

Measurement and Interpretation of Nonlinear Mechanical Energy Losses in High Polymer Fibers

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Synopsis

Dynamic mechanical loss measurements were made on fibers at large tensile strains which caused nonlinear viscoelastic behavior. Measurements on fibers from polyethylene, polypropylene, nylon 66, nylon 4 and an experimental polymer led to seven energy loss peaks for each sample in the temperature range of 120–350°K. The peaks were evenly spaced in temperature at intervals of 30–35°K. rather than at unequal temperature intervals of approximately 100–150°K. normally observed under conditions of linear viscoelastic behavior. In every case, the array of evenly spaced peaks occurred only at temperatures below the glass transition temperature. The temperatures at the energy loss peaks were virtually independent of crystallinity and molecular orientation and were interpreted in terms of polymer molecular structure. The data could be explained only by a single mechanism, common to all polymers, which could operate in a quantized manner, e.g., diffusional motion of molecular chain segments. To account for the constant temperature spacing between peaks of a given sample, it was necessary to assume that the rate controlling step in the energy loss process is the return of a displaced segment to equilibrium. Calculations from the experimental data indicated that peaks at higher temperatures stem from displaced molecular segments which experience high potential energy barriers and which have to be excited to higher skeletal vibrational energies to overcome the barrier. Precedence for this interpretation is provided by Tanaka and Ishida, who have associated molecular vibrations with the well-known β loss peaks in polymers.

Introduction and Preliminary Discussion

The dynamic mechanical loss behavior of polymers has been discussed extensively for both polymer solutions and solid polymer.¹ Virtually all studies carried out in depth have been made under conditions such that a sinusoidal strain imposed on a sample produces a sinusoidal stress. Normally there is a time lag between stress and strain which provides an unambiguous measure of the energy dissipated as heat during each mechanical cycle. In these cases, the material is said to exhibit linear viscoelastic behavior.

In the present work, fibers from high polymers were subjected to a moderately large static extension, which was near the fiber yield strain, and samples were subsequently subjected to a superimposed, large dynamic strain. Under these conditions, a sinusoidal strain did not produce a sinusoidal stress, and the material is said to exhibit nonlinear viscoelastic behavior.

These nonlinear measurements generated much more extensive data than conventional, linear measurements. This additional information took the form of previously unobserved loss peaks along with those normally measured at low strains. Measurements on polyethylene, polypropylene, nylon 66, nylon 4, and an experimental polymer led to approximately seven energy loss peaks for each sample in the temperature range of 110–360°K. The peaks were evenly spaced in temperature at intervals of 30–35°K. rather than at unequal temperature intervals of 100–150°K., as normally observed under conditions of linear viscoelastic behavior. In every case, the array of evenly spaced loss peaks occurred only at temperatures below the glass transition temperature.

A possible explanation for the presence of these additional loss peaks is based on the observation that (1) the present nonlinear measurements produced a large-scale motion of molecular segments in which the degree of molecular orientation increased and decreased periodically with dynamic strain during each mechanical cycle and (2) no such change occurred under conditions of linear measurements. The more vigorous molecular motion characteristic of nonlinear measurements may have induced the additional loss peaks not found in the linear measurements. The changes in molecular orientation were determined from continuous measurements of sound velocity during cycling.²

The temperatures of the multiple loss peaks were virtually independent of crystallinity and molecular orientation and were interpreted in terms of the polymer molecular structure. Correlations of these data for polymers of widely different molecular structure showed that the loss peaks could not be explained in terms of molecular motion at specific bond sites such as side group motion or hindered rotation about single bonds. The existence of many loss peaks for a polymer so simple in structure as polyethylene defies the proposition that each loss peak stems from a totally different type of molecular motion.

The unavailability of a separate mechanism for each peak and the equal temperature spacing between peaks of each sample imply a single mechanism which can operate in some quantized fashion. The only simple mechanism which applies to all polymers, regardless of their structure, and for which there is precedence, is the diffusional motion of molecular chain segments. This interpretation has been advanced by Sauer and Woodward¹ for at least one polyethylene peak; Zener³ has discussed it in more general terms.

The present interpretation assumes that short chain segments are capable of occupying at least two different stable positions and that a mechanical disturbance will cause segments to move from a position of low potential energy to a less stable position having higher potential energy. For this, or any process, to produce mechanical energy losses, there must be a potential energy barrier preventing displaced segments from returning immediately to the more stable, lower energy position, and displaced segments must be activated by normal thermal fluctuations to overcome the energy barrier.

It was shown that the equal temperature spacing between successive peaks for a sample leads directly to the conclusion that the activation energies of the peaks are integral multiples of an energy constant. To account for this fact it was necessary to assume that the rate controlling step in the energy loss process is the return to equilibrium over the potential barrier. On the basis of this assumption, peaks at higher temperatures would stem from displaced molecular segments which experience higher potential energy barriers and which have to be excited to higher thermal vibrational energies to overcome the barrier. In this way the vibrational energy necessary to overcome the barrier becomes the effective activation energy.

This development permitted the calculation of an activation energy constant from the temperature spacing characteristic of each polymer studied. Values correlated well with molecular skeletal vibration energies which suggested that the rate controlling step in the multiple energy loss processes may be the thermal excitation of molecular skeletal vibrations. Precedence for this interpretation is provided by Tanaka and Ishida,⁴ who have associated molecular vibrations with the well-known β loss peaks in polymers.

Experimental

All measurements were made on fibers which were stretched 2% at room temperature and held at a fixed length for the duration of the experiment. Samples were dried under nitrogen for 1 hr. and subsequently cooled to liquid nitrogen temperatures while under dry nitrogen. Measurements were made as the samples warmed to room temperature and subsequently heated to near the polymer melting point.

A probe, attached to the center of the 20-in. fiber samples, was mounted on the sensing element of a strain gage. The strain gage and probe were continuously cycled in the direction of the fiber axis at a rate of 1.0 cycles/sec. over a total dynamic strain of 1%. The strain gage measured the resulting cyclic stress in the fiber. The dynamic strain was measured by a second gage which oscillated with the first and which had its sensing probe attached to the center of a stationary spring. Both the dynamic stress and strain were recorded on a Visicorder direct recording oscillograph (Minneapolis-Honeywell).

In the case of linear viscoelastic behavior, a sinusoidal strain produces a stress which also varies sinusoidally with time. Such linear data are normally described by the phase angle between stress and strain δ and the ratio of the peak stress to peak strain, i.e., the elastic storage modulus E' . The imaginary component of the complex modulus (or loss modulus, E'') is related to these parameters by:

$$E'' = E' \tan \delta \quad (1)$$

In the case of the nonlinear data obtained in this work, the measured stress was not sinusoidal, even though samples were cycled in the sinusoidal fashion. Consequently, the phase angle had no precise meaning and did not describe the mechanical energy losses.

