

The Dynamic Mechanical Properties of Nylons

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INTRODUCTION

In an article by Schmieder and Wolf¹ mechanical loss data are presented as a function of temperature for a number of nylons. Somewhat similar data have been reported by Woodward, Sauer, Deeley, and Kline.^{2,3} All members of the series of nylons investigated by these authors showed four dispersion regions over the temperature range from 80 to 530°K., with the exception of a result observed for completely dried sample.³

The mechanisms advanced by Schmieder and Wolf to account for the three peaks occurring at about 170°K., 250°K., and 350°K. essentially involve cooperative movement of either unstressed or stressed segments of polymer chains in the amorphous regions. Other tentative interpretations were proposed by Woodward and his co-workers: the loss peak occurring at about 250°K. is attributed to segmental motion involving amide groups in the amorphous regions which are not hydrogen-bonded to other amide groups, and the loss peak occurring at about 350°K. is considered a probable result of the breaking of hydrogen bonds in the amorphous parts.

To investigate this problem more fully, the dynamic mechanical properties of a number of nylons and its closely related family of polymers have been studied. All measurements of elastic modulus and damping factor herein reported were made by a vibrating reed method.

EXPERIMENTAL

Samples

Table I lists the complete series of polymers. The polymers were melted at temperatures below their decomposition points, extruded through a small hole into water, and spun into a monofilament. All samples were undrawn monofilaments with no preferred molecular orientation. Samples were dried *in vacuo* over P₂O₅ at room temperature for a

month before measurement. Density was measured at 25°C. by the flotation method. The solvents employed were mixtures of toluene and carbon tetrachloride.

TABLE I
Polymer Series

Polymer (repeating unit)	Density, g./cc.
—NH(CH ₂) ₃ CO—	1.2479
—NH(CH ₂) ₆ CO—	1.1573
—NH(CH ₂) ₆ CO—	1.0948
—NH(CH ₂) ₇ CO—	1.0687
—NH(CH ₂) ₈ CO—	1.0518
—NH(CH ₂) ₉ CO—	1.0316
—NH(CH ₂) ₁₀ CO—	1.0255
—NH(CH ₂) ₄ NHCO(CH ₂) ₇ CO—	1.0973
—NH(CH ₂) ₆ NHCO(CH ₂) ₇ CO—	1.0762
—NH(CH ₂) ₇ NHCO(CH ₂) ₇ CO—	1.0598
—NH(CH ₂) ₈ NHCO(CH ₂) ₇ CO—	1.0578
—NH(CH ₂) ₁₀ NHCO(CH ₂) ₇ CO—	1.0443
—NH(CH ₂) ₆ NHCO(CH ₂) ₄ CO—	1.1330
—NH(CH ₂) ₇ NHCO(CH ₂) ₅ CO—	1.0849
—NH(CH ₂) ₈ NHCO(CH ₂) ₆ CO—	1.0902
—NH(CH ₂) ₉ NHCO(CH ₂) ₇ CO—	1.0425
—NH(CH ₂) ₁₀ NHCO(CH ₂) ₈ CO—	1.0323
—NH(CH ₂) ₄ NHCO(CH ₂) ₈ CO—	1.1003
—O(CH ₂) ₄ OCO(CH ₂) ₈ CO—	—
—NHCONH(CH ₂) ₆ —	1.0613
—(CH ₂)—	0.9424

Method

The vibrating reed method was used. The apparatus and calculating procedure were the same as those employed in a previous study.⁴ A small reed specimen was sinusoidally excited at the clamped end. The frequency of resonance f and the band width for the forced vibration of the reed Δf were observed. The mechanical loss is then given by the ratio of Δf to f , and the dynamic modulus E is obtained to a first-order approximation from the frequency by the relation:

