Cryogenic Relaxations of Polystyrene and Poly(fluorinated Styrenes)

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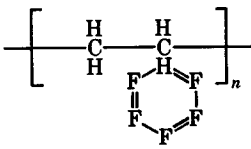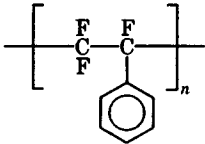*The Dow Chemical Company, Midland, Michigan 48640*

Synopsis

The effect of structural and morphologic modifications of styrene and fluorinated sty-
rene polymers on their internal friction was studied by means of a free-oscillating tor-
sional pendulum at temperatures from 300° to 4.2°K and frequencies of 1 to 2 Hz.
Atactic and isotactic polystyrene gave the previously observed δ and β' loss peaks at 38°
and 100°K, respectively.   These losses decrease in intensity with crystallinity in isotac-
tic polystyrene but remain relatively unchanged in uniaxially drawn atactic polymer.
Atactic polypentafluorostyrene showed an intense δ loss peak at 52°K and a broad
shoulder around 100°K, which extends toward the β' relaxation.   In poly-α,β,β-tri-
fluorostyrene, the δ loss peak is largely suppressed, the logarithmic decrement showing
only broad maxima at 22° and 100°K.   Plasticization of atactic polystyrene with 2%
mineral oil gives rise to a sharp loss maximum at 100°K, which does not occur in the pure
atactic polymer.

INTRODUCTION

Several internal friction maxima have been observed in polystyrene below
its glass transition temperature: a broad shoulder, β', around 300°K at fre-
quencies below 40 Hz,[1–4] a peak, γ, at 100–150°K,[2–6] and a peak, δ, near
40°K.[7,8]   The position and strength of these loss peaks change markedly
with various structural factors, such as molecular weight, tacticity, nature
of chain ends, chemical substitution, crosslinking, and crystallinity.   As a
result of this complex behavior, their structural origin is not well estab-
lished.   The δ maximum has been attributed to motions of the phenyl side
groups,[7,8] while the γ and β' relaxations have been tentatively associated
with motions of special main chain segments, such as head-to-head se-
quences.[2,3,5]

This work investigates the dependence of the low-temperature relaxations
on the molecular organization of atactic and isotactic polystyrene.   It also
presents data on the effect of chemical substitution (fluorination) and
processing additives on the low-temperature relaxation behavior.   The in-
ternal friction studies were conducted on a previously described free-

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TABLE I

Composition and Characteristics of the Polymer Samples

Sample Code	Description	$\bar{M}_v \times 10^{-3}$	T_g, °C
S690	atactic polystyrene (Styron 690)[a] compression molded at 150°C	800	100
DrnS690	S690 drawn uniaxially 5× at 105°C (Δn = .026)[b]	800	100
QIPS	isotactic polystyrene, quenched from the melt, amorphous	350	240[c]
AIPS	isotactic polystyrene, crystallized from the melt isothermally for 24 hr at 170°C (50% crystalline)	350	240[c]
P5FS	poly-2,3,4,5,6-pentafluorostyrene, atactic, compression molded	230	125
P3FS	poly-α,β,β-trifluorostyrene, atactic, compression molded	280	202

[a] Trademark of the Dow Chemical Company.

[b] Optical birefringence, measured with green light.

[c] Crystalline melting temperature.

oscillating torsional pendulum[9] designed and constructed in these laboratories. This instrument operates at temperatures from 300° to 4.2°K and frequencies of 1 to 2 Hz. It is capable of measuring log decrement values down to 10^{-4} using thin-film specimens. The composition and characteristics of the polymer samples used in this study are listed in Table I. The polystyrene samples were provided by courtesy of the Dow Chemical Company, while the poly(fluorinated styrenes) were kindly provided by Dr. Leo Wall of the National Bureau of Standards.

