

# Polystyrene Crosslinked with Oligomeric and Polymeric Poly(Dimethyl Siloxane) Derivatives. Thermal and Dynamic Mechanical Studies

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## SYNOPSIS

Styrene has been copolymerized with various bifunctional poly(dimethyl siloxane) crosslinkers having molar masses in the range 200–35,000. Calorimetric and rheological measurements show that the crosslinkers change  $T_g$ ,  $T_{11}$ , and  $T_{exo}$ , as well as melt viscosity and elasticity of polystyrene. These changes are strongly dependent on the molar mass of the crosslinker. Increasing the length of the siloxane crosslinker lowers  $T_g$  and melt viscosity, if the molar mass of the crosslinker is in a range 200–2000. Copolymerizing styrene with a bifunctional poly(dimethyl siloxane) having molar mass near 35,000 leads to a phase-separated polymer where polystyrene phase largely retains its original properties.

## INTRODUCTION

The introduction of silicone-containing groups into styrene monomer has been shown to be an effective way to change the properties, such as  $T_g$ , stiffness, and gas permeability of polystyrene. Especially the glass transition temperature is dramatically altered when styrene monomer is substituted with a silicone-containing group. Recently, Kawakami et al.<sup>1</sup> reported the effects of *p*-oligo(dimethyl siloxanyl) substituents of polystyrene on  $T_g$  and oxygen permeability of the polymer. Polymers with linear oligo(dimethyl siloxanyl) substituents showed glass transition varying from 136 to  $-10^\circ\text{C}$ ,  $T_g$  decreasing with an increase in the number of silicone atoms in the side groups. Saigo et al.<sup>2</sup> have synthesized poly(alpha-methyl styrene)s with silicone-containing allylic *p*-substituents. Also in this case  $T_g$  decreased considerably with increasing length of the linear substituent.

Copolymers composed of poly(dimethyl siloxane) and polystyrene blocks have received considerable attention due to the interesting possibility to utilize

them as thermoplastic elastomers. The properties of the block copolymers of polystyrene (PS) and poly(dimethyl siloxane) (PDMS) depend critically on the size of the chemically differing blocks because PS and PDMS are mutually noncompatible. PS and PDMS blocks tend to demix and to form separate microphases in the solid polymer.<sup>3–5</sup>

Polymers obtained by copolymerizing styrene with oligomeric or polymeric bifunctional PDMS derivatives are the subject of this study. These are fairly complex polymers, whose properties are affected by at least two competing trends. First, crosslinking is generally considered to prevent the translation of the polymers by each other, and they also slow down the segmental motion. These changes in the dynamic state of the polymer are macroscopically detected as insolubility, elasticity, and increasing  $T_g$ . Second, a flexible pendant PDMS chain tends to increase the free volume around the PS molecule, and it thus lowers the glass transition temperature.

When styrene is reacted with small amounts of the oligomeric or polymeric crosslinking agent, the product is not necessarily a network, but a strongly branched (in this case PDMS-grafted) polystyrene. It is not yet clearly established how noncompatible side chains affect the properties of a solid polymer.

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Also, polymeric crosslinkers as such have not been studied very intensively. Very recently, a report has been published on the synthesis of bifunctional poly(dimethyl siloxane)s to be used as polymeric crosslinkers in high-impact strength polymers.<sup>6</sup> Gelation of polystyrene caused by poly(oxyethylene) crosslinkages has also been investigated.<sup>7</sup>

The aim of the present study is to find out how these factors—crosslinking on one hand and introduction of the flexible siloxane groups on the other—change the properties of polystyrene. Rheological properties of the copolymers will be discussed and correlated with the differential scanning calorimetry (DSC) data.