The classical method of treating these nonlinear data is to plot stress against strain over a complete cycle and calculate the energy dissipated during the cycling from the area of the hysteresis loop. When divided by the total dynamic strain, this energy corresponds to the loss modulus E'' for linear behavior, since both are measures of the absolute energy dissipated per cycle, per unit dynamic strain.

To simplify the present calculations, the following approach was taken.

As discussed above, the stress-measuring probe was attached to the center of the fiber samples, and this served to average gross differences in the stress-strain behavior during the extension and retraction parts of the cycle. When this composite stress was plotted against strain, the resulting hysteresis loop had exactly the same area as the loop obtained when the fiber was cycled at its end, after proper normalization for sample length. This method of treating the data was shown to be justified from simple geometrical arguments.

When the composite stress (measured at the center of the fiber) was plotted against time, a nearly but not exactly sinusoidal curve was obtained. An apparent phase angle between strain and the composite stress was measured at various parts of the cycle and the values were averaged. Then, an apparent loss modulus E'' was calculated from eq. (1) and compared with the actual area of the hysteresis loop (normalized to unit dynamic strain). The two methods of calculation were found to be in agreement within limits of experimental error. This agreement stemmed from the fact that the composite stress versus time curve was very nearly a sine wave when measured by oscillating the center of the specimen.

For purposes of convenience and comparison with linear loss measurements the present results are reported in terms of apparent loss modulus E'' .

The units used in reporting the present data are typical for mechanical measurements on textile fibers, i.e., grams of force per denier, where denier is a measure of the linear density of the fiber sample. Specifically, denier is the weight, in grams, of 9×10^5 cm. fiber. Moduli of textile fibers are normally calculated in these units, rather than in dynes/cm.², to circumvent the difficulties of determining the cross-sectional area or the volume density of small, irregularly shaped textile fibers.

The relationship between the two systems of units involves the volume density ρ of the sample and the acceleration due to gravity g , and is given by:

$$E' \text{ (g./den.)} = E' \text{ (dynes/cm.}^2\text{)}/9 \times 10^5 g \rho \quad (2)$$

The loss moduli E'' in the two systems bear the same relationship. In the present system, energy losses have the units of gram-centimeters of energy per unit sample length of unit denier; or, in short, grams/denier.

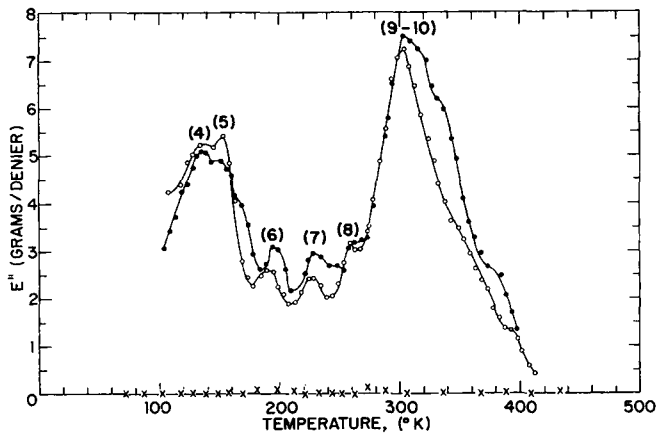


Fig. 1. Apparent loss modulus vs. temperature: (●, ○) for separate specimen of a linear polyethylene fiber drawn 10×; (×) for a steel spring.

As described in later sections, the present nonlinear measurements have led to the observation of many loss peaks, evenly spaced in temperature, which have not been previously reported. Naturally, the apparatus rather than the samples was initially suspected as the source of this unusual behavior. However, this was shown not to be the case by making measurements on springs which showed no significant losses at any temperature, and by measuring samples with a wide range of lengths and diameters. Also the mechanical frequency was varied from 0.1 to 10 cycles/sec., and some samples were cycled at the end rather than at the center. All of these variables produced no significant change in the experimental results.

Data in Figure 1 show the apparent loss moduli obtained in experiments on two different specimens of a fiber from linear polyethylene. While the actual values of the apparent loss moduli were not identical at all temperatures, the temperature at each of the numbered peaks was reproduced within about 3°K., and it is the latter which concerns the present development. The significance of the numbers assigned to the various peaks will be discussed in a later section. Loss moduli measured on a steel spring showed no significant losses as indicated by the crosses near the bottom of Figure 1.

Multiple Loss Peak Behavior

When the apparent loss moduli E'' of polyethylene and polypropylene fibers were plotted against the temperature of measurement, an array of loss peaks, evenly spaced in temperature were observed for each sample at temperatures below the glass transition. The height of the loss peaks varied with sample history (thermal treatments, stretch), but the temperature of each loss peak was virtually independent of sample treatment.

Figure 2 shows the relationship between E'' and temperature for a polypropylene fiber drawn 6× (crystallized in the α -form) and two linear poly-

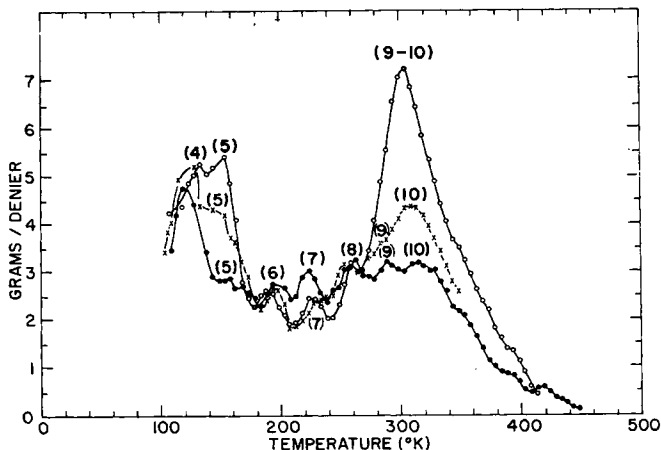


Fig. 2. Plots of (O) apparent loss modulus E'' vs. temperature for linear polyethylene, drawn $10\times$; (X) $3E''$ for linear polyethylene, undrawn; (●) E'' for polypropylene, drawn $6\times$.

ethylene samples: one drawn $10\times$ and one undrawn. These samples show a remarkable similarity in the position of the loss peak on the temperature axis. The lowest peak temperature, which varied from 120 to 130°K . for the three samples was designated as peak 4 since, as described later, three peaks are believed to exist at lower temperatures. Peak 5 is near 150°K . for all three samples. Similarly, each of the samples have comparable temperatures for peaks 6, 7, and 8.

