

Effects of Physical Aging on Viscoelastic and Ultrasonic Properties of Poly[1-(trimethylsilyl)-1-propyne] Films

Akira TANAKA,* Koh-hei NITTA, Ryuichi MAEKAWA,
Toshio MASUDA, and Toshinobu HIGASHIMURA

*Department of Polymer Chemistry, Faculty of Engineering, Kyoto University,
Yoshida-honmachi, Sakyo-ku, Kyoto 606, Japan*

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ABSTRACT: Effects of physical aging and heat-treatment on the viscoelastic and ultrasonic properties of poly[1-(trimethylsilyl)-1-propyne] (designated as PTMSP) films were examined. The loss modulus and loss tangent decreased with physical aging and heat-treatment, and the attenuation coefficient increased. However the storage modulus and ultrasonic velocity little changed with heat-treatment. This indicates that no conformational change occurs in backbone carbon with physical aging and heat-treatment, but aggregation of substituents may change. Accordingly, reduction in gas-permeability with physical aging is ascribable to the change in the aggregation of substituents. Furthermore, we found that casting solvents and catalysts affect viscoelastic and ultrasonic properties of PTMSP films as well as gas-permeability.

KEY WORDS Poly[1-(trimethylsilyl)-1-propyne] / Ultrasonic Property /
Physical Aging / Gas-Permeability / Aggregation / Viscoelastic Property /

Most polymers such as poly(dimethyl siloxane) and *cis*-polyisoprene show high gas-permeability in the rubbery state and their high gas-permeability can be mainly due to their flexible backbones and resultant high free volume. Poly[1-(trimethylsilyl)-1-propyne] (designated as PTMSP) has attracted much attention as a polymer showing significantly high gas-permeability¹⁻⁴: PTMSP has a higher gas-permeability even in the glassy state than poly(dimethyl siloxane) in the rubbery state. It is well known that physical aging of some polymers below T_g affects the physical properties such as density, modulus, and the rate of enthalpy relaxation.⁵⁻¹⁰ Also in the case of PTMSP, gas-permeability is a little reduced by physical aging or heat-treatment.^{3,4}

Under non-equilibrium extra forces will make conformation of polymer molecules unusual, and sometimes lead to local ag-

gregation. Local aggregation is often frozen in the glassy state particularly for polymer molecules having rigid chains and/or high molecular weight, but it gradually disappears (or melts) by thermal agitation.

To elucidate the behavior of gas permeability, it seems to be necessary to examine the change in molecular aggregation with physical aging. For this purpose, ultrasonic measurements are useful, because ultrasonic propagation is sensitive to small scale changes in the material structure.^{11,12} In this study, we measured ultrasonic and dynamic mechanical properties of PTMSP films in the process of physical aging or heat-treatment.

We found that the solubility property of PTMSP changes with polymerization catalyst.¹ We presumed that the solubility change was due to geometric structure rather than molecular weight. To examine the effect of the

* To whom correspondence should be addressed.

geometric structure on the molecular aggregation, we used PTMSP's prepared with different catalysts.

EXPERIMENTAL

PTMSP polymers were synthesized using group 5 transition metal chlorides (TaCl_5 and NbCl_5) as catalysts.¹ Polymer synthesized with TaCl_5 , designated as PTMSP-Ta has weight average molecular weight of 8.5×10^5 , while polymer synthesized with NbCl_5 , designated as PTMSP-Nb 3.2×10^5 . PTMSP-Ta was soluble both in toluene and *n*-hexane, while PTMSP-Nb was soluble in toluene but not in *n*-hexane. This indicates that the geometric structure between PTMSP-Ta and PTMSP-Nb polymers is different.

Films of *ca.* 150 μm in thick were prepared by casting from 5 wt% of toluene and *n*-hexane solutions in the case of PTMSP-Ta, designated as Ta-tol and Ta-hex films, respectively. In the case of PTMSP-Nb, films of *ca.* 150 μm in thick were prepared by casting only from 5 wt% of toluene solution, designated as Nb-tol films. The films thus prepared were furthermore evacuated by a vacuum pump at room temperature for 3 days. More evacuation than 3 days brought no significant weight loss in the cast films: it is considered that the solvent hardly remains in the films after evacuation for 3 days. According to the X-ray diffraction,² small angle X-ray scattering (SAXS),¹³ and dynamic mechanical studies,¹⁴ PTMSP films were found to be in the amorphous state.