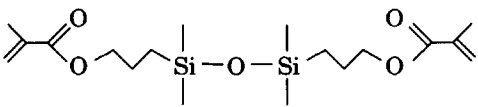
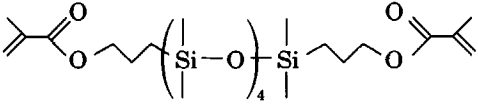
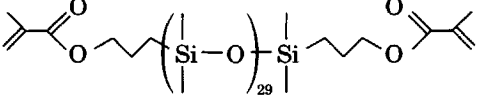
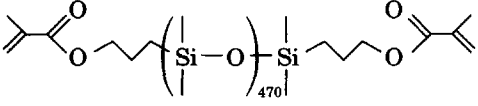
The copolymers are investigated calorimetrically, not only by measuring  $T_g$  but also by studying the thermal transitions occurring at  $T > T_g$ . With thermomechanical and calorimetric measurements PS, as well as some other amorphous polymers, has been observed to undergo a second-order phase transition at a certain temperature  $T > T_g$ . The exact nature of this transition is not yet definitely understood. It seems evident that when heating PS, it does not transform into a true liquid state at  $T_g$  but forms a so-called fixed fluid. At  $T_{11}$ , which usually equals 1.2  $T_g$ , a liquid-liquid transition occurs, and the mac-

romolecules gain liquidlike motional freedom. The flow properties of the polymer have been observed to change at this point.<sup>8-11</sup> It has been shown that processing PS above or below  $T_{11}$  leads to products with different end use properties.<sup>12</sup> The occurrence of the  $T_{11}$  transition is interesting not only from the rheological point of view, but it has also more fundamental consequences. Theoretical considerations concerning the glass transition are usually based on the assumption that amorphous polymers are in an equilibrium liquid state at temperatures above  $T_g$ .

Measurements on the PS samples with narrow molar mass distributions have shown that  $T_{11}$  is dependent on the molar mass (on  $M_n$  but not on  $M_w$ ) in a same way as  $T_g$ ;  $T_{11}$  increases with increasing size of the polymer but reaches an asymptotic value with further increase of  $M_n$ . This implies that the  $T_{11}$  transition has a similar free-volume basis as the glass transition, but the  $T_{11}$  transition involves a longer chain segment length or possibly the entire molecule. This interpretation is further supported by the observation that the  $T_{11}$  transition disappears when the polymer is crosslinked.<sup>8</sup>

$T_{11}$  of polystyrene can be detected as an endothermic change in the slope of the heating thermogram. In addition, during the first heating run in

**Table I Structure and Amount of Crosslinkers. Abbreviations for the Polymers**

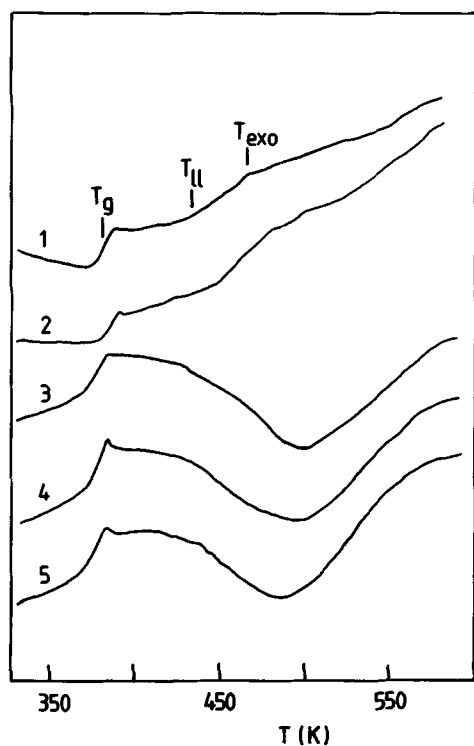
Crosslinker	Sample	mol %	wt %	Abbreviation
	1	0.023	0.08	PSX 200
	2	0.13	0.46	
	3 (x)	0.29	1.04	
	4 (x)	0.55	1.96	
	5 (x)	0.89	3.10	
	1 (x)	0.17	0.99	PSX 400
	2 (x)	0.43	2.34	
	3 (x)	0.62	3.38	
	4 (x)	0.92	4.94	
	1	0.04	0.99	PSX 2000
	2	0.21	4.76	
	3 (x)	0.43	9.09	
	4 (x)	0.71	14.5	
	5 (x)	0.93	18.0	
	1 (xx)	0.001	0.34	PSX 35000
	2	0.002	0.67	
	3	0.004	1.48	
	4	0.01	4.12	
	5	0.06	16.4	
	6	0.34	54.3	

(x) Insoluble samples.