$$E = \rho(16\pi^2/a_0^4r^2) l^4 f_0^2$$

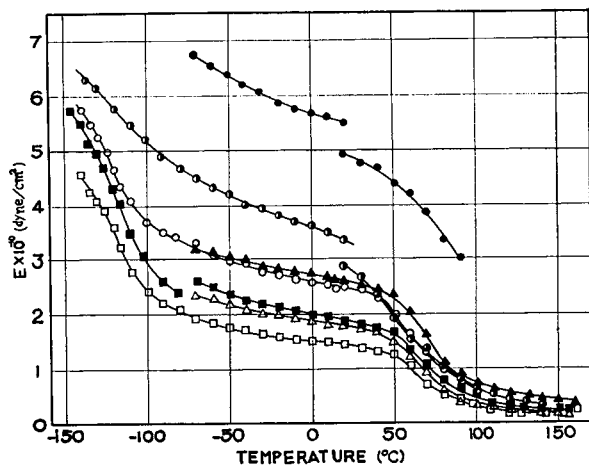


Fig. 1. Elastic modulus vs. temperature for ω -amino acid polymers: (●) nylon 4; (◐) nylon 6; (○) nylon 7; (▲) nylon 8; (△) nylon 9; (■) nylon 10; (□) nylon 11.

Here ρ is the density, l is the length of the reed, r is the radius of the cross section, and a_0 , a constant which is associated with the mode of vibration, equals 1.875 for the first mode. For measurements in vacuum, the entire apparatus was placed inside a closed vessel and surrounded by the thermal media. The temperature of the sample was controlled by a surrounding oil, electrically heated for temperatures up to 200°C., and by Dry Ice and ethanol for temperatures down to -70°C. Temperatures below -70°C. were attained by using liquid nitrogen. A copper-constantan thermocouple was used to measure the temperature.

RESULTS AND DISCUSSION

Measurement of a sample was separated into two parts. After completion of the first test of the sample from 20°C. down to -140°C., the sample was stored in a desiccator for a week and a new run was made over the temperature range increasing from 20°C. to a temperature at which sagging of the sample prevented further measurement. The effects of increasing temperature on the Young's modulus and loss angle of undrawn monofilaments of polyamides obtained from ω -amino carboxylic acids or their derivatives are shown in Figures 1-3. The results indicate the presence of at least four dispersion regions characterized by a drop in the modulus accompanied by a peak in the loss angle. These dispersions are found at about -120°C., -40°C., 90°C. and near the melting temperature. In general, the magnitude of the elastic modulus rises with an increase of the amide group concentration in the molecular chains.

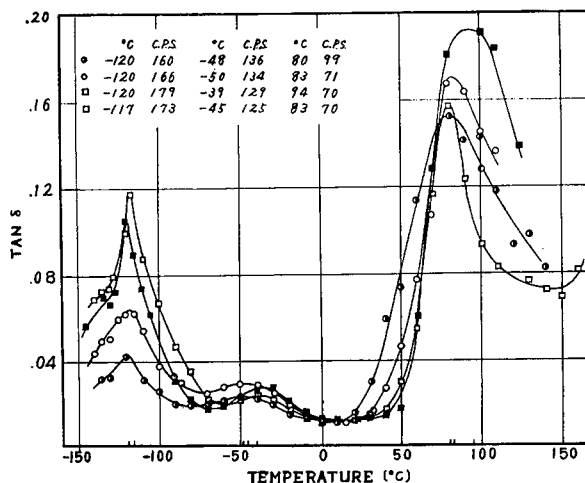


Fig. 2. $\tan \delta$ vs. temperature for amino acid polymers: (◐) nylon 6; (○) nylon 7; (■) nylon 10; (□) nylon 11.

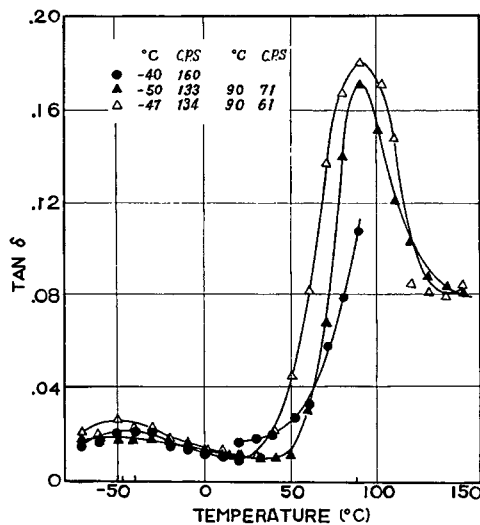


Fig. 3. $\tan \delta$ vs. temperature for amino acid polymers: (●) nylon 4; (▲) nylon 8; (△) nylon 9.