Dynamic mechanical properties of PTMSP films were measured at 110 Hz between room temperature and 200°C using Rheovibron Model DDV-IIc (Toyo Baldwin Co., Ltd.). Ultrasonic attenuation coefficient and velocity were measured between room temperature and 100°C. The gas-permeability coefficient was determined using a K-315-N gas-permeability apparatus (Rikaseiki Co., Japan) equipped with a MKS Baratron detector: The reservoir is separated by a piece of circular membrane (or test film) with 4 cm diameter. The downstream side is evacuated to about 0.1 mmHg, and the upstream side is provided with a permeate at 1 atm. One can measure the pressure in the downstream side as a function of time. When a steady-state condition is satisfied, one can determine the permeation coefficient from the rate of increase in pressure using Fick's law. Density of film specimens was measured using a floatation method.

RESULTS

Table I gives permeability coefficients of oxygen and nitrogen and density for Ta-tol, Ta-hex, and Nb-tol films both in as-cast and heat-treated states. In the cases of Ta-tol and Nb-tol films, the gas-permeability coefficient was considerably reduced by heat-treatment. In the case of Ta-hex films, however, reduction was very little: The gas-permeability coefficient in the as-cast state was as low as that in the heat-treated state. Density of heat-treated films was higher than that of as-cast films both for

Table I. Gas-permeability coefficient and density for Ta-tol, Ta-hex, and Nb-tol films

		Ta-tol		Ta-hex		Nb-tol	
		As-cast	Heat-treated	As-cast	Heat-treated	As-cast	Heat-treated
Gas-Permeability	O_2	5.81	1.61	1.86	1.60	5.50	2.08
Coefficient ^a	N_2	3.89	0.78	1.01	0.85	3.73	0.69
Density/ g cm^{-3}		0.9350	0.9386	0.9478	0.9491	0.9260	0.9279

^a In units of $\frac{\text{cm}^3 (\text{S.T.P.}) \text{ cm}}{\text{cm}^2 \text{ s cm Hg}} \times 10^7$.

PTMSP-Ta and PTMSP-Nb polymers.

Figure 1 shows the temperature dependencies of dynamic viscoelastic coefficients for as-cast (*i.e.*, 2-days-aged at room temperature) and aged (*i.e.*, 50-days-aged at room temperature) Ta-tol films. Storage modulus E' slightly decreased with increasing temperature. The loss modulus E'' and loss tangent $\tan \delta$ ($=E''/E'$) monotonously decreased. Thus, there was no dispersion in the entire range of temperatures measured in this work. The glass transition temperature of this polymer is above 200°C.¹³

It should be noted that we observed a large difference in E'' and $\tan \delta$ between as-cast and aged films. Those of aged films were significantly lower than those of as-cast films in the entire range of temperatures. In contrast, we observed little difference in E' between as-cast and aged films.

Figure 2 shows the effect of heat-treatment on E' , E'' , and $\tan \delta$ for Ta-tol films. Heat-treatment was carried out at 100°C for 15 hours. E'' and $\tan \delta$ decreased by heat-treatment in the entire range of temperatures. In contrast, E' did little change with heat-treatment. The effect of heat-treatment was quite similar to that of physical aging at room temperature.

