

Stress Relaxation of Polytetrafluoroethylene in the Vicinity of Its Glass Transition Temperature at about 130°C.

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Synopsis

Measurements of compressive stress relaxation for molded polytetrafluoroethylene were carried out at different temperatures over the range 60–150°C., at 5°C. increments under a small strain (less than 0.3%). By the application of the so-called Ferry's reduction method, three master curves were obtained with good overlapping from a series of stress relaxation curves obtained at different temperatures for the same specimen. This polymer has two temperatures at which the three master curves cross and the reduction method becomes entirely inapplicable. Those two temperatures are about 80 and 100°C. It may be concluded that this polymer has two first-order transitions at about 80 and 100°C., and the states above and below these temperatures are quite different, as in the case of the transition observed for this polymer at about 20°C., which has been confirmed to be a first-order transition in crystal structure. The reduction factors a_T at different temperatures were plotted in logarithmic scale against the reciprocals of the absolute temperatures. From the slope of those three $\log a_T$ vs. $1/T$ curves, the diagrams of the apparent activation energy vs. temperature were obtained. There were two sharp maxima at about 120 and 130°C. in the diagram, where this polymer also has two irregular changes in other viscoelastic properties. It is conceivable that these changes at 120 and 130°C. are second-order transitions occurring in the amorphous region of the polymer.

Introduction

Polytetrafluoroethylene (PTFE) has various transitions. Two kinds of first-order transitions have been found. The first consists of two closely spaced room-temperature transitions at about 20 and 30°C.,¹⁻¹⁶ and the second occurs at about 330°C. which is the crystal melting point.^{7,9,17} In addition to these first-order transitions, two second-order transitions, that is, glass transitions, have been discovered at about -90°C.¹⁸⁻²⁶ and at about 130°C.^{20-25,27-30} In regard to the transition at about 130°C., however, discrepancies exist in certain publications: some authors have claimed the transition occurs in the amorphous region,^{20-22,23,30} but others have contended it occurs in the crystalline region.²³⁻²⁵

For the amorphous polymers, it is well known that the so-called Ferry's reduction method²¹ gives a useful means of constructing the relaxation time spectra over a wide range of time from the rheological data of limited time range at different temperatures.

For crystalline polymers, such as polytrifluorochloroethylene and polyethylene, Ferry's reduction method was reported to be inapplicable by Tobolsky and his co-workers.^{32,33} Nagamatsu and his co-workers,^{15,16} however, found that Ferry's reduction method could be applied to some crystalline polymers, namely, polytrifluorochloroethylene, isotactic polypropylene, nylon 6, polyethylene, and PTFE. In their studies, the whole course of the measurements were carried out under the smallest values of strain, and the specimens were carefully conditioned before each measurement. Especially with PTFE, they offered a good example of the relation between the rheological behavior and the room-temperature transition, using the method of tensile stress relaxation for ribbonlike specimens in the temperature range of 15–70°C.¹⁵

In the previous paper,³⁰ the thermal expansion study of PTFE in the vicinity of its glass transition temperature at about 130°C. has been reported. This paper deals with the viscoelastic properties of PTFE in the temperature range of 60–150°C., on the basis of the results obtained through the method of compressive stress relaxation in a way similar to that used by Nagamatsu and others, and several transitions or distinct changes observed are discussed.

Experimental Procedure

Several PTFE specimens of cylindrical shape, 15 mm. in diameter and 40 mm. in length, with different crystallinity, molded from Teflon, were used for the stress relaxation measurements. The direction of the axis of the specimen was in accordance with that of the pressure applied in molding. The molding of the blocks from the resin powder was carried out very carefully so as to minimize the void content in them. Cylindrical specimens were machined from the molded blocks and were annealed carefully to relax the stress caused by molding and machining.

Measurements of the specific gravity were made by water displacement method according to ASTM D-792, method A, with the cylindrical specimens, and by a density-gradient technique according to ASTM D-1505, with thin films obtained in machining the specimens from the molding blocks.

The crystallinity of the specimens was estimated not only from the results obtained by these specific gravity measurements, but also from the infrared absorption of the thin films.^{13,14,34} The values obtained by the method of water displacement for the cylindrical specimens assuming the void content to be zero, are given in this paper.