RESULTS

Figure 1 shows internal friction measurements for two atactic polystyrene samples, a compression-molded, isotropic specimen and a sample drawn uniaxially 5×. Both specimens show at 38°K the δ relaxation originally observed by Sinnott.[7] Except for a slight broadening of the internal friction peak, uniaxial drawing has no appreciable effect on the relaxation behavior. There is no trace of the γ relaxation in the 100–160°K
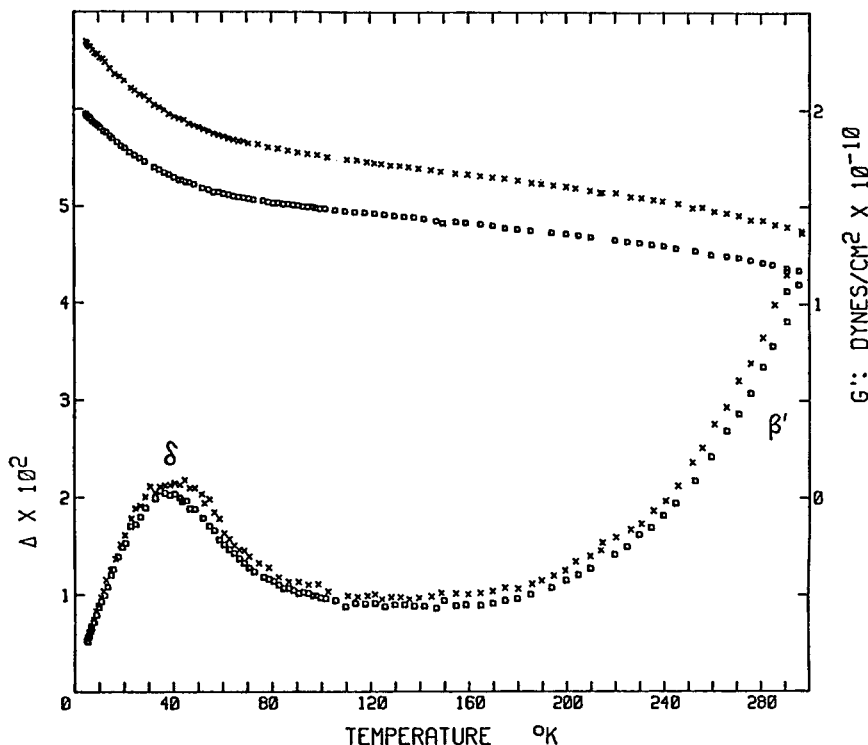
Fig. 1. Effect of orientation on the internal friction of atactic polystyrene at 1 Hz:
(□) isotropic atactic PS (Styron 690); (×) atactic PS, drawn uniaxially 5 × at 105°C.

region in either specimen. Above 200°K the log decrement increases rapidly, reaching a level of 0.05 at room temperature. This corresponds to the peak intensity of the β' relaxation observed at this temperature.[2,10]

Internal friction measurements on amorphous and semicrystalline isotactic polystyrene samples are shown in Figure 2. The relaxation spectra are similar to that of the atactic polymer, showing the δ loss peak at 38°K and rising toward the β' relaxation above 200°K. In the amorphous specimen these loss peaks have intensities comparable to those of the atactic polymer. These are reduced by about 25% in the semicrystalline specimen.

Figure 3 shows internal friction spectra of the two fluorinated polystyrenes and compares them with that of atactic polystyrene. The polymer with side-group fluorination (P5FS) shows an intense δ relaxation at 52°K. In addition, it has a very broad shoulder around 100°K, which extends toward the β' relaxation. The polymer with main-chain fluorination (P3FS) shows a markedly different internal friction spectrum. There is no easily discernible δ loss, only a smeared-out relaxation with maxima around 22° and 100°K. The loss level is considerably lower than that of P4FS sample and, below 80°K, lower than that of atactic polystyrene. Above 160°K
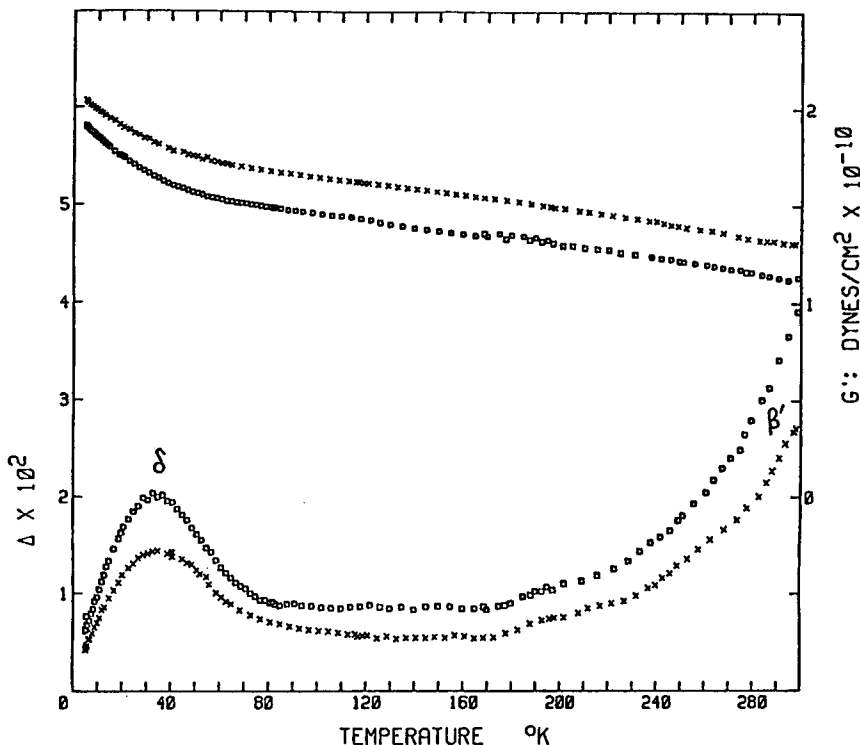
Fig. 2. Effect of crystallinity on the internal friction of isotactic polystyrene at 1 Hz: (□) isotactic PS, melt quenched (amorphous); (×) isotactic PS, crystallized at 170°C (50% crystalline).