The polypropylene sample showed both peaks 9 and 10; the undrawn polyethylene sample had a hint of a peak near 290°K ., which was presumed to correspond to the peak 9 for polypropylene. The drawn polyethylene sample exhibited a single large peak which encompassed both peaks 9 and 10. In all cases, the storage modulus E' exhibited a precipitous decrease in the temperature range of peaks 9 and 10, indicating that the glass transition

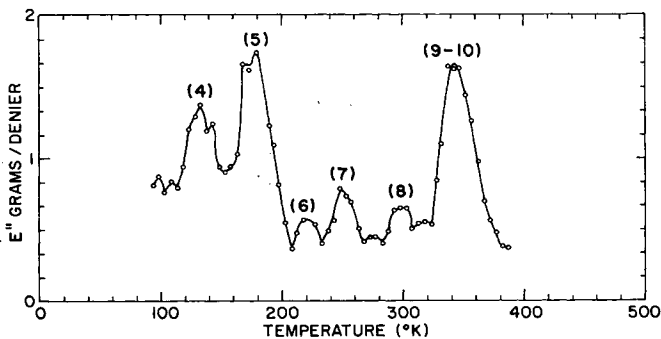


Fig. 3. Apparent loss modulus vs. temperature for nylon 66, undrawn.

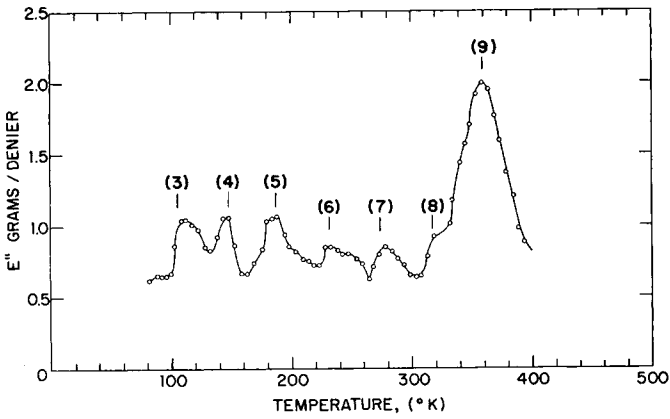


Fig. 4. Apparent loss modulus vs. temperature for nylon 4, undrawn.

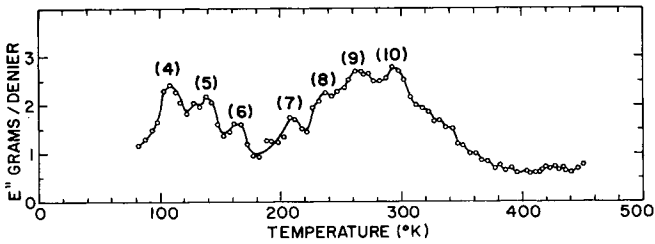


Fig. 5. Apparent loss modulus vs. temperature for experimental polymer.

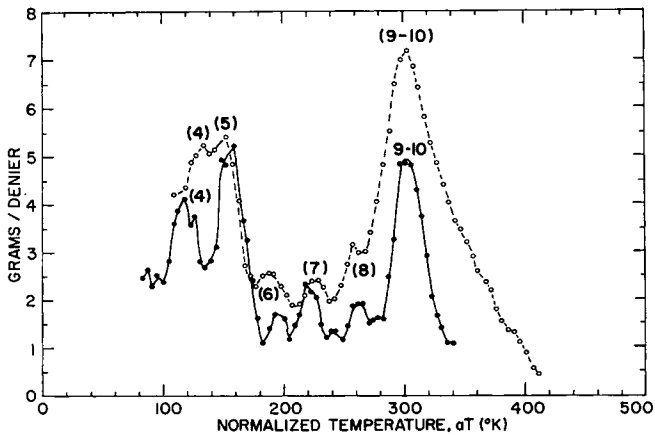


Fig. 6. Plots of (O) apparent loss modulus E'' vs. normalized temperature scale (aT) for drawn, linear polyethylene, $a = 1.0$; (●) $3E''$ for nylon 66, $a = 0.88$.

TABLE I

Peak number	Temperature of E'' peaks, °K.										Normalized peak temperature aT , °K.		
	Linear polyethylene					Drawn polypropylene					Experimental polymer		
	Undrawn	Drawn	Drawn	Nylon 66	Nylon 4	Drawn polypropylene	Nylon 66	Nylon 4	Experimental polymer	Nylon 66	Nylon 4	Experimental polymer	
3													
4	127	132	118	132	110	118	145	108	118	90	108	108	
5	150	153	158	175	186	158	186	136	152	119	148	148	
6	192	188	198	220	232	198	232	165	195	153	186	186	
7	230	225	222	250	278	222	278	210	222	190	228	228	
8	255	258	262	298	320	262	320	237	263	228	258	258	
9	285	303	288	343	359	288	359	265	303	262	290	290	
10	308		313			313		292		294	320	320	

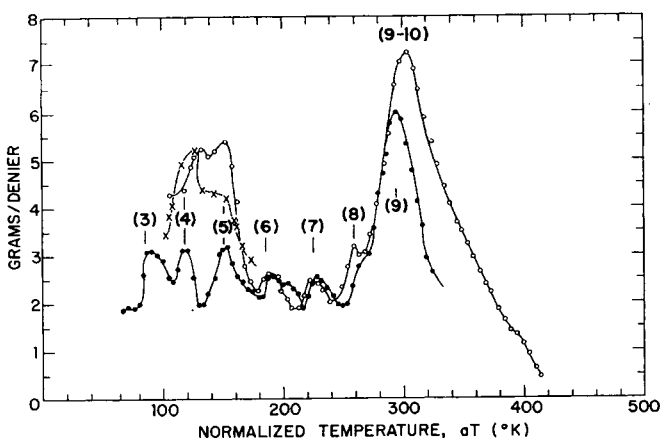


Fig. 7. Plots of (O) apparent loss modulus E'' vs. temperature for drawn, linear polyethylene, $a = 1.0$; (X) $3E''$ for undrawn linear polyethylene, $a = 1.0$; (●) $3E''$ for undrawn nylon 4, $a = 0.82$.