The apparatus for the measurement of compressive stress relaxation is shown in Figure 1. The arrangement consists of a specimen *S* of cylindrical shape (15 mm. in diameter and 40 mm. in length), a pressing rod *R*, a guider *G* for the rod, a lever *E*, counterbalances *E* and *F* for the rod and the lever, respectively. *L* is a load cell of bonded type with capacity of 10 kg. and with sensibility of 0.424 mv./kg. at 6 v. input voltage. The strain gauge *U* is of the unbonded type with capacity of ± 2.5 mm. full-

scale strain and with sensibility of 4.92 mv./mm. at 3 v. input voltage. A driving screw D pushes down the load cell L against the lever E; B is the battery supplying the potential to the load cell L or the strain gauge U. A voltmeter V determines the potential supplied to the load cell or the strain gauge; and the stress and strain, respectively, of the specimen are recorded on the instruments I and J. H is a heater and T is a temperature regulator.

Prior to each measurement at an arbitrary temperature, the specimen was set in the apparatus under no load at that temperature for about 1.5 hr. Subsequently, after the dead weight was added to the specimen in the direction of the axis by turning the driving screw D, so as to impart a strain of about 0.02 mm. (0.05%), the specimen was kept for 100 min. under the given strain at the test temperature. During that period, the stress relaxed

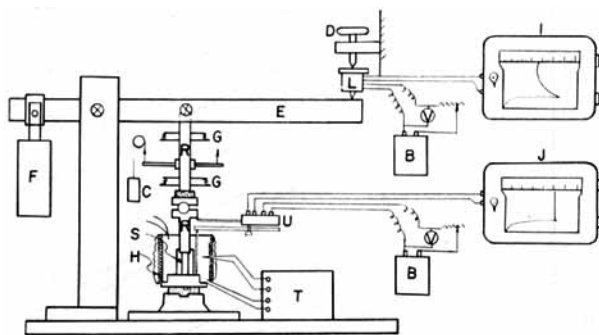


Fig. 1. Schematic diagram of the apparatus for measurement of compressive stress relaxation: (S) specimen; (R) pressing rod; (G) guides for the pressing rod; (E) lever; (C) counterbalance for the pressing rod; (F) counterbalance for the lever; (L) load cell; (U) strain gauge; (D) driving screw; (B) battery; (V) voltmeter; (I) recorder for the stress; (J) recorder for the strain; (H) heater; (T) temperature regulator.

and became almost constant. This preconditioning removed gaps or uneven contact between the both bottom surfaces of the cylindrical specimen and the pressing rod or the base; this procedure was convenient for determining the zero point of the strain required for measurement of stress relaxation.

At that state, an additional strain was given to the specimen, and the measurement was carried out as follows. The driving screw D was turned rapidly to push down the lever E through the load cell L, and the specimen S was pressed. The additional strain thus applied to the specimen, less than 0.1 mm. (0.25%), was measured by the strain gauge U and recorded electrically. The additional stress originating from the additional strain was detected by the load cell L, converted into an electrical potential, and recorded in the recorder I. After the specimen was strained, the relaxation of the stress was measured during 50 min. at an arbitrary constant temperature and under a constant strain.