the loss level increases more rapidly, approaching that of P5FS in the β' relaxation region.

Figure 4 compares the internal friction of atactic polystyrene with 2% mineral oil additive with that of the pure atactic polymer. The effect of the additive is quite remarkable. It lowers the temperature of the δ relaxation by 10°K and decreases its intensity. In addition, it gives rise to a pronounced loss peak at 110°K, which does not occur in pure atactic or isotactic polystyrene. Repeated experiments with several polystyrene specimens have confirmed this behavior. These effects are not seen in specimens processed identically but without the mineral oil and are, therefore, attributed to this additive.

DISCUSSION

The internal friction studies of isotactic polystyrene (Fig. 2) show the δ relaxation to decrease in intensity with crystallinity. This behavior is in accordance with the suggested mechanism for the δ relaxation, which involves multiple-mode librations of the phenyl side group.[7,11] The arrangement of chain segments in a crystalline lattice is expected to hinder these
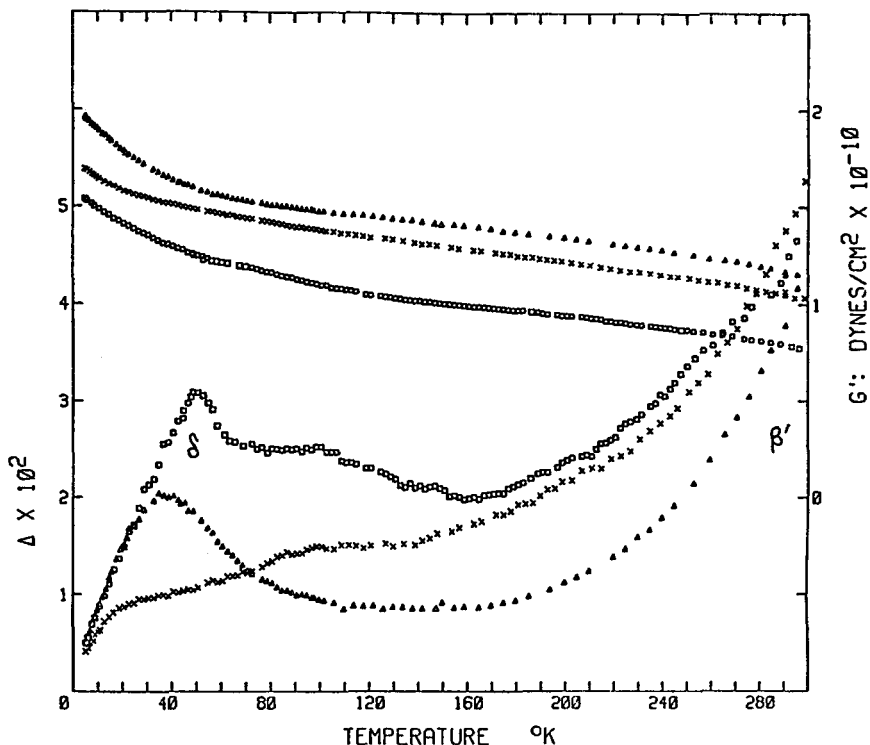
Fig. 3. Internal friction of poly(fluorinated styrenes):   (X) poly-α,β,β-trifluoro-styrene, atactic; (□) poly-2,3,4,5,6-pentafluorostyrene, atactic; (Δ) atactic PS.

side-group motions, thus decreasing the intensity of the relaxation. The presence of crystallinity also reduces the β' loss. This is consistent with the tentative assignment of this loss to local relaxations of main-chain segments in regions of enhanced mobility.[2,3,5] The occurrence of this loss in polystyrene samples with bulky chain ends or low molecular weight species, previously observed by Buchdahl and Nielsen,[1] is also consistent with this mechanism, since the endgroups and short chains create defect areas with enhanced local chain mobility. Experiments with a well-characterized atactic polystyrene sample show no appreciable effect of uniaxial orientation on the low-temperature relaxations (Fig. 1). However, the molecular orientation of this sample is quite modest ($\Delta n = 0.026$) despite the high draw ratio and is probably not sufficient for showing anisotropic relaxation effects, if indeed they do exist.