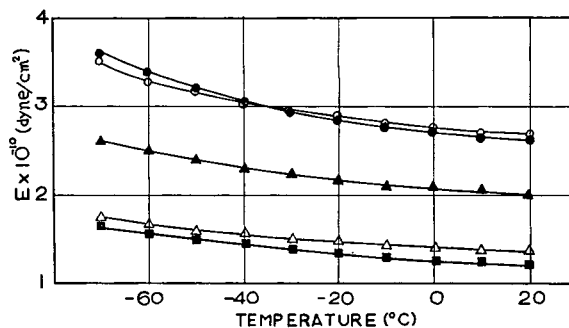


Fig. 4. Elastic modulus vs. temperature in the β -dispersion region for nylons: (●) nylon 66; (○) nylon 77; (▲) nylon 88; (△) nylon 99; (■) nylon 1010.

It is customary to label the different dispersion regions as α , β , γ , etc., descending from higher temperature. It is believed that the α peak reflects the onset of chain mobility accompanying the crystalline melting process, and there seems to be little doubt that the α' peak occurring at about 90°C. reflects the onset of motion of large chain parts caused by the breaking of intermolecular bridging in the amorphous regions. However, the experimental data concerning the molecular mechanism of the β dispersion observed at about -40°C. are not so extensive as that of the α' dispersion. It was, therefore, one of the major objects of this work to obtain more dispersion, and a major part of the experiments were concentrated upon this point.

A series of tests similar to those described above was also made in the β dispersion temperature range on a series of polyamides which were prepared from dicarboxylic acids and diamines. The results are shown in Figures 4-7. In Figure 8 the areas under the β dispersion loss peaks for the above series of specimens are plotted against the number of amide groups per 100 chain atoms. There is rather good correlation of the areas with the density of the amide groups for the series prepared from dicarboxylic acids and diamines, but a poorer one for a series obtained from ω -aminocarboxylic acids. However, according to these experiments the areas under the β dispersion peak obtained from the results of the same experiments on different samples of the same polymer material are, in general, not easily reproducible. As already pointed out by Woodward and his co-workers,^{2,3} the magnitude of the loss factor in the α' and β dispersion region is sensitive to the absorbed water content. Therefore, the discrepancy may be due to an undetectable difference in the content of the combined residual water. More detailed and precise experiments would be required to confirm the correlation between the β dispersion and the density of amide groups in the molecular chain.

To investigate more fully the effects of the molecular mechanisms on the β dispersion, the dynamic properties of a closely related family of polymers were measured. The effect of the polar groups in the polyamide on the β dispersion may be specifically explored by comparing polyesters and polyamides of the same concentration of polar groups per unit chain length. The structural formulas of polytetramethylene sebacate and polytetramethylene sebacamide appear in Table I, in which the -NH- groups of the amide group has been replaced by the -O-. In the polyamides

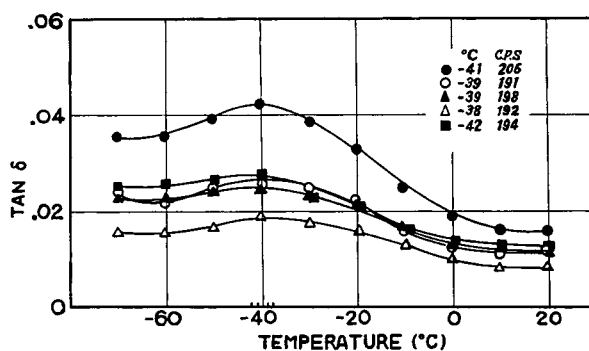


Fig. 5. $\text{Tan } \delta$ vs. temperature in the β -dispersion region for nylons: (●) nylon 66; (○) nylon 77; (▲) nylon 88; (△) nylon 99; (■) nylon 1010.

