \propto \exp(-\beta T)$ [$\beta > 0$], the apparent contradiction is not resolved but rather enlarged. Then we must introduce a positive thermal expansion term that represents the thermal expansion of the string along its path and modify eq 25 as

$$\frac{\partial\epsilon}{\partial T} \simeq \alpha_+ - \frac{C}{2}\left\langle \frac{1}{\rho v^2} \right\rangle \tag{51}$$

where the second term of eq 25 is neglected. For further discussion, we make the hypothesis that the transvese modes are divided approximately into two parts: (i) the flexural modes, which have one small value of $\rho v^2 = G_e$ and their total heat capacity C_e, and (ii) the other transverse modes, which have a very large value of ρv^2 and so do not contribute to the summation in eq 20, etc. Under such a hypothesis, the term $C\langle 1/\rho v^2\rangle/2$ in eq 51 can be replaced with $C_2/2G_2$. Then from the data listed in Table II, α_+ is estimated as 4.1×10^{-6} K^{-1} for PRD 49 and 0.9×10^{-6} K^{-1} for Kevlar 49. These values of α are comparable to the thermal expansion coefficient of diamond ($\alpha = 1.1 \times 10^{-6}$ K^{-1} at 300 K and 3.2×10^{-6} K^{-1} at 600 K)[34] as a typical example of isotropic and covalently bonded crystals.

From the above discussion the necessity and the order of α_+ is understandable. As a next step, we take into account the temperature dependences of α_+ and G_e and rewrite eq 17 under the assumption of monodisperse G_e as

$$\epsilon \simeq \frac{\sigma}{E_0} - \frac{1}{2}\frac{C_e T}{G_e + \sigma} + \frac{1}{2}AT^2 \tag{52}$$

where $(1/2)AT^2$ corresponds to the second term of eq 41 (the above-estimated values of α_+ are considered as the averaged value of AT). We assume further that

$$G_e = G_{e,0}\exp(-\beta T) \tag{53}$$

Figure 2 shows the theoretical results based on eq 52 in comparison with the experimental results for PRD 49.[2] The calculated curves are well coincident with the experimental plots, where the following parameters are utilized: $G_{e,0} = 2.0$ GPa, $\beta = 0.00085$ K^{-1}, $C_e = 22 \times 10^3$ J m^{-3} K^{-1}, $A = 5.6 \times 10^{-9}$ K^{-2}, and $E_0 = 210$ GPa. The total heat capacity of the transverse mode C is estimated as 106 $\times$ 10^3 J m^{-3} K^{-1} by using the relation $C = 4\mathbf{k}_B/(abc)$, where a, b, and c are the lattice constants of the orthorhombic PBA crystal[35] and the numerical factor 4 is the number of vibrational directions (=2) times the number of the

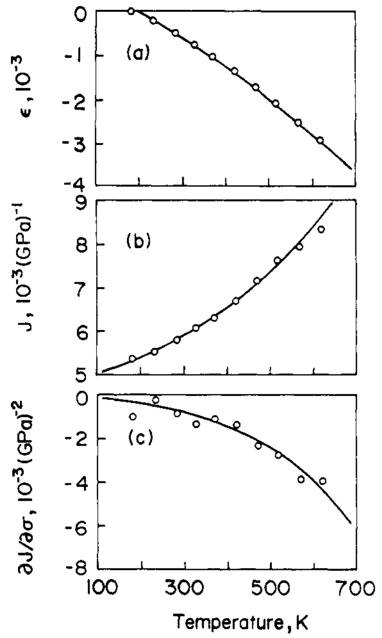

Figure 2. Temperature dependences of (a) ϵ, (b) J, and (c) $\partial J/\partial\sigma$ for PRD 49 under the stress $\sigma = 0.15$ GPa. The solid lines are the theoretical curves; $C_e = 22 \times 10^3$ J m^{-3} K^{-1}, $G_{e0} = 2.0$ GPa, $\beta = 0.00085$ K^{-1}, $E_0 = 210$ GPa, and $A = 5.6 \times 10^{-9}$ K^{-2}. In (a) the zero point of the strain is arbitrary.

chains in the unit cell (=2). The estimated heat capacity of the flexural modes C_e is about 20% of that of all the transverse modes. The magnitude G_e and the temperature dependence β are comparable to those for isotropic polymer materials in the glassy state.[36] (It is considered that such a modulus reflects mainly the intermolecular potential as similarly as ρv^2.) The value of E_0, 210 GPa, is nearly equal to the value estimated by linear extrapolation of plots of E_t vs. T to 0 K, 215 GPa.[2] This accordance suggests the reasonableness of such an extrapolation.

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