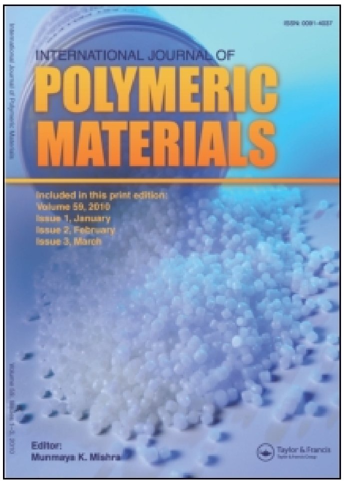

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I. A. Tumanova[a]; O. B. Semenov[a]; Yu. G. Yanovsky[a]
[a] Institute of Petrochemical Synthesis Leninsky, Moscow GSP-1, USSR

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Evaluation of Branching in Polyvinyltrimethylsilane on the Basis of Analysis of the Temperature Dependence of Mechanical Losses

I. A. TUMANOVA, O. B. SEMENOV, and YU. G. YANOVSKY

Institute of Petrochemical Synthesis Leninsky Prospekt 29 Moscow GSP-1, 117912, USSR

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The relaxation transitions in polyvinyltrimethylsilane in the region of 60, 120, and 180°C have been studied by means of the dynamic method. We have investigated the effect of branching on the magnitude and position of the maximum of mechanical losses.

Polyvinyltrimethylsilane (PVTMS) is the first representative of a new class of silicon-hydrocarbon polymers—polyvinyltriorganosilanes.[1–6] It is known[7–9] that the polymerization of vinyltrimethylsilane (VTMS) initiated by n-butyl-lithium is complicated by the occurrence of secondary reactions which give rise to branching in macromolecules. With high degrees of conversion there is formed a highly branched polymer, while the samples produced at low conversions remain practically linear. Branching has a substantial effect on the physico-mechanical properties of polymers,[10–17] and that is why the evaluation of branching is extremely important. The generally adopted method of calculation of the degree of branching **m** in polymers is the method proposed by Zimm and Kilb,[18] according to which **m** is determined from the amount of deviation of the dependence of log $\eta]$ on log [M] from the straight line.

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In the present work, an attempt is made to establish the relation between dissipation losses and branching in PVTMS on the basis of the analysis of the relaxation transitions determined by dynamic experiments (involving small-amplitude cyclic deformations).

Samples of PVTMS were synthesized in glass ampoules without mixing according to the procedure described in the literature.[7–8] The conditions of synthesis and the characteristics of the materials obtained are given in Table I. The average number of branches—the degree of branching—per one macromolecule of PVTMS (**m**) was calculated on the assumption of a three functional branching in accordance with the method described in the literature[18] and available data.[7]

TABLE I

Conditions of synthesis and characteristics of PVTMS samples

No.	T, °C	Time, hours	$M_W \times 10^5$	Number of branches, **m**	Yield, % by weight	T_g	T_α
1	25	0.5	0.36	0	7.0	170	—
2	40	4	2.00	0	19.5	170	—
3	40	6	3.34	0	15.6	170	—
4	40	22	6.18	0.80	26.2	170	120
5	40	55	8.80	2.60	37.0	175	145
6	50	6.0	4.00	0.5	18.4	170	—
7	50	100	10.24	4.40	55.8	187	150
8	60	20	7.05	1.70	41.7	170	120
9	60	50	9.15	3.60	61.4	175	135
10	60	100	10.18	5.40	71.5	180	145
11	80	2	4.57	0.7	23.3	173	—
12	80	9	7.34	1.80	43.6	180	130
13	80	22	8.43	2.5	55.5	185	150
14	65		12.50	3.1	32.4	195	150

Note: sample No. 14 was obtained in a metallic reactor with mixing.

The molecular-mass distribution (MMD) of the materials under study was investigated by the fractionation, gel-chromatographic and sedimentation techniques.[9]

The dynamic characteristics were measured by means of an automatic torsional pendulum of the model ATM-1[19] and the dynamic moduli of elasticity in shear, G', and the loss tangent tan δ were calculated. The experiments were conducted at a vibration frequency of 1 Hz in the temperature range 20–220°C. The samples were used in the form of films about 1 mm thick, which were obtained from a 10% solution of PVTMS in carbon tetrachloride and dried to constant weight in vacuum at 50°C. The density was also measured.