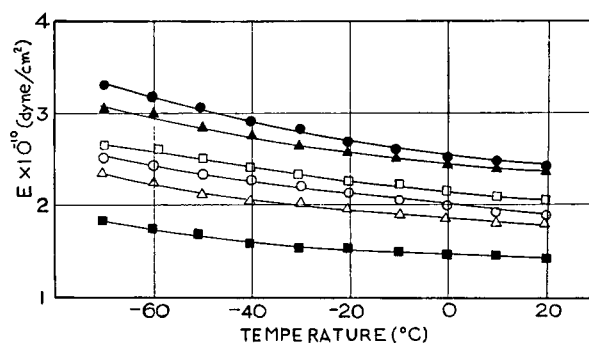


Fig. 6. Elastic modulus vs. temperature in the β -dispersion region for nylons: (●) nylon 49; (○) nylon 69; (▲) nylon 79; (△) nylon 89; (■) nylon 99; (□) nylon 109.

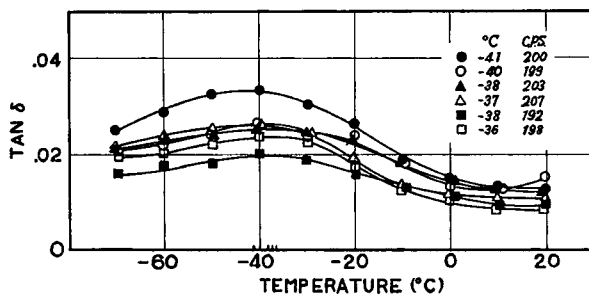


Fig. 7. $\text{Tan } \delta$ vs. temperature in the β -dispersion region for nylons: (●) nylon 49; (○) nylon 69; (▲) nylon 79; (△) nylon 89; (■) nylon 99; (□) nylon 109.

probably only few of the amide groups may be free from hydrogen bonding, whereas in the polyesters the corresponding substituent is an ester link and its thermal motion is constrained only by the dipole-dipole interaction from the adjacent polar groups. The loss angles of both polymers are shown in Figure 9. The curve for polyester is similar in appearance to that of the polyamide, but some interesting differences are observed in the γ - and β -dispersion regions. In the lowest temperature

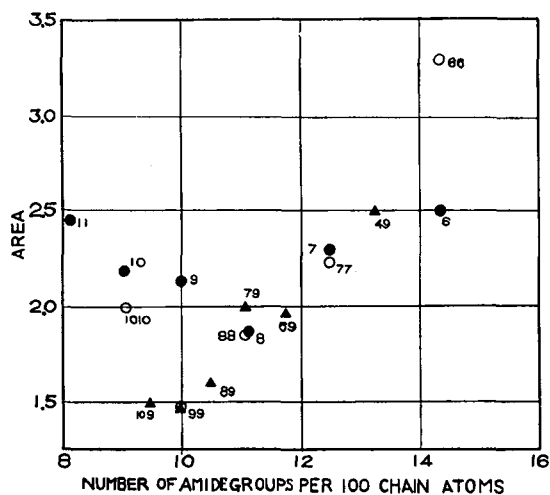


Fig. 8. Plot of the area under the β -dispersion peak against the number of amide groups per 100 chain atoms.

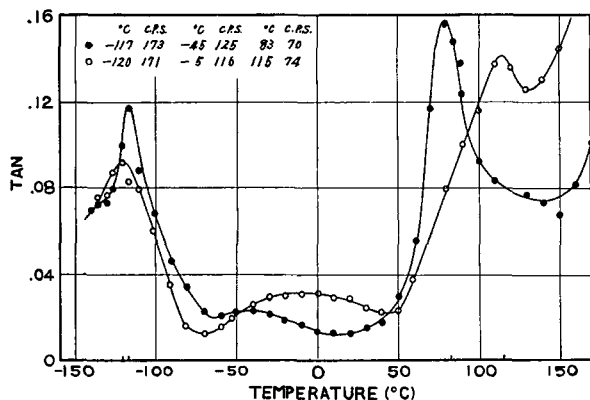


Fig. 10. Tan δ vs. temperature for (O) polynonamethylene urea and (●) nylon 11.