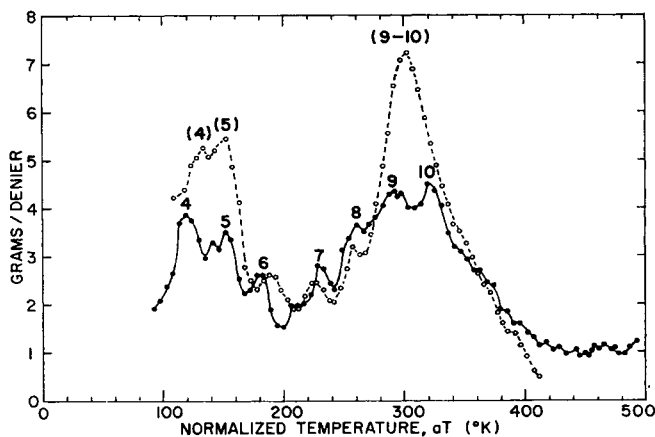
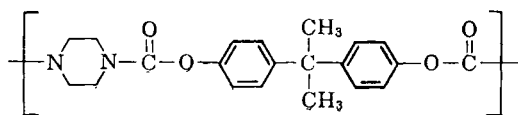


Fig. 8. Plots of (O) apparent loss modulus E'' vs. normalized temperature scale for drawn, linear polyethylene, $a = 1.0$; (●) $1.6E''$ for experimental polymer, $a = 1.09$.

is in this region. As stated earlier, the multiple loss peaks occurred only at temperatures below the glass transition.

Multiple loss peaks similar to those observed in polyethylene and polypropylene were found in certain condensation polymers. The three examples described below include an undrawn fiber of nylon 66 (Fig. 3), of nylon 4 (Fig. 4), and of the following experimental polymer from diphenylolpropanol and piperazine (Fig. 5):



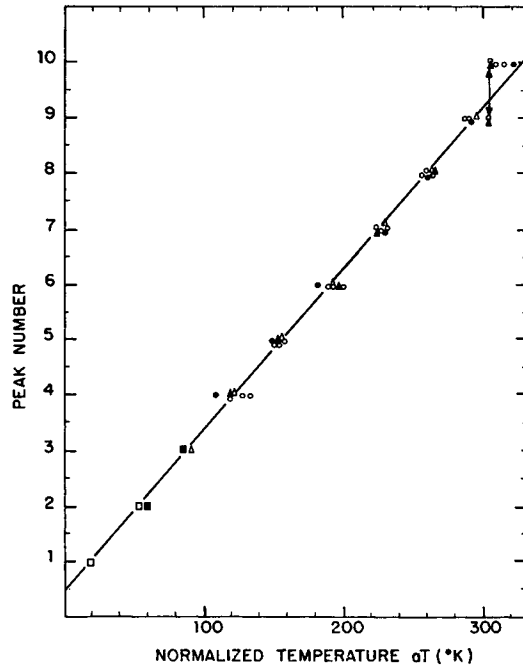


Fig. 9. Plots of peak number vs. normalized temperature scale: (O) polyethylene and polypropylene, this work; (▲) nylon 66, this work; (Δ) nylon 4, this work; (●) experimental polymer, this work; (□) polypropylene, data of Sinnott;⁵ (■) liquid hydrocarbons, data of Young.⁶

The similarity between these data and the polyhydrocarbon loss behavior was striking when the apparent loss moduli were plotted against a normalized temperature scale. In Figure 6 the abscissa is designated aT , where T is the temperature and a is a normalization constant having a value of 1.0 for polyethylene and 0.88 for nylon 66. In Figures 7 and 8 the normalization factors are 0.82 and 1.09 for nylon 4 and the experimental polymer, respectively. As in the case of the polyolefins, the storage modulus E' exhibited a precipitous decrease in the temperature range of peaks 9 and 10, indicating that the glass transition is in this temperature region.

The fact that the multiple loss peaks are evenly spaced in temperature is shown in Figure 9, where the assigned peak numbers are plotted against the normalized temperature scale. The ambiguities associated with unresolved peaks 9 and 10 may result from the presence of the glass transition in this temperature region. The intercept of one-half at absolute zero is treated in a later section. Data for peaks 3–10 are summarized in Table I.

It must be emphasized that not all nonlinear loss measurements were so easily correlated as those described above. For example, the data for all measurements on highly drawn nylon 66 fibers showed the characteristic multiple peaks but: (1) in some patterns, an occasional small peak was completely missing; (2) in other cases, a small peak appeared out of place

while the remaining peaks were positioned at the characteristic, equal temperature intervals; and (3) in still other incidences, a single broad peak appeared in place of two small peaks. However in every case, the data showed the general character of the multiple loss peaks but with the occasional irregularities mentioned above. No attempt has been made to interpret the significance of these irregularities.

As illustrated in a later section, it appears that the nonlinear loss peaks measured between -200 and $+200^{\circ}\text{C}$. include those obtained by linear measurements plus additional ones. With this fact in mind, the present data in Figure 9 were correlated with earlier measurements of loss peaks associated with temperatures below -200°C . for frequencies near 1 cycle/sec.

Sinnott⁵ has observed a peak at 19°K . (peak 1) and another at 52°K . (peak 2) for polypropylene. Peak 2 was observed along with peak 1 for a highly crystalline polypropylene sample, but only peak 1 was observed in a sample of low crystallinity. While Sinnott made measurements at 7 cycles/sec., the temperature of these peaks should be near the values for 1 cycle/sec., since it is usually necessary to change frequency by several orders of magnitude to observe significant changes in peak temperature.

There is evidence of both peaks 2 and 3 in measurements on liquid hydrocarbons but it is not certain that the same mechanisms are responsible for loss peaks observed in solid polyhydrocarbons and in hydrocarbon liquids. Nevertheless, a comparison of the data is highly suggestive, as shown below.

Young⁶ reported loss peaks for 2-methylbutane and 3-methylpentane which he observed acoustically at frequencies of several megacycles. He obtained activation energies for the peaks, which permitted calculation of the peak temperature for a 1 cycle/sec. dynamic measurement. This calculation led to a temperature of 83°K . (peak 3) as indicated in Figure 9. Further measurements on 2,3-dimethylbutane led to peak 2.

Young attributed peaks 2 and 3 to rotation about a carbon atom with two and one methyl side groups, respectively. While his data for *n*-pentane showed an increasing loss with decreasing temperature, they did not completely define a peak over the experimental temperature range. Young gave no interpretation of these data. While we have neither confirmed nor

TABLE II
Parameters Calculated from Energy Loss Data

Polymer	Temperature normalization factor a	Product of S and $a \times 10^2$, $^{\circ}\text{K}^{-1a}$
Polyethylene	1.00	2.92
Polypropylene	1.00	2.92
Nylon 66	0.88	2.57
Nylon 4	0.82	2.39
Experimental polymer	1.09	3.18

^a Slope of line in Figure 9 = $2.92 \times 10^{-2}/^{\circ}\text{K}$.

disproven Young's interpretations for peaks 2 and 3, we have shown that the liquid hydrocarbon data fit into the multiple loss peak scheme illustrated in Figure 9.