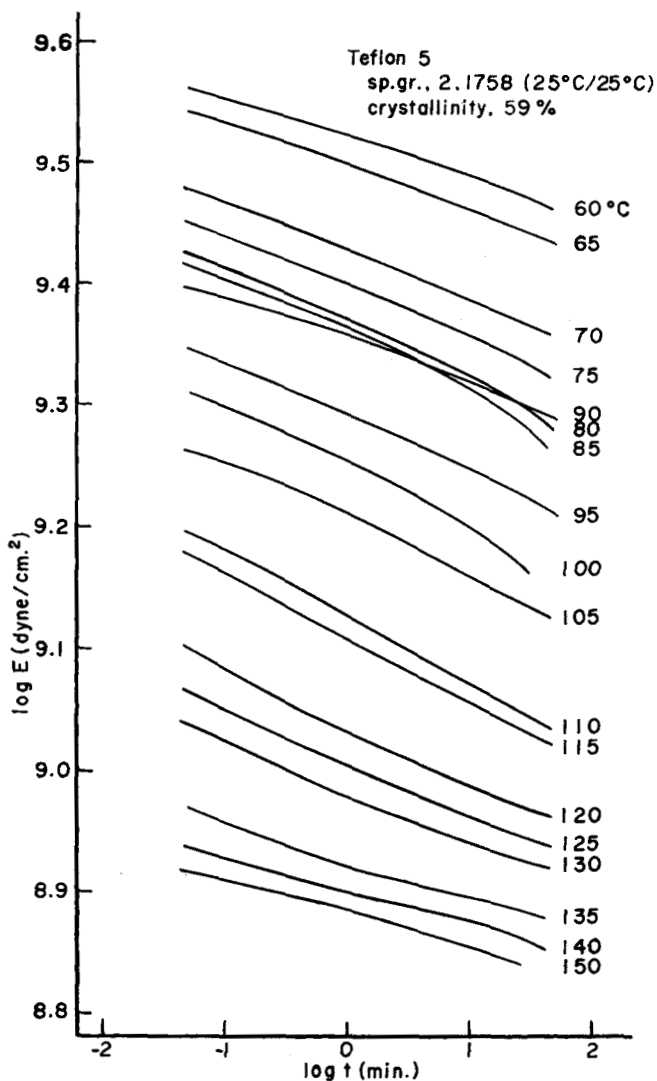


Fig. 2. Stress relaxation curves of polytetrafluoroethylene (Teflon 5) between 60 and 150°C.

After the measurement had been completed, the load was removed, and the specimen was left at room temperature for 12–24 hr. before the measurement at the next higher temperature was begun. The same specimen was used for a series of measurements at nineteen different temperatures in rising order, in the range from 60 to 150°C. at intervals of 5°C. Each measurement was carried out once or twice in 24 hr. In every measurement the total strain did not exceed 0.3%. If the strain was kept below 0.3%, the strain recovery after each measurement was almost complete, and linearity between stress and strain was obtained.

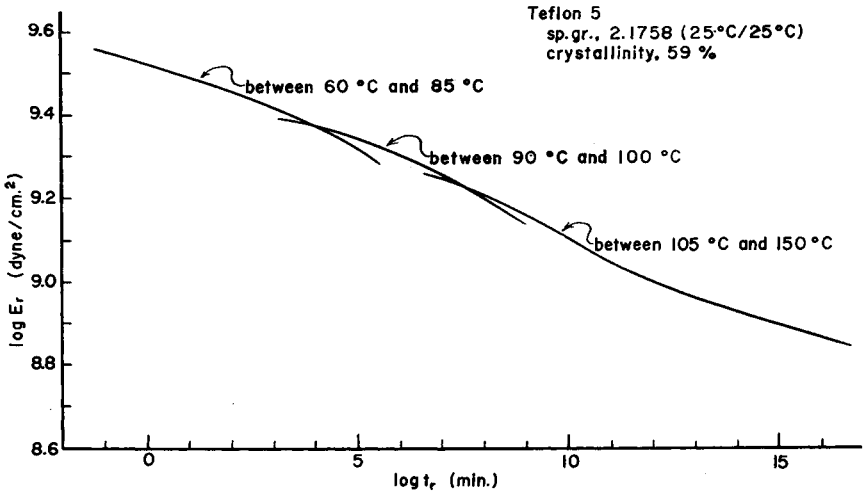


Fig. 3. Stress relaxation master curves of polytetrafluoroethylene (Teflon 5) reduced to 60°C.