region where the γ peak is found, the damping maximum and the area under the curve of the polyester are considerably smaller than those for the polyamide. This may be due to the higher degree of crystallinity in the former. In the next dispersion region, near -50°C ., a large increase in the height is shown for the polyester as contrasted to the polyamide. Yager and Baker^{5,6} have observed the dielectric properties of some linear polyesters and presented reasons for supposing that the β dispersion of the linear polyester is attributable to the onset of rotational motion of the ester groups in the molecular chains. Woodward and his co-workers proposed an interpretation that the β dispersion of the polyamide is due to segmental motion involving amide groups which are not hydrogen-bonded to other amide groups. If this hypothesis is correct, then the depression in the height of the β peak for

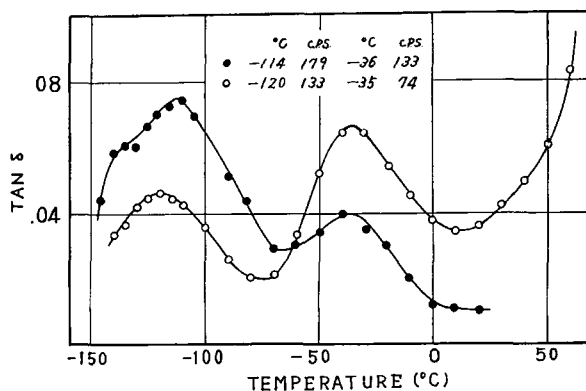


Fig. 9. Tan δ vs. temperature for (O) polytetramethylene sebacate and (●) polytetramethylene sebacamide.

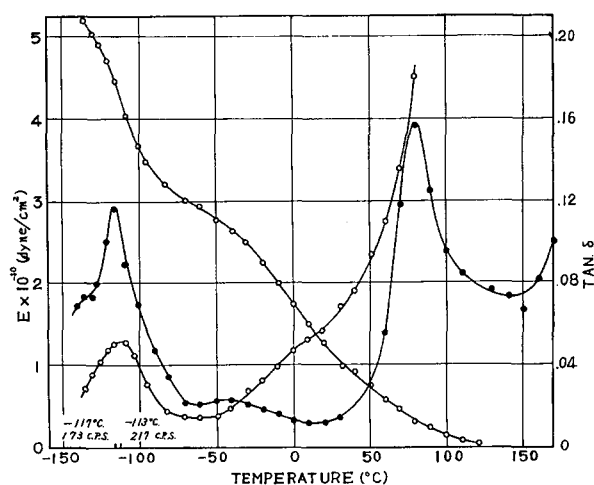


Fig. 11. Elastic modulus and tan δ vs. temperature for (O) polyethylene and (●) nylon 11.

the polyamide as compared with the polyester is the behavior one would expect from the fact that in the polyamide only a few amide groups are free from hydrogen bonding.

Further support for this hypothesis comes from a comparison of the behavior of a polyurea and a polyamide. Figure 10 shows the loss angle of polynonamethylene urea, with the curve for nylon 11 for direct comparison. The polynonamethylene urea has the same concentration of polar groups in the molecular chain as nylon 11. The cohesion of a urea group is presumably greater than that of an amide group. Therefore, the melting point and the temperatures of the dispersion which are related to the onset of the segmental motion involving the urea groups should be higher than those of the corresponding polyamide. It can be seen in Figure 10 that the behavior of polynonamethylene urea is

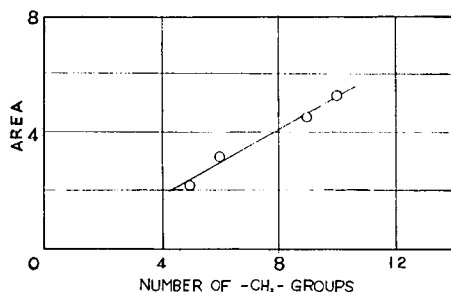


Fig. 12. Plot of the area under the γ -dispersion peak against the number of CH_2 groups in the repeating unit for amino acid polymers.

almost identical with that of the nylon 11. In the γ -dispersion region the damping peak shows approximately the same height and the same area under the loss curve. In the β and α' dispersions, while the heights of the loss peaks remain approximately unaltered, the temperatures at the loss maximum are shifted to higher values. The results given here support the above prediction, and suggest that the β dispersion of the polyamide is also related to the segmental motion involving the amide groups.