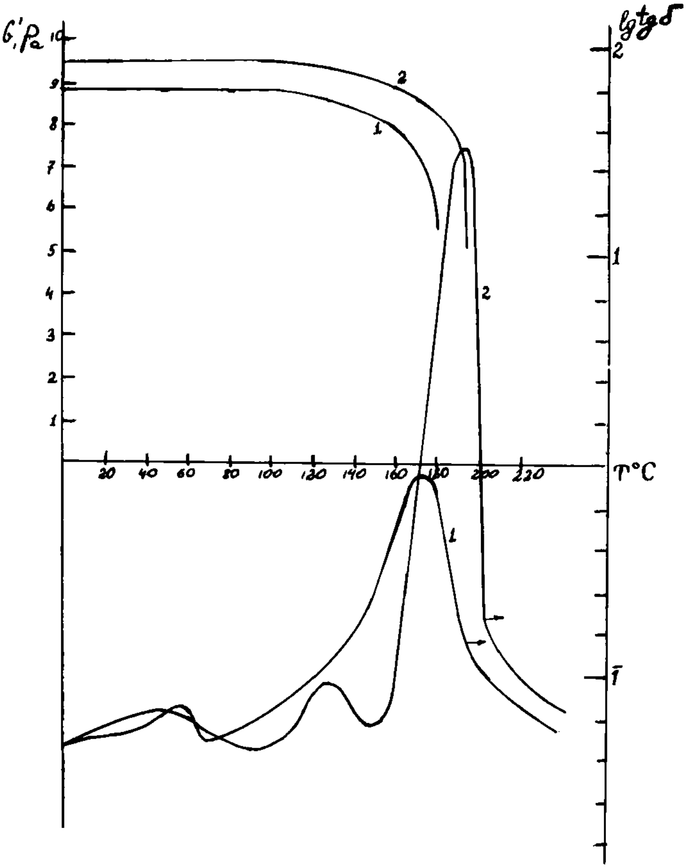

FIGURE 1 Temperature dependences of the modulus of elasticity and the loss tangent for samples of polyvinyltrimethylsilane. The curves 1 and 2 correspond to linear and branched samples, respectively.

Figure 1 presents typical results of dynamic tests for samples of PVTMS of the molecular masses 7.34×10^5 and 0.36×10^5 (Table I, Nos. 1 and 12) in the form of the curve of G' and the loss tangent tan δ versus temperature. It is seen that in the temperature range of 20–220°C there are observed three maxima of the loss tangent in the region of 60, 130, and 180°C for a highly branched polymer (No. 12) and only two maxima at 60 and 170°C for a sample of the expected linear structure. On the curve showing the variation of the density ρ as a function of temperature (Figure 2, curve 1) there are observed two kinks for sample No. 12 at the temperatures 60, 120, and 180°C. Analogous dependences have been obtained for samples of PVTMS of other molecular masses and structure. High values of the elastic modulus in the

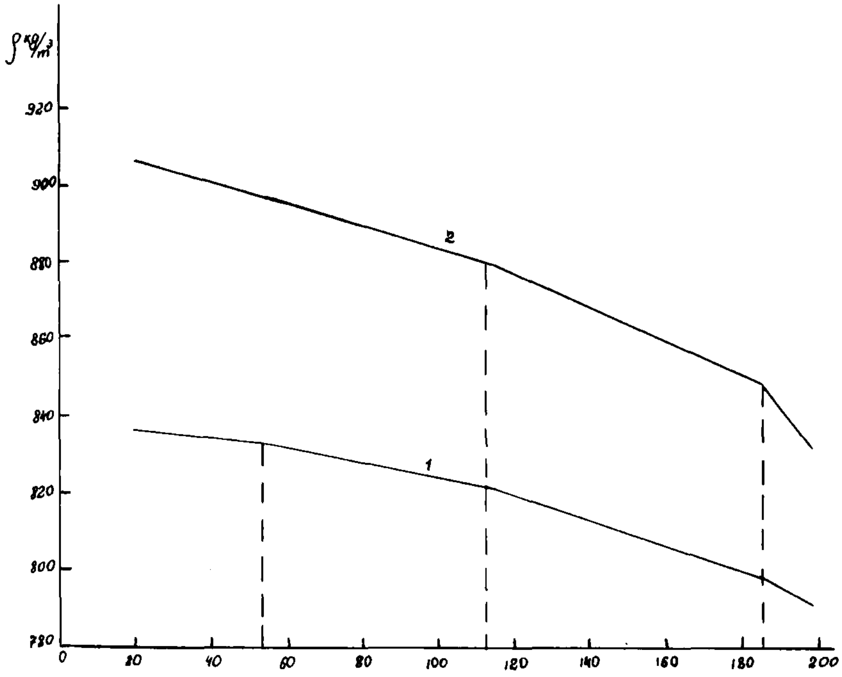

FIGURE 2 Temperature dependence of the density of PVTMS: curve 1 corresponds to the first cycle of heating; curve 2 = repeated heating.

range of 20–180°C (G' amounting to about 10^9 Pa) are evidence that in this temperature range the polymer is in the glassy state.