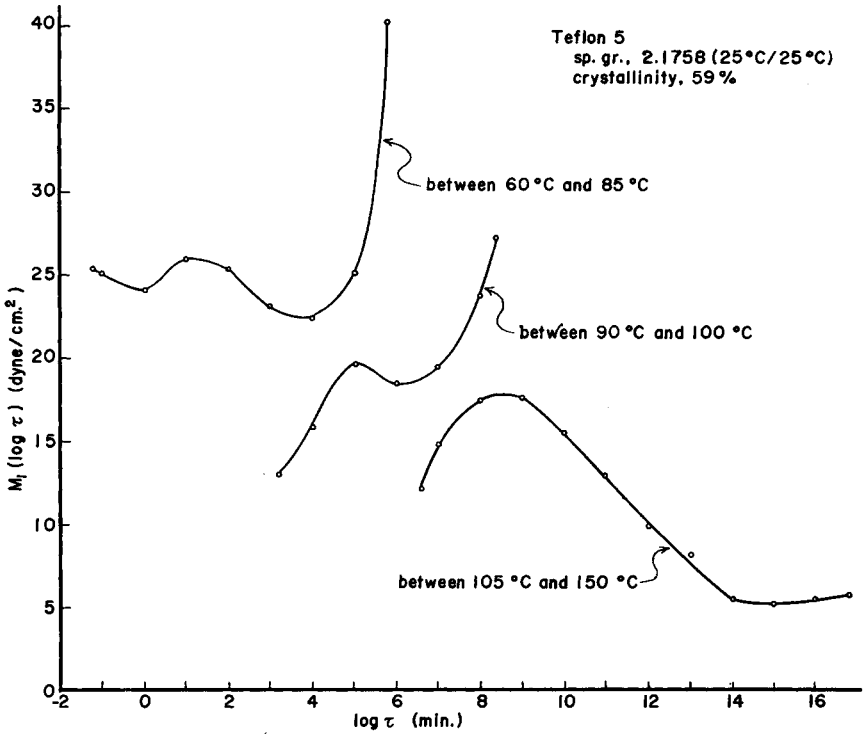


Fig. 4. Relaxation time spectra of polytetrafluoroethylene (Teflon 5). Ordinate value should be multiplied by 10^8 .

Results

Several series of stress relaxation curves were obtained, an example of which is shown in Figure 2. A series of those curves obtained at different temperatures with the same specimen was divided into three groups. As is shown in Figure 3, three master curves were then obtained with good overlapping by the application of Ferry's reduction method, which is

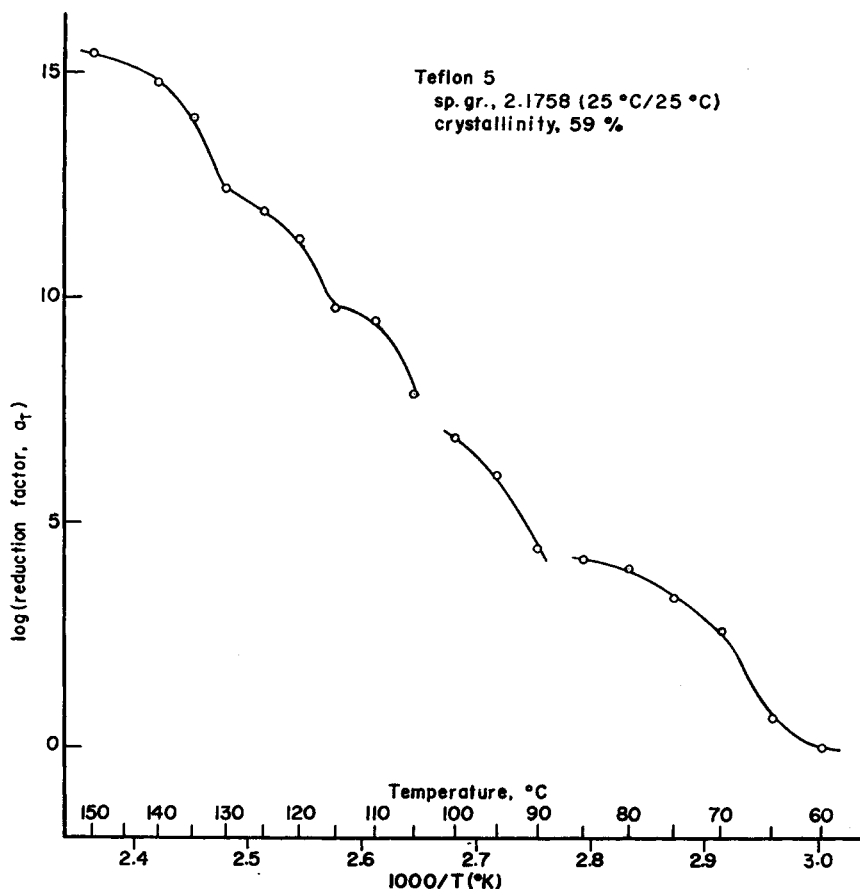


Fig. 5. Relation between Ferry's reduction factor a_T and temperature for polytetrafluoroethylene (Teflon 5).

shifting those curves along the time axis so as to overlap each other. Those three master curves correspond to the three groups of curves in Figure 2 obtained in the temperature ranges of 60–85°C., 90–100°C., and 105–150°C., respectively.