In Figure 3, E' , E'' , and $\tan \delta$ measured at 50, 100, and 150°C after films were heat-treated at 100°C for a given time and plotted against heat-treatment time are shown. E' little changed with heat-treatment time. In contrast, E'' and $\tan \delta$ decreased with increasing heat-treatment time. From the initial decrease of E'' in the figure, we estimated the reduction rate k at the heat-treatment temperature of 100°C. As already demonstrated in Figure 1, E'' decreased with aging. From the initial decrease on the plot of E'' against aging period, we estimated the reduction rate k at room temperature. The reduction rate k is related to the activation energy ΔH for a concerned mechanism by the following equation.

$$k = A \exp(-\Delta H/RT) \quad (1)$$

where T is the heat-treatment temperature in K , R the gas constant, and A a positive constant. Figure 4 shows the plot of the logarithm of k against $1/T$, which includes two sets of data. One is data when heat-treatment was carried out at 100°C, and the other when aging was carried out at room temperature. For each set, three reduction rates were determined from E'' measured at 50°C, 100°C,

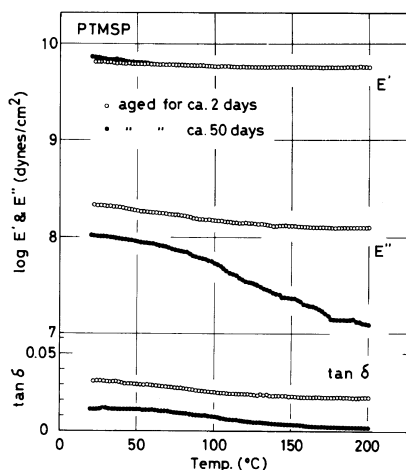


Figure 1. Effects of aging on E' , E'' , and $\tan \delta$ for Ta-tol films.

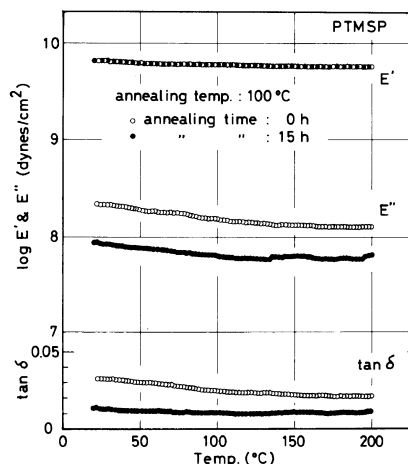


Figure 2. Effects of heat-treatment on E' , E'' , and $\tan \delta$ for Ta-tol films.

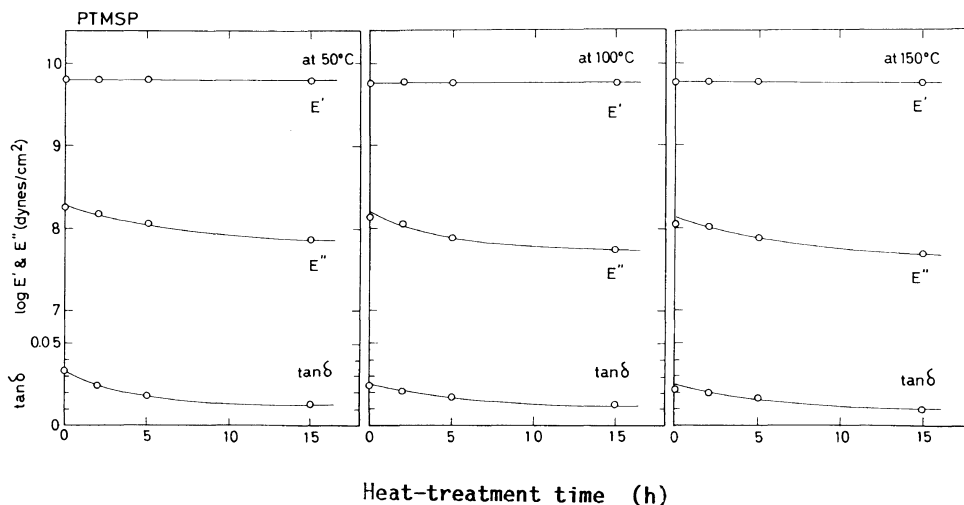


Figure 3. Variation of E' , E'' , and $\tan \delta$ at 50, 100, and 150°C with heat-treatment time for Ta-tol films.