It has been proposed that the γ -peak reflects the onset of cooperative movement of $-\text{CH}_2-$ groups between amide linkages in the amorphous parts, and is considered to be the same mechanism as that contributing to an analogous peak in polyethylene (Fig. 11). As pointed out by Schmieder and Wolf, the most significant feature of this process is the way in which it is affected by changes in the length of the methylene chain between amide linkages. The height of the loss peak and the elasticity increment associated with this process increase with increasing length of the methylene chain, while the temperature at the loss maximum remains unchanged. The areas under the γ peaks are plotted against the number of methylene groups in the repeating unit for a series of the amino-acid polymers in Figure 12. The result shows that the area increases with increasing number of methylene groups.

It is interesting to note the form of the γ loss peak of the nylons (Fig. 2). It appears that another small loss peak exists on the lower temperature side. This small loss peak cannot be resolved completely, but appears as an excrescence on the side of the large γ peak. It was observed that this excrescence is obscured as the degree of crystallinity of the specimen is increased by thermal treatment. It is not yet confirmed whether this shoulder peak re-

flects the onset of thermal motion involving extremely flexible atomic groups or is due to an incidental cause.

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Synopsis

A study of the dynamic mechanical properties of a series of polyamide polymers and some related polymers has been made over a wide temperature range at about 100 cycles/sec. by means of a vibrating reed method. The character of the β dispersion of the polyamides occurring at about -40°C . is discussed in relation to the chemical structure of the polymers particularly to the amide groups. It is shown that the β dispersion of the linear condensation polymers of this type is influenced by the properties of the polar groups in the molecular chains. The data supports the view recently postulated by Woodward and his co-workers that the β peak in the polyamides is due to a segmental motion involving nonhydrogen-bonded amide groups. Finally the correlation between the γ process occurring at about -120°C . and molecular structure is discussed.

Résumé

Une étude des propriétés mécaniques dynamiques a été faite sur une série de polymères polyamides et sur certains polymères analogues sur une grande échelle de température à 100 cycles/sec. utilisant une méthode à plume vibrante. Les caractères d'une dispersion β de la polyamide à 40° sont discutés en fonction de la structure chimique des polymères, particulièrement de ceux des groupes amides. Il est montré que la β dispersion des polymères linéaires de condensation de ce type est influencée par les propriétés des groupes polaires dans la chaîne moléculaire. Les données appuient les vues récentes de Woodward et collaborateurs qui montrent que le pic β dans les polyamides est dû aux mouvements segmentaires des groupes amides non liées par un pont hydrogène. Finalement, la corrélation entre le processus γ à -120°C .; et la structure moléculaire est discuté.

Zusammenfassung

Die dynamisch-mechanischen Eigenschaften einer Reihe von Polyamidpolymeren und einiger verwandter Polymerer

wurde in einem weiten Temperaturbereich bei etwa 100 Hertz nach einer Vibrationsmethode untersucht. Das Verhalten der bei -40°C . auftretenden β -Dispersion des Polymeren wurde in seiner Beziehung zur chemischen Struktur, besonders den Amidgruppen, der Polymeren diskutiert. Es wird gezeigt, dass die β -Dispersion der linearen Kondensationspolymeren von diesem Typus von den Eigenschaften der polaren Gruppen in den Molekülketten abhängig ist. Die Ergebnisse bilden eine Stütze

für die kürzlich von Woodward und Mitarbeitern vertretene Ansicht, dass das β -Maximum bei den Polyamiden auf eine Bewegung von Kettensegmenten unter Beteiligung von wasserstoffbrückenfreien Amidgruppen zurückzuführen ist. Schliesslich wird eine Diskussion der γ Beziehung zwischen den bei etwa -120°C . ablaufenden Vorgängen und der Molekülstruktur gegeben.

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