The internal friction data of the fluorinated polystyrenes represents a limited attempt to study the effect of a controlled change in chemical structure on the relaxation behavior of the polymer. Fluorination is expected to cause a small increase in chain bulkiness as well as considerable increase in interchain forces, due to the high polarity of the substituent. These effects are reflected in the glass transition temperatures of samples P5FS and P3FS,
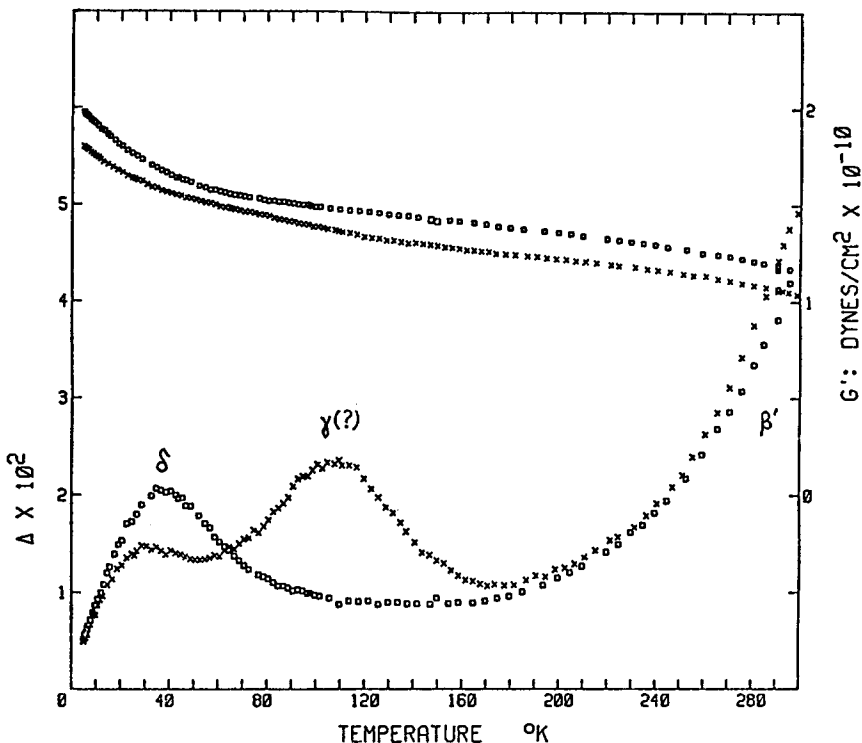
Fig. 4. Effect of mineral oil addition on the internal friction of atactic polystyrene at 1 Hz; (□) atactic PS (Styron 690); (×) atactic PS with 2% mineral oil additive.

which show an increase of 25° and 102°C, respectively, over atactic polystyrene (see Table I). It is noteworthy that main-chain fluorination, which involves only three fluorine atoms, is more effective in increasing T_g than side-group substitution by five fluorines.

Examination of Figure 3 shows that fluorination has little effect on the β' relaxation but changes drastically the internal friction in the δ loss region. The shift of the δ peak to higher temperatures in P5FS may be due to hindrance of side-group motion by the main-chain fluorines. The dynamic mechanical data provide no information on the nature of the weak maxima in the 100°K region. It is possible that NMR studies of these polymers may elucidate the nature of molecular motion at these temperatures.

Of considerable interest is the effect of the 2% mineral oil additive, mechanically blended with atactic polystyrene, on the internal friction of the plasticized system shown in Figure 4. The intensity of the loss peak at 110°K due to the additive is quite disproportionate to its small concentration, indicating that the hydrocarbon molecules participate very effectively in the transfer of external strains to molecular motions. Current investigations by means of cryogenic tensile experiments seek to determine whether this relaxation correlates with an increase in the ductility of the oil-ex-

tended polymer at these temperatures. A careful analysis of these phenomena may yield valuable information on the mechanism of external plasticization.

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