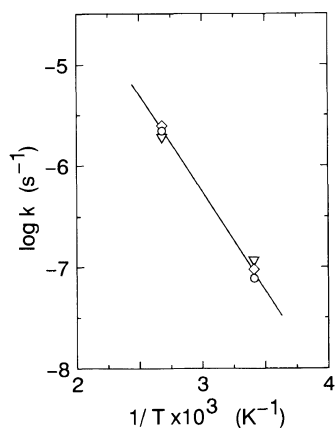


Figure 4. Arrhenius plot of k for Ta-tol films. k is the reduction rate of the dynamic loss modulus with heat-treatment and T the absolute temperature, \circ , \diamond , and ∇ denote the reduction rate of E'' measured at 50, 100, and 150°C, respectively.

and 150°C. All points lay on a straight line, whose slope gave an activation energy of *ca.* 9.0 kcal mol⁻¹. Fluctuation in the activation energy becomes ± 2 kcal mol⁻¹ at most, even if one overestimates the variation of room temperature (from 10 to 30°C). The magnitude of enthalpy indicates that structural changes occurring in the process of aging or heat-treatment are small.

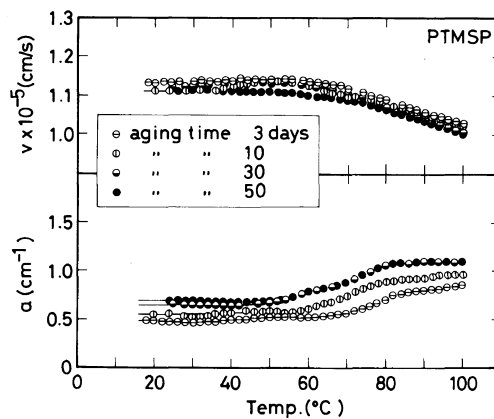


Figure 5. Variation of ultrasonic velocity and the attenuation coefficient with temperature at various aging times for Ta-tol films.

Figure 5 shows the temperature dependencies of velocity and attenuation coefficient for Ta-tol films having different aging times. The longer the aging time, the attenuation coefficient became higher in the entire range of temperatures and began to increase at lower temperatures. The temperature was 70°C for as-cast films (3-days-aged films), and 50°C for aged films (more than 30-days-aged films). However, variation of velocity with temperature as well as the magnitude of velocity was

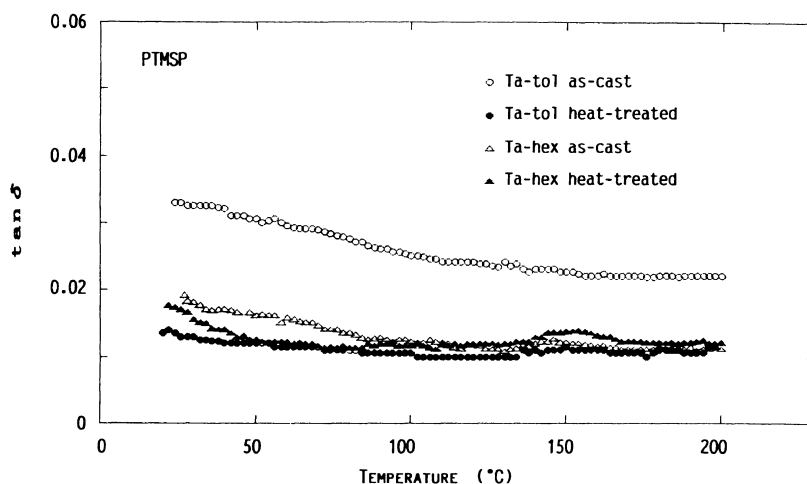


Figure 6. Effects of heat-treatment on temperature dependence curve of $\tan \delta$ compared between toluene-cast and hexane-cast films for PTMSP-Ta polymers. Heat-treatment was carried out at 100°C for 15 hours.

little dependent on aging time. We examined the effects of heat-treatment time on the attenuation coefficient and velocity. The effects of heat-treatment time on the attenuation coefficient and on velocity were quite similar to those of aging time.

In Figure 6, we compared the effect of heat-treatment on $\tan \delta$ between Ta-tol and Ta-hex films. The heat-treatment was carried out at 100°C for 15 hours. $\tan \delta$ decreased with heat-treatment in the almost entire range of temperatures both for Ta-tol and Ta-hex films. However, the decrease with heat-treatment was quite small for Ta-hex films. In the case of Ta-hex films, $\tan \delta$ in the as-cast state was as low as that in the heat-treated state.