As has been shown by X-ray structure analysis, samples of PVTMS have an amorphous structure with regions of ordered macromolecules: on the X-ray photographs there are observed two rings with $\alpha = 5.6$ and 9.7 Å and a strong gaseous background. This indicates that the maxima on the curves of tan δ versus temperature are due to the relaxational nature and are associated with the variation of the mobility of the macromolecule and its separate parts.

The maximum on the curve of tan δ versus T at 180°C is due to the transition of the polymer from the glassy to the rubbery state. This is evidenced by the sharp decrease of the modulus of elasticity G' from 10^9 to about 10^5 Pa. The temperature region of the transition of PVTMS from the rubbery to the viscofluid state could not be attained in real experiments since it is above the decomposition temperature of the polymer.[3,4] The considerable variation of the slope of the curve of density versus temperature in the region of 180°C and the transition from low expansion coefficients characteristic of the glassy state to high coefficients specific to the rubbery state, just as in the case of dynamic investigations, allows one to conclude that the transition in the region of 180°C is associated with vitrification.

The maximum recorded on the curve of tan δ versus T at 60°C may be accounted for by the relaxation processes associated with the mobility of the side trimethylsilyl groups —$Si(CH_3)_3$ about the —C—Si— bonds. An indirect evidence of this is the change (decrease) of the magnitude of this maximum on the curve of tan δ versus T and the absence of a kink on the curve of ρ versus T (Figure 2, curve 2) upon repeated heating of the PVTMS sample. It may be supposed that the gradual repeated heating of the samples during dynamic investigations produces an effect analogous to annealing and contributed to the orientation of the —$Si(CH_3)_3$ groups in a certain definite direction. This creates favourable conditions for a more ordered arrangement of portions of macromolecules and, as a consequence, their denser packing. Indeed, the comparison of the density of the original PVTMS samples at 20°C with that of the samples subjected to heating at 200°C shows that the value of ρ increases, respectively, from 0.835 to 0.905 g/cm^3. The suppositions advanced are in good agreement with the results of X-ray structure analysis of unannealed and annealed PVTMS films. Thus, for example, when PVTMS samples were annealed during 24 hours at 160°C, there was observed an increase of the average size of the ordered regions in the macromolecules from 30 to 60 Å.

The relaxation transition detected in the region of 120°C is probably due to the mobility of those portions of the macromolecular chain which contain long side branches. Figure 3 shows the temperature dependences of the loss tangent for PVTMS samples which were synthesized at 60°C and which had different degrees of branching (see Table I). It is seen that for samples with a large value of **m** there is observed an increase of the intensity of the loss maximum at 120°C and their shift to the side of higher temperatures. Figure 4 is a plot of the area of the maximum of the α-transition (S_α) for PVTMS samples produced at various temperatures against the number of branches **m**. The dependence of S_α on **m** is approximated by a straight line that passes through the coordinate origin (the α-transition is practically absent and $S_\alpha = 0$ for linear macromolecules), which points to the existence of a sufficiently simple relationship between the magniture of dissipation losses and the degree of branching of the macromolecules.

It should be noted that the variation of the intensity of the maximum for samples of different degrees of branching on the curve of tan δ versus T is also observed in the region of 180°C. The dependence of the area of the maximum of mechanical losses at $T_g(S_g)$ on **m** is given in Figure 5. In this particular case, the experimental data are approximated by two curves—one for samples synthesized at 40–60°C and the others for polymers produced at 80°C. The point of intersection of the curves with the ordinate corresponds