In summary, the temperature normalization factor a for each of the samples is listed in Table II along with the slope S of the line in Figure 9 and the product Sa . The significance of these parameters will be discussed in a later section.

Comparisons with Earlier Measurements

Willbourn⁷ has shown that the temperatures of $\tan \delta$ peaks for branched polyethylene depend on sample history (Fig. 10). However, the product of loss modulus (E'' , in units of grams/denier) and density (ρ , in units of

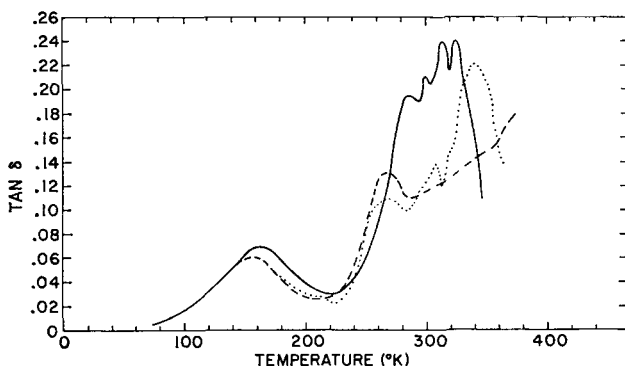


Fig. 10. Loss tangent vs. temperature for branched polyethylene: (—) quenched; (...) partially annealed; (---) fully annealed. Data of Willbourn.⁷

grams/cubic centimeter) was calculated from Willbourn's data and plotted against temperature. The data showed only two significant loss peaks which were little affected by sample history (Fig. 11). These two loss peaks correspond to peaks 5 and 8 (Fig. 12). Willbourn's data for a 14% methyl-substituted polymethylene show peaks 5 and 7 only (Fig. 13). The polyhydrocarbon multiple loss peaks measured in this work appear to include those reported in earlier work along with several additional peaks.

In a similar fashion, the multiple loss peaks observed in this work for nylon 66 were compared to the well known α , β , and γ peaks reported by Willbourn (Fig. 14). The present data show two peaks (4 and 5) in lieu of the γ peak; when the temperature of the γ peak was multiplied by the normalization factor for nylon 66 (0.88) the product aT fell between the values for peaks 4 and 5 in Figure 9. The fact that the γ peak encompasses the temperature range for peaks 4 and 5 suggest that the γ peak may be composed of two unresolved loss peaks. The β peak corresponds to peak 7 but extends over the temperature range of peaks 6 through 8, in much the same manner that the γ peak extends over the range of peaks 4 and 5.

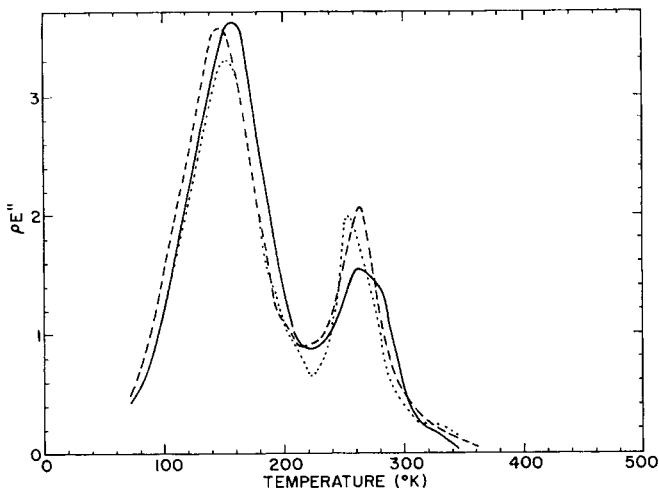


Fig. 11. Product of density ρ (g./cc.) and loss modulus E'' (g./den.) for branched polyethylene, calculated from data of Willbourn:⁷ (—) Quenched;⁷ (...) partially annealed; (---) fully annealed.

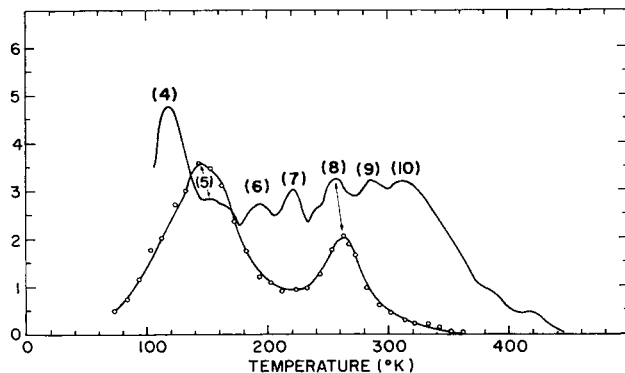


Fig. 12. Plots of (O) Willbourn's data⁷ on branched polyethylene, $\rho E''$ vs. temperature; (—) drawn polyethylene, this work, E'' vs. temperature.

The α peak falls at 326°K., which is somewhat below the present 9–10 peak; when the temperature of the α peak was multiplied by the normalization factor for nylon 66 the resulting value of 287°K. for aT was identical to the value for peak 9 (Fig. 9). The 9–10 loss peak measured in the present work falls between peaks 9 and 10 as indicated in Figure 9 and is taken as an unresolved combination of two peaks as discussed earlier.

Interpretations

It appears that the temperature at which loss peaks occur is determined by the polymer molecular structure and not by the physical structure (crystallinity, molecular orientation) of the actual sample. Examples are

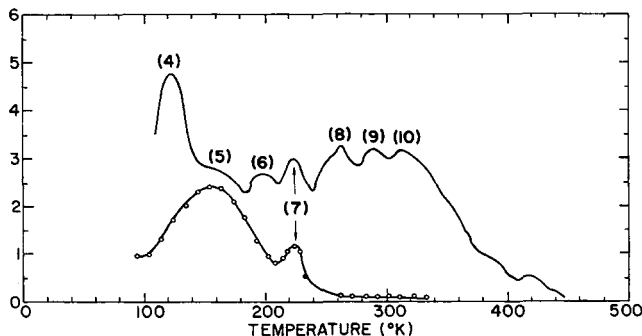


Fig. 13. Plots of (O) Willbourn's data⁷ on methyl branched polymethylene, $\rho E''$ vs. temperature; (—) drawn polyethylene, this work, E'' vs. temperature.