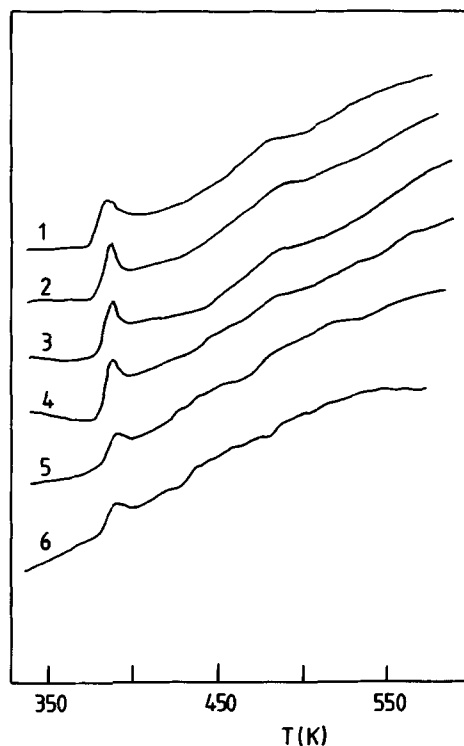
(xx) All the PSX 35000 samples from turbid solutions in  $\text{CHCl}_3$ .

DSC an exothermic change may be detected above  $T_{ll}$ . The onset of the exotherm is designated as  $T_{exo}$ . The exotherm has been suggested to be due to the viscous flow of the polymer and/or to the wetting of the surface of the DSC sample pan during the flow process.  $T_{exo}$  depends on the molar mass of the polymer; above a critical  $M_w$  (the entanglement molar mass  $M_c$ )  $T_{exo}$  begins to increase without limit. The observation that  $T_{exo}$  is dependent on the mass average of the molar mass is equivalent with the fact that  $T_{exo}$  is observed to depend on the zero shear melt viscosity. Furthermore,  $T_{exo}$  is to some extent dependent on the physical form of the sample (pellet, powder, film).<sup>13</sup>

Several contradictory results concerning the existence of  $T_{ll}$  have been published (see, e.g., Refs. 14 and 15), and the discussion concerning the existence and the true nature of the liquid-liquid transition has not yet settled. In the present case, the transitions  $T_{ll}$  and  $T_{exo}$  were observed for several PDMS-PS copolymers. It seems very possible that by measuring  $T_g$ ,  $T_{ll}$ , and  $T_{exo}$ , information may be obtained concerning the crosslinking efficiency of the bifunctional PDMS derivatives with varying molar masses.



**Figure 1** Thermograms of the series PSX 200. The measured transition temperatures are indicated by vertical straight lines.