These three master curves could not be superimposed on each other by simple translation along the time axis. They crossed in two regions, namely, in the temperature range between 85 and 90°C., and between

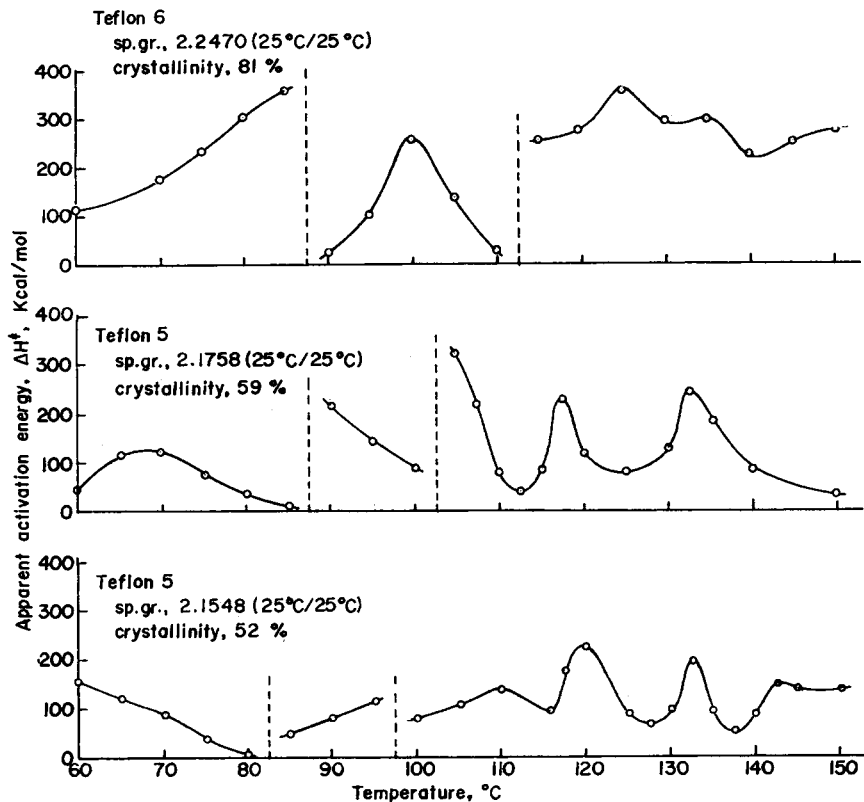


Fig. 6. Relation between the apparent activation energy ΔH^\ddagger of Ferry's reduction factor a_T and temperature in the method of stress relaxation for polytetrafluoroethylene (Teflon 5, Teflon 6).

100 and 105 $^\circ\text{C}$., where this polymer has two remarkable changes in its viscoelastic properties.

The relaxation time spectra were obtained from those three relaxation master curves, using the so-called first-order approximation method.³⁵ The spectra thus obtained from the master curves in Figure 3 are shown in Figure 4.

Figure 5 shows the reduction factors a_T at different temperatures plotted on a logarithmic scale against the reciprocals of the absolute temperatures $1/T$; three curves were obtained. From the slope of these three curves (Fig. 5) at each temperature, assuming the reduction factor a_T to be in accordance with the Arrhenius equation, the relation between the apparent activation energy and temperature was obtained for Teflon 5; this is shown in Figure 6 together with those of other samples. As is clearly seen in Figure 6, there are two sharp maxima at about 120 and 130 $^\circ\text{C}$., where this polymer has two irregular changes in its other viscoelastic properties.

Discussion

As has been mentioned above, the experimental results show that PTFE has four fairly distinct irregularities in its viscoelastic properties, namely, at about 80, 100, 120, and 130°C.

The irregularities at 120 and 130°C. appear in the form of two sharp maxima in the apparent activation energy versus temperature diagram. This type of irregularity is often seen as the second-order transitions of other polymers.^{36,37} The existence of the transition at about 130°C. for PTFE has already been found through different methods.^{20-25,27-30} It is conceivable that these two changes are second-order transitions occurring in the amorphous region, in comparison with other results for this polymer,^{20,30} which had been observed not as double changes but as a single one.

On the other hand, the two other irregularities at about 80 and 100°C. have a quite different character from those at 120 and 130°C. The stress relaxation master curve or the relaxation time spectrum for PTFE is split into three different parts above and below these two temperature regions. A similar kind of rheological irregularity was observed for this polymer at about 20°C,^{15,16} which has been confirmed to be a change in crystal structure¹⁰⁻¹⁴ and to be a first-order transition.^{6,8,9} Thus, from the rheological point of view, the irregularities at about 80 and 100°C. are believed to be first-order transitions.