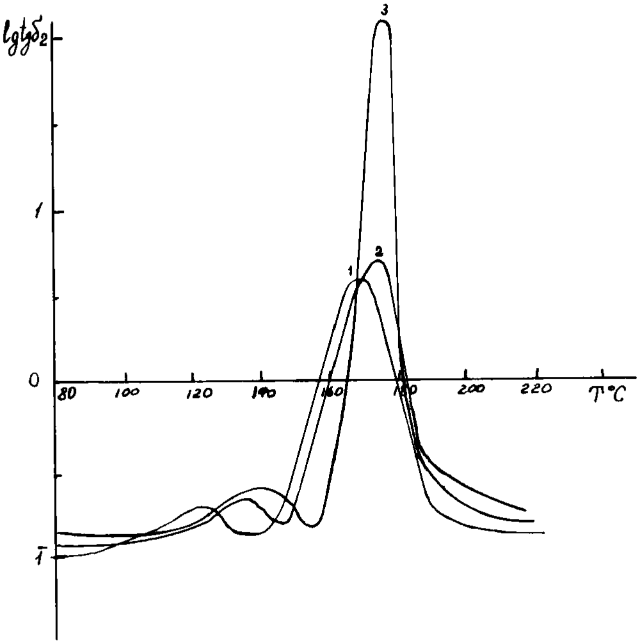

FIGURE 3 Temperature dependence of the loss tangent of PVTMS samples of different degrees of branching. The curves 1–3 correspond to the following degrees of branching, respectively: 1.0, 3.60, 5.40.

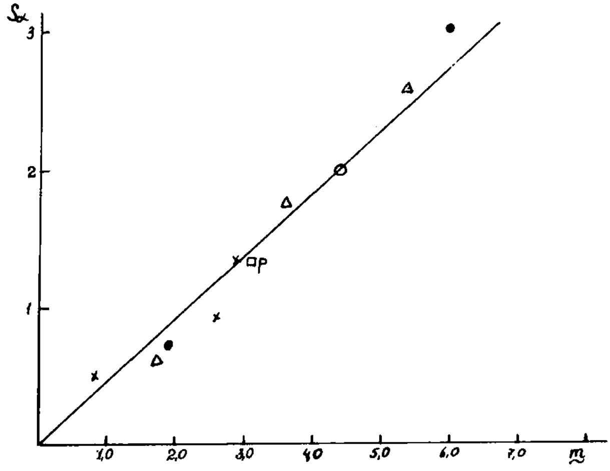

FIGURE 4 The magnitude of the area of dissipation losses in the region of the α-transition, S_α (arbitrary units) for PVTMS samples of various degrees of branching (x = samples synthesized at 40°C, ○ = at 50°C, Δ = at 60°C, ● = at 80°C, □p = samples produced in a metallic reactor).

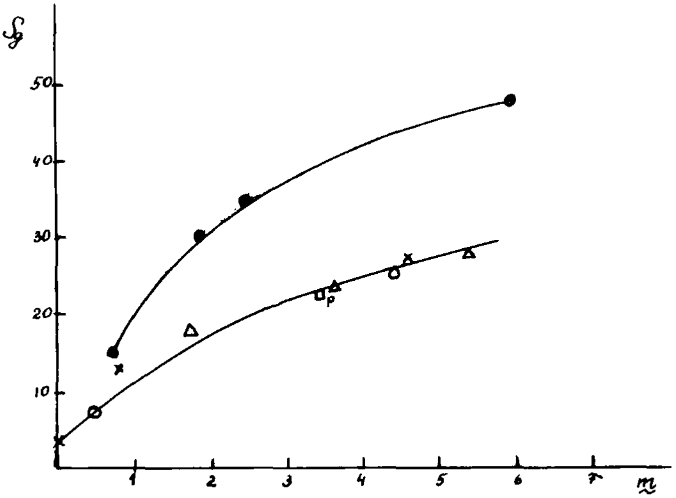

FIGURE 5 The magnitude of the area of dissipation losses in the region of transition through the glassy state, S_g (arbitrary units) for PVTMS samples of different degrees of branching (the designations are the same as in Figure 4).

to S_g for samples Nos. 2 and 3 with the suspected linear structure of macromolecules. The existence of various relationships between S_g and **m** may apparently be attributed to the effect not only of the number of branches (the quantity **m**) but also of their length, which varies depending on the conditions of polymerization of PVTMS and increases with rise of temperature, on the magnitude of dissipation losses in the region of virtification of the polymer.

Thus, the analysis of the dependences of tan δ on T for PVTMS of different degrees of branching indicates that there exists a simple relationship between the magnitude of the dissipation losses and the degree of branching of macromolecules.

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