In Figure 7, we compare the effects of heat-treatment on the attenuation coefficient between Ta-tol and Ta-hex films. In the case of Ta-hex films, the effect of heat-treatment on the attenuation coefficient was quite small; the attenuation coefficient was high even in the as-cast state, and they were comparable to those of heat-treated films.

In Figure 8, we compare the effects of heat-treatment on $\tan \delta$ between Ta-tol and Nb-tol films. The heat-treatment was also

carried out at 100°C for 15 hours. $\tan \delta$ decreased with heat-treatment in the almost entire range of temperatures both for Ta-tol and Nb-tol films. However, the decrease with heat-treatment was smaller for Nb-tol films than that for Ta-tol films.

In the case of Nb-tol films, $\tan \delta$ increased above 170°C both for as-cast and heat-treated films. This may be due to the onset of glass transition. Such different behavior for PTMSP-Nb polymers was also found in the solubility as described above: PTMSP-Ta is soluble both in toluene and *n*-hexane. However, PTMSP-Nb is insoluble in *n*-hexane, although the latter has lower molecular weight than the former. The different behavior of the two samples seems associated with the content of *cis* and *trans* conformers. In the case of the attenuation coefficient, we observed little difference between Ta-tol and Nb-tol films not only in the effect of heat-treatment but also in the temperature dependence.

The storage modulus and ultrasonic velocity little changed with heat-treatment also in the cases of Ta-hex and Nb-tol films. Both storage modulus and ultrasonic velocity were in order of Nb-tol, Ta-tol, Ta-hex films. This order is

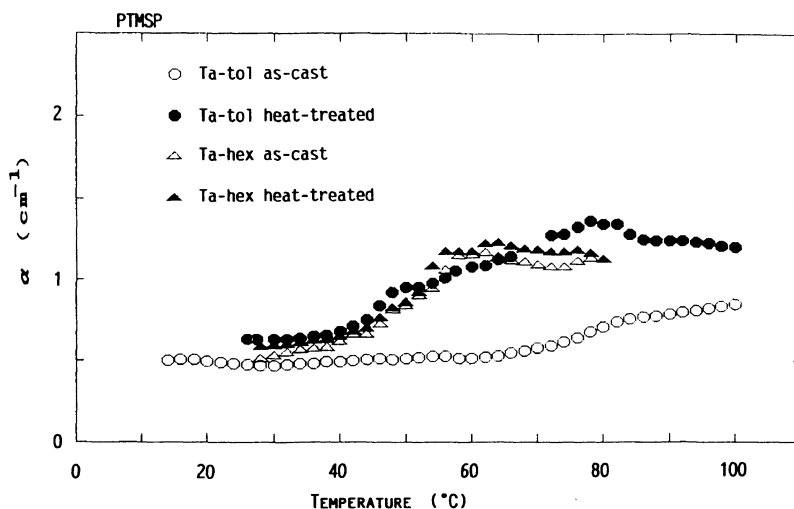


Figure 7. Effects of heat-treatment on temperature dependence curve of the attenuation coefficient compared between toluene-cast and hexane-cast films for PTMSP-Ta polymers. Heat-treatment was carried out at 100°C for 15 hours.