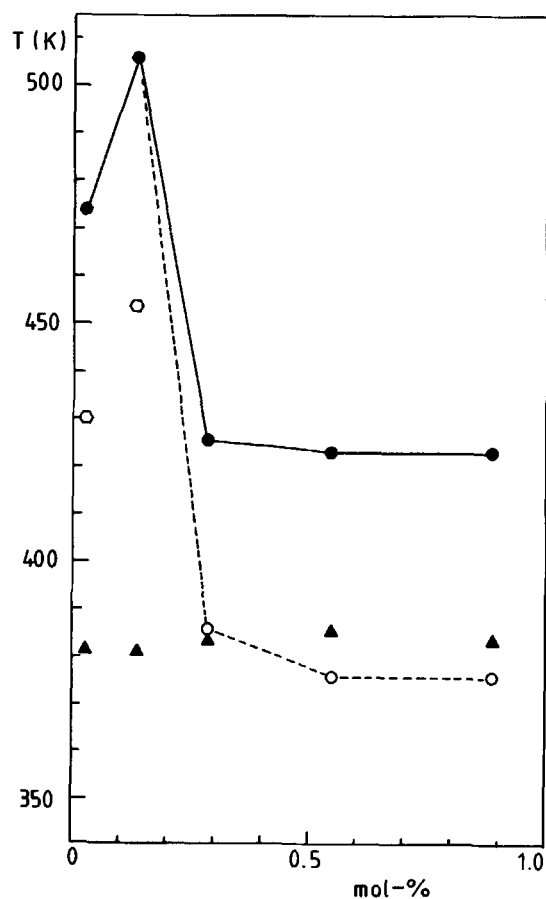


**Figure 2** Thermograms of the series PSX 35000.

## EXPERIMENTAL

The samples were, with one exception, bulk polymerized in test tubes under nitrogen atmosphere. Typically 6 g of styrene and 50 mg of dibenzoyl peroxide were mixed in a test tube, and a known amount of crosslinker was added. The mixture was deaerated with flowing nitrogen gas. The tube was sealed and heated at 70°C for 24 h. The structure and the amount of the crosslinkers are shown in Table I, which also gives the abbreviations for the samples. The crosslinkers were synthesized by endcapping hydrogen-terminated PDMS (Petrarch Systems) with allyl methacrylate, using a hydrosilylation<sup>16</sup> reaction. The molar masses of the crosslinkers were estimated from the viscosity data and proton NMR spectra. The crosslinker with molar mass of about 35,000 could not be reacted with styrene in a test tube due to macroscopic phase separation during polymerization. The polymerization was performed in an aqueous suspension stabilized with gelatin for 8 h at 80°C.

The polymers were repeatedly purified by precipitating with methanol from a chloroform solution and dried at 70°C. In case of insoluble polymers the ground samples were allowed to swell in chloroform for several days; after adding methanol, the polymer



**Figure 3** Transition temperatures for the series PSX 200.  $T_g$  ( $\blacktriangle$ ),  $T_{11}$  ( $\circ$ ),  $T_{exo}$  ( $\bullet$ ). Open circles are for the dried gel fraction, filled circles for the whole sample.

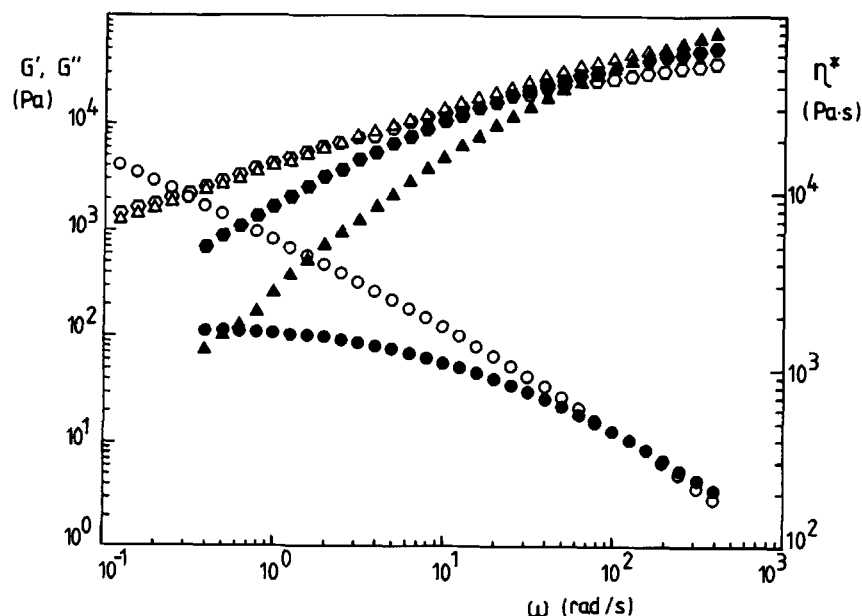
was collected and dried. Exceptionally, sample series PSX 400 was purified by extraction with toluene in a soxhlet apparatus; this series thus differs from the others, i.e., it contains only the insoluble gel fraction.

Thermal analysis was performed with a Perkin-Elmer DSC2. The samples (usually 8 mg) were heated in open sample pans with a heating rate 40 K/min from 323 to 603 K. The transition points  $T_{11}$  and  $T_{exo}$  were obtained from these measurements. Because thermal degradation may occur during the heating,  $T_g$  of polystyrene was measured with separate samples, again in open pans, as follows. The polymer was heated to 423 K, cooled quickly to 323, and the thermogram (323–423 K) was then registered with a heating rate 40 K/min. Because most of the samples contain very small amounts of siloxane crosslinker, no trials were made to measure  $T_g$  of PDMS.

The dynamic mechanical measurements were performed with a Rheometrics System Four rheometer in nitrogen atmosphere at 220°C. The softened samples were measured between two plates with a diameter of 25 mm. Strain was kept low enough so that the measurements were all done well in the linear range.

## RESULTS AND DISCUSSION