According to the results obtained here, it may be concluded that two types of transitions occur at relatively closely spaced temperatures, namely, two first-order transitions at about 80 and 100°C., and two second-order transitions at about 120 and 130°C. Each of these multiple transitions may be observed at fairly different temperatures owing to the time scale of observations, e.g., the frequency in dynamic, electrical, or nuclear magnetic resonance measurements, or the speed of rising temperature in thermal measurements. Moreover, some of the transitions may appear vaguely or disappear, depending on the observation methods, the accuracy of the measurements, or the nature of the specimen (crystallinity or anisotropy).

As has been mentioned, there are two opposite explanations of the transition at about 130°C. for PTFE: some authors believe it to occur in the amorphous region,^{20-22,28,30} but others attribute it to a change in the crystalline region.²³⁻²⁵ The discrepancy may be attributed to the fact that the two different types of multiple transitions of PTFE might be confused, because they exist in the relatively narrow range of temperature.

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Résumé

On a effectué des mesures de relaxation de la tension en compression sur des échantillons de polytétrafluoroéthylène moulés. Les mesures ont été faites dans un domaine de température variant de 60 à 150°C, la température étant élevée par incrément de 5°C, la déformation restait petite (moins de 0.3%). En appliquant la méthode de réduction dite de Ferry, on a obtenu trois courbes maîtresses, chaque courbe étant construite à partir de courbes de relaxation de la tension obtenues à diverses températures par un même échantillon. Ce polymère possède deux températures auxquelles les trois courbes maîtresses se recoupent ce qui entraîne la caducité de la méthode de réduction. On en conclut que le polymère possède deux températures de transition de premier ordre aux environs de 80 et de 100°C, l'état physique étant très différent de part et d'autre de ces températures. On a rencontré une transition analogue pour ce polymère aux environs de 20°C et on a pu montrer qu'il s'agissait dans ce cas d'une transition de premier ordre de la structure cristalline. On a porté en graphique le logarithme du facteur de réduction en fonction de l'inverse de la température absolue et on en a tiré l'énergie d'activation apparente du phénomène. On a noté surtout deux maxima aigus vers 120 et 130°C,

températures à laquelle changent les propriétés viscoélastiques. Il serait également possible que les deux transitions soient des transitions de second ordre amorphe se produisant dans la fraction amorphe.

Zusammenfassung

Die Messung der Kompressions-Spannungsrelaxation wurde an Spritzguss-Polytetrafluoroäthylen bei verschiedenen Temperaturen im Bereich zwischen 60 und 150°C bei steigender Temperatur in Abständen von 5°, bei kleiner Verformung (weniger als 0,3%) ausgeführt. Durch Anwendung der sogenannten Reduktionsmethode von Ferry wurden aus einer Reihe von bei verschiedener Temperatur an der gleichen Probe erhaltenen Spannungs-Relaxationskurven drei sich gut überdeckende Masterkurven erhalten. Das Polymere besitzt zwei Temperaturen, bei welchen sich die drei Masterkurven kreuzen und die Reduktionsmethode nicht mehr angewendet werden konnte. Diese beiden Temperaturen lagen bei etwa 80 und 100°C. Man kann daraus schliessen, dass das Polymere bei etwa 80 und 100°C zwei Umwandlungen erster Art besitzt und dass die Zustände oberhalb und unterhalb dieser Temperaturen vollständig verschieden sind, so wie es bei der beidiesem Polymeren bei etwa 20°C beobachteten Umwandlung der Fall ist, welche als Kristallstrukturumwandlung erster Art bestätigt wurde. Die Reduktionsfaktoren a_T bei verschiedenen Temperaturen wurden logarithmisch gegen den Reziprokwert der absoluten Temperature aufgetragen. Aus der Neigung der drei $\log a_T - 1/T$ - Kurven wurden Diagramme für die scheinbare Aktivierungsenergie gegen die Temperatur erhalten und es traten zwei scharfe Maxima bei etwa 120–130°C auf, wo das Polymere zwei unregelmässige Änderungen anderer viskoelastischer Eigenschaften besitzt. Man kann annehmen, dass es sich dabei um zwei Umwandlungen zweiter Art im amorphen Bereich handelt.

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