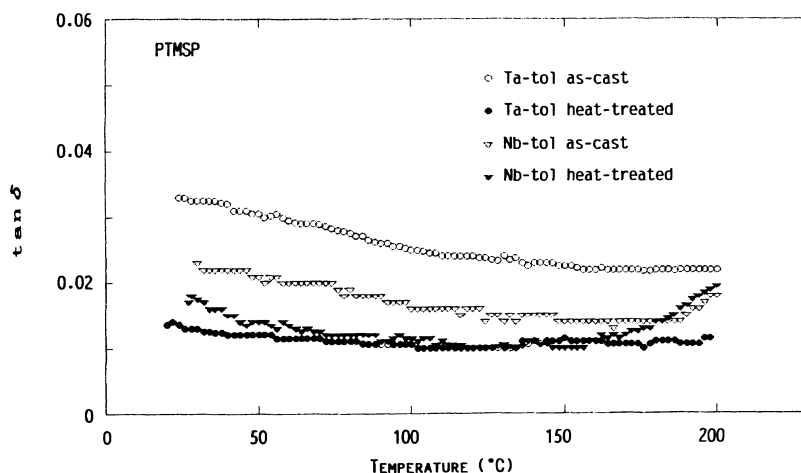


Figure 8. Effects of heat-treatment on temperature dependence curve of $\tan \delta$ compared between PTMSP-Ta and PTMSP-Nb polymers. Casting solvent was toluene. Heat-treatment was carried out at 100°C for 15 hours.

also the same as the one found on the magnitude of density (see Table I).

To summarize findings: (1) The higher the gas-permeability, the loss modulus (or $\tan \delta$) became higher and the ultrasonic attenuation coefficient lower. (2) Loss modulus (or $\tan \delta$) decreased with physical aging or heat-treat-

ment and the attenuation coefficient increased. For Ta-hex films, the effect of aging or heat-treatment was considerably small. (3) storage modulus and ultrasonic velocity little changed with physical aging or heat-treatment.

DISCUSSION

There are many processes responsible for sound attenuation in solid materials. They include viscothermal absorption, heat-conduction, coupling with thermal vibration, and sound scattering due to dislocation and boundaries.

According to previous papers,^{12,14} PTMSP films prepared in the similar condition are in the glassy state below 200°C. Therefore, one can rule out sound scattering due to dislocation and boundaries. Thermal processes will be possible mechanisms, because viscothermal motion raises $\tan \delta$, and the interaction of thermal motion with sound waves¹⁵ raises the attenuation coefficient.

However, one can also rule out thermal motion of main chains, because storage modulus and velocity little change with aging or heat-treatment. Here, the thermal motion of substituents remains as a possible mechanism. If one assumes that the thermal motion of substituents is somewhat restrained in the as-cast state and that the restraint is released in the aged or heat-treated state, one can consistently explain the results: $\tan \delta$ was higher and the attenuation coefficient lower in the as-cast state than in the heat-treated state.

Thus, change in the aggregation state of substituents causes change in $\tan \delta$ and attenuation coefficient with aging or heat-treatment. Accordingly, the change in gas-permeability is ascribable to change in the aggregation state of substituents.

We propose the following hypothesis: Substituents (*i.e.*, trimethylsilyl group) will make a special aggregation with solvent. The aggregation state will somewhat remain in dry state, because the solution is too viscous to alter the aggregation during solvent evaporation. The aggregation of substituents will continue long in existence, even though it is heterogeneous and unstable in dry state. It is due to the matter that the glass transition temperature of PTMSP is considerably high.

However, thermal agitation causes the homogenization of heterogeneous aggregation, and then substituents is mobilized. The time required for the homogenization can be of the order of day at room temperature. The attenuation coefficient becomes high as physical aging proceeds (*i.e.*, day by day). Heterogeneous aggregation can be expected to raise free energy (or lower entropy) of polymers. Accordingly, heterogeneous aggregation acts as a loss component (or an energy absorber) with respect to mechanical excitation. Thus, the decrease in the heterogeneous aggregation leads to decrease in $\tan \delta$. The increase in the attenuation coefficient can be explained by mobilized substituents. An activation energy around 9.0 kcal mol⁻¹ is quite reasonable for the above mechanism.

In the case of *n*-hexane solution, however, no special aggregation may be formed between substituents and solvents. As a result, $\tan \delta$ is low and the attenuation coefficient is high in the as-cast state. This hypothesis, especially the effect of solvent on the aggregation state of substituents will be examined in the future.

In conclusion, the higher gas-permeability for as-toluene-cast PTMSP films is due to a mechanism such that gas molecules permeate through sparse sites formed by the heterogeneous aggregation of substituents. During physical aging or heat-treatment, however, heterogeneous aggregation changes towards homogeneous one. This results in decrease of sparse sites. Consequently, the gas-permeability decreases with aging and heat-treatment. The increase in density with heat-treatment supports the mechanism above.

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