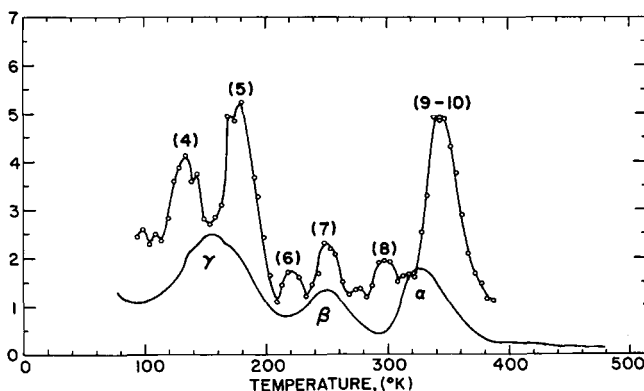


Fig. 14. Plots of (—) Willbourn's data⁷ on nylon 66, $\rho E''$ vs. temperature; (O) undrawn nylon 66, this work, $3E''$ vs. temperature.

given in Figure 2 for oriented (highly drawn) and unoriented polyethylene fibers, and in Figure 11 (Willbourn's data) for annealed and quenched polyethylene. While the temperature of each loss peak in Figure 2 was little affected by molecular orientation, the overall magnitude of the energy losses was found to be much greater for the oriented sample.

Certainly the common behavior of polymers of widely different molecular structure (Fig. 9) cannot be explained in terms of molecular motion at specific bond sites such as side group motion or hindered rotation about single bonds.^{6,8} The existence of many loss peaks for a polymer so simple in structure as linear polyethylene defies the proposition that each loss peak stems from a totally different type of molecular motion.

The unavailability of a separate mechanism for each peak and the equal temperature interval between peaks for a given sample imply a single mechanism which operates in some quantized fashion. The only simple mechanism which applies to all polymers, regardless of their structure, and for which there is precedence, is the diffusional motion of molecular chain

segments. This interpretation has been mentioned by Sauer and Woodward¹ for at least one polyethylene peak; Zener³ has discussed it in more general terms.

In the diffusion mechanism, a short chain segment is capable of occupying at least two different stable positions and a mechanical disturbance will cause the segment to move from a position of low potential energy to a less stable position having higher potential energy. For this, or any process, to produce mechanical energy losses, (1) there must be a potential energy barrier preventing the displaced segment from returning immediately to its more stable, lower energy position, and (2) displaced segments must be activated by normal thermal fluctuations to overcome the energy barrier.

As stated earlier, we are forced to assume that this mechanism operates in some quantized manner to give the observed array of loss peaks evenly spaced in temperature. To express this idea in more quantitative terms, a comparison is drawn between an empirical expression for the line in Figure 9 and the well known Eyring expression commonly used to describe energy loss behavior.^{1,9}

The correlations in Figure 9 are described by the relation

$$2N_p - 1 = 2SaT_p \quad (3)$$

where N_p is assigned peak number, S is slope of the line in Figure 9, a is temperature normalization factor, and T_p is peak temperature. Values of S , a , and their product are given in Table II for samples studied. The Eyring relationship^{1,9} is expressed by

$$\Delta E_p = k(\ln 1/\tau_p - \ln f)T_p \quad (4)$$

where ΔE_p is activation energy, k is Boltzman's constant, τ_p is a time constant, and f is experimental mechanical frequency.

These two expressions have the same form and the Eyring expression applies to the data in Figure 9 only if the logarithm of the time constant for the multiple peaks of a given sample are approximately equal,

$$\ln \tau_p \simeq \ln \tau \quad (5)$$

where $\ln \tau$ is constant for the multiple peaks of a given sample. Eliminating the peak temperature from eqs. (3) and (4) and introducing eq. (5) yields

$$\Delta E_p = (2N_p - 1)\Delta E_0 \quad (6)$$

where

$$\Delta E_0 = (k/2)[\ln (1/\tau f)/Sa] \quad (7)$$

and is constant among all peaks for a given sample.

An explanation of the quantization of the activation energy and the corresponding equal temperature interval between loss peaks was postulated by assuming that the rate-controlling step in the energy loss process is the return of a displaced segment to equilibrium over a potential energy barrier.

By this assumption, the effective activation energy will be the thermal vibrational energy to which a segment must be excited to overcome the potential barrier and return to equilibrium. Since the vibration energy is quantized, so would be the effective activation energy [eq. (6)]. This interpretation would mean that peaks at the higher temperatures would stem from displaced molecular segments which experience higher potential energy barriers and which must be excited to higher thermal vibrational energies to overcome the barrier.

It would be instructive to measure the activation energies of the multiple loss peaks to test the validity of eq. (6). A further instructive test would be to see if the logarithm of the time constants are approximately the same for the multiple peaks of a given sample. However, the present apparatus could not cover a wide enough frequency range to permit these measurements.

The fact that eq. (6) shows the activation energy to be odd multiples of an energy constant stems from the intercept of one-half in Figure 9. It was not possible to get a good fit of the data by drawing the line through the origin. This behavior might be explained by the LaPorte rule,¹⁰ i.e., any excited segment can return directly to the ground state vibration energy only if it is excited to an odd quantum state.

While the above hypothesis is consistent with present observations, it has not been rigorously proven. Further experimentation involving the determination of activation energies and time constants for the multiple loss peaks would be a logical step in testing the validity of the present approach.

Calculation of Structural Parameter from Energy Loss Data

The above explanation for the quantization of activation energies and the equal temperature interval between peak amounts to taking the energy constant in eq. (6) as a molecular vibration energy. Equation (6) becomes:

$$\Delta E_p = (2N_p - 1)h\nu \quad (8)$$

and from eq. (7),

$$Sa = (k/2h\nu)(\ln 1/\tau - \ln f) \quad (9)$$

where ν is some unspecified molecular motional frequency and h is Planck's constant.

Equation (9) relates the experimental quantities to two parameters, ν and τ . Before this expression could be used to calculate any molecular structural parameter, it was necessary to make the following assumption which seems justified in light of present data: once a displaced segment becomes excited with the energy required to overcome the potential barrier, the time required for it to return to equilibrium is of the order of a few molecular vibrations. This would mean that the logarithm of the reciprocal time constant ($\ln 1/\tau$) would be approximately equal to (but slightly less than) the logarithm of the vibrational frequency ($\ln \nu$).

It was found that published values of activation energy¹ for the low temperature loss peaks of polyethylene (β and γ peaks) and values for loss peaks measured on liquid hydrocarbons⁶ are essentially in agreement with this assumption. This was shown by: (a) calculating ν from eq. (8) by using published values of the activation energy for a given peak and the appropriate N_p , depending on the temperature of the loss peak at an experimental mechanical frequency of 1 cycle/sec., (b) comparing the calculated values of $\ln \nu$ with published values of $\ln 1/\tau$.

As described by Sauer and Woodward,¹ published values of activation energies determined on solid polymers are subject to very large errors.

TABLE III
Activation Energies and Time Constants for Liquid Hydrocarbons^{a, b}

Peak Number	ΔE_p , kcal./mole	$\log \nu$	$\log 1/\tau_p$	$\log \nu/\log (1/\tau_p)$
2	3.3	13.5	11.8	1.11
3	4.7	13.7	12.0	1.08

^a Calculated from data of Young.⁶ ^b Note: data give $\log \nu$ (base 10); in equations we use $\ln \nu$ (base e).

TABLE IV
Theoretical and Experimental Frequencies

Description	Frequency, cm. ⁻¹				
	Linear polyethylene (LPE)	Polypropylene (PP)	Nylon 66	Nylon 4	Experimental polymer
Chain stretching (theoretical ^a)	477	412	~412-477	~412-477	—
Experimental ^b	353 ± 10	353 ± 10	407 ± 10	437 ± 10	327 ± 10
Twisting (theoretical ^a)	195	118	~118-195	~118-195	—
Transverse vibration (theoretical ^a)	<10	<10	<10	<10	—
Coiling (theoretical ^a)	<10	<10	<10	<10	—

^a Theoretical values from infrared data.

^b Experimental values from mechanical energy loss data.

Certainly the values reviewed by Sauer and Woodward are too scattered to permit any quantitative justifications of the present assumption; however, it was found that typical activation energies for the β and τ peaks in polyethylene led to $\ln \nu$ values identical with values of $\ln 1/\tau$ calculated from published data.¹

The scatter in the activation energy data for solid polymers does not exist in the case of liquid hydrocarbons, and these data permit a more quantitative test of the correctness of the hypothesis. As shown in Table III, values of $\ln \nu$ and $\ln 1/\tau$ agree within 8-11% and the values of $\ln \nu$ are the larger, as expected.

On assuming, then

$$\ln \nu = \ln 1/\tau \quad (10)$$

and on recognizing that the present measurements were made at a mechanical frequency of 1 cycle/sec., eq. (9) becomes

$$\nu/\ln \nu = k/2hSa \quad (11)$$

This expression permits the calculation of ν from experimental values of Sa . The calculated values in Table IV are discussed in the following section and are compared with molecular skeletal vibration frequencies calculated from infrared data.

Comparisons with Molecular Skeletal Frequencies

The low frequency skeletal vibrations of polymer molecules contribute to polymer heat capacity and also describe the mechanical response of the individual molecules. These frequencies have been calculated for several polymer molecules by Zbinden and others¹¹⁻¹³ from infrared absorption data using a molecular model consisting of a series of masses connected by springs.

Zbinden has grouped these so called "acoustical frequencies" into four types of motion: (1) chain stretching; (2) chain twisting, about the molecular axis; (3) transverse chain vibration (violin string motion); and (4) chain coiling (cork screw fashion).

When the ends of a chain segment are fixed (possibly by entanglements, molecular folds), the motion of any one mass within the segment will influence the motion of all other masses. If the segment is made to vibrate in tension, for example, the energy will be partitioned among several

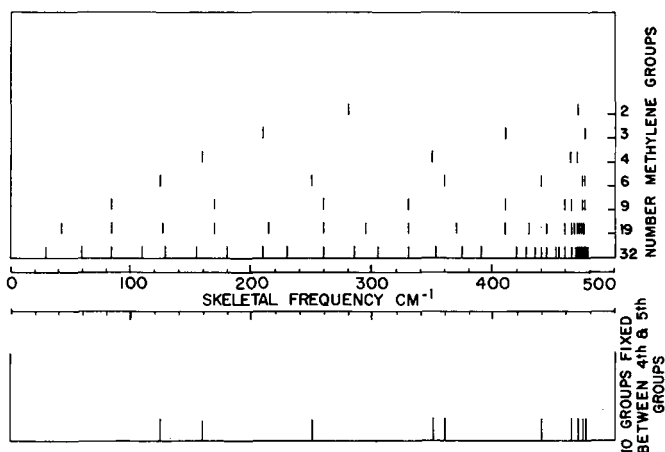


Fig. 15. Calculated skeletal frequencies for: (top) hydrocarbon chains with various numbers of methylene groups and (bottom) a ten-methylene chain, rigidly fixed between the fourth and fifth group.

different frequencies and the number of frequencies will equal the number of masses involved in the cooperative motion, i.e., the number of modes of vibration will depend on segment length.

The bar graph in Figure 15 shows the vibrational frequencies as calculated by Zbinden for stretching linear polyethylene (LPE) molecules of various chain lengths from 2 to 32 methylene groups. The longer the chain, the more densely populated the frequency range from 470 to 477 cm.^{-1} . In the limit of infinitely long chains, the population at 477 cm.^{-1} becomes infinitely greater than the population at any other frequency. Therefore, the most probable skeletal frequency for vibrating long LPE molecules in tension is near 477 cm.^{-1} .

The lower frequencies participate in the vibrational behavior of a molecule, but for segments greater than about nine methylene groups, the magnitude of their contribution would be small compared to those associated with frequencies near 477 cm.^{-1} . The most probable frequency for the other modes of vibration were derived from Zbinden's data and are listed in Table IV for LPE and polypropylene (PP) along with estimated frequencies for nylon 66 and nylon 4.

Skeletal frequencies for nylon 66 were approximated from Zbinden's calculations by assuming that all hydrogen bonds are formed and provide a complete barrier to the vibration of the methylene groups in the acid and amine portion of the chain. The tensile vibration frequencies were taken as the sum of those for 4 and 6 methylene groups (Fig. 15). These frequencies cluster mostly between 465 and 476 cm.^{-1} , i.e., a nominal theoretical frequency of about 470 cm.^{-1} .

If the hydrogen bonds in nylon 66 do not provide complete isolation of the amine and acid portions of the chain, one would still expect a theoretical value near those for LPE and PP. This is concluded from the similarity in values of the linear density and force constants for deforming isolated molecules of nylon 66 and linear polyolefins.^{12,4} Consequently, the theoretical frequencies for nylon 66 (Table IV) are assumed to be near the values for polyethylene, polypropylene, and the values calculated assuming that hydrogen bonding provides a vibrational barrier to the methylene groups. A similar approach was taken for nylon 4.

The molecular structure of the experimental polymer is too complicated to permit any direct estimation of its theoretical frequency from Zbinden's data. However, it is clear that the effect of rings in the polymer chain would increase both the stiffness and the mass per unit chain length. Since the vibrational frequencies are related to the ratio of stiffness to mass, the two effects tend to cancel so that the theoretical frequencies could be similar to values for the other polymers in Table IV.

Experimental frequencies determined from mechanical energy loss data are included in Table IV for comparison with the theoretical values. In all cases, the experimental frequencies lie between the theoretical values for chain stretching and twisting; are nearer the theoretical for stretching; and are much greater than the values for transverse vibration and coiling.

It is emphasized that the theoretical frequencies were derived for hypothetical, isolated, single chain molecules while the experimental values represent the behavior of molecules in the solid state. For this reason the experimental frequencies are not expected to agree precisely with any single theoretical value. However, intermolecular bonding in the solid state is expected to have a relatively small effect on the skeletal frequencies;¹² and therefore, qualitative agreement between the experimental and theoretical values is expected.

The differences in the experimental frequencies for the polyolefins and the two nylons are suggestive of the effect of hydrogen bonding on molecular properties, but any detailed interpretation of the data are beyond the scope of the present subject.

This work has shown that the multiple energy loss peaks obtained under nonlinear viscoelastic behavior must stem from a mechanism common to polymers of widely different structure, and the diffusional motion of chain segments is the logical mechanism. The present results only suggest that (1) the rate-controlling step in energy loss by this diffusion process is the thermal excitation of skeletal vibrations in polymer chain segments and (2) that chain stretching vibrations, chain twisting vibrations, or some combination of these motions are involved when a displaced molecular segment gains sufficient thermal energy to overcome an energy barrier and return to its equilibrium position.

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References

1. Sauer, J. A., and Woodward, *Rev. Mod. Phys.*, **32**, 88 (1960).
2. Moseley, W. W., Jr., *J. Appl. Polymer Sci.*, **3**, 266 (1960).
3. Zener, C., *Elasticity and Anelasticity of Metals*, Univ. Chicago Press, Chicago, Ill., 1948.
4. Tanaka, T., and Y. Ishida, *J. Phys. Soc. Japan*, **15**, 261 (1960).
5. Sinnott, K. M., *SPE Trans.*, **2**, 65 (1962); L. T. Muus, G. McCrum, and F. C. McGrew, *SPE J.*, **15**, 368 (1959).
6. Young, J. M., Ph.D. Thesis, Univ. of Notre Dame; summarized by J. M. Young and A. A. Petraskas, *Bull. Am. Phys. Soc.*, **1**, 122 (1956).
7. Willbourn, A. H., *Trans. Faraday Soc.*, **54**, 717 (1958).
8. Myushima, S., *Structure of Molecules*, Academic Press, New York, 1954.
9. Powell, R. E., and H. Eyring, *Advances in Colloid Science*, Interscience, New York, 1942.
10. Kauzmann, W., *Quantum Chemistry*, Academic Press, New York, 1957.
11. *Advances in Spectroscopy*, Vol. I, H. W. Thompson, Ed., Interscience, New York, 1959.
12. Zbinden, R., personal communication of work to be published in book form; method of calculation summarized in *J. Mol. Spectroscopy*, **3**, 654 (1959).
13. Lin, T. P., and J. L. Koenig, *J. Mol. Spectroscopy*, **9**, 228, 243 (1962).
14. Lyons, W. J., *J. Appl. Phys.*, **29**, 1429 (1958).

Résumé

On a effectué des mesures d'amortissement mécanique dynamique à des élongations suffisamment grandes pour causer un comportement viscoélastique non-linéaire. On a déterminé sur des fibres de polyéthylène, de polypropylène de nylon 66, de nylon 4 et d'un polymère expérimental sept pics d'amortissement pour chaque polymère situé dans un domaine de température variant de 120 à 350°K. Des pics sont espacés de manière uniforme et situés à des intervalles de 30–35°K alors qu'on observe usuellement des intervalles inégaux de l'ordre de 100–150°K. Dans chacun des cas étudiés, les pics d'amortissement étaient situés à des températures inférieures à la température de transition vitreuse. Les températures auxquelles se produisaient ces pics d'amortissement ne dépendent ni de la cristallinité, ni du degré d'orientation des polymères, et on a interprété les résultats en se basant sur la structure moléculaire des polymères étudiés. Ces résultats s'expliquent seulement si l'on admet un mécanisme unique commun pour les polymères étudiés. Il s'agirait d'une diffusion de segments de la chaîne polymérique suivant un processus quantifié. Afin de justifier l'espacement régulier des pics d'amortissement, il est nécessaire de penser que l'étape limitative du processus d'amortissement est le retour d'un segment déplacé à sa position d'équilibre. Des calculs effectués à partir des données expérimentales montrent que les pics situés à des températures plus élevées, proviennent de la diffusion de segments moléculaires déplacés qui doivent traverser des lumières de potentiel plus élevées et être excités à un plus haut état énergétique pour traverser ces lumières. Tanaka et Ishida ont déjà utilisé cette interprétation lorsqu'ils ont attribué les pics d'amortissement β des polymères à des vibrations moléculaires.

Zusammenfassung

Messungen des dynamisch-mechanischen Verlustes wurden an Fasern bei grosser Zugspannung, die zu nichtlinearem viskoelastischen Verhalten führte, durchgeführt. Messungen an Fasern aus Polyäthylen, Polypropylen, Nylon 66, Nylon-4 und einem Versuchspolymeren führten im Temperaturbereich von 120–130°K bei jeder Probe zu sieben Energieverlustmaxima. Die Maxima waren in Intervallen von 30–35°K gleichmässig über den Temperaturbereich verteilt und nicht in ungleichmässigen Intervallen von etwa 100–150°K wie sie normalerweise unter den Bedingungen des linearen viskoelastischen Verhaltens beobachtet werden. In allen Fällen traten die gleichmässig verteilten Maxima nur bei Temperaturen unterhalb der Glasumwandlungstemperatur auf. Die Temperaturen der Energieverlustmaxima waren praktisch unabhängig von Kristallinität und Molekülorientierung und wurden anhand der Molekülstruktur interpretiert. Die Ergebnisse liessen sich nur durch einen einzigen, für alle Polymeren gemeinsamen Mechanismus erklären, und zwar durch eine gequantelte Diffusionsbewegung von Molekülkettensegmenten. Zur Erklärung der konstanten Temperaturabstände zwischen den Maxima einer gegebenen Probe musste eine Rückkehr eines vorgelagerten Segments zum Gleichgewicht als geschwindigkeitsbestimmender Schritt angenommen werden. Rechnungen auf Grund der Versuchsdaten zeigen, dass Maxima bei höheren Temperaturen durch verlagerte Molekülsegmente bedingt sind, die höhere potentielle Energiebarrieren zu überwinden haben und daher zu höheren Skelettschwingungsenergien angeregt werden müssen. Eine ähnliche Interpretierung wurde schon von Tanaka und Ishide gegeben, welche die Molekülschwingungen mit den wohlbekannten β -Verlustmaxima bei Polymeren in Verbindung gebracht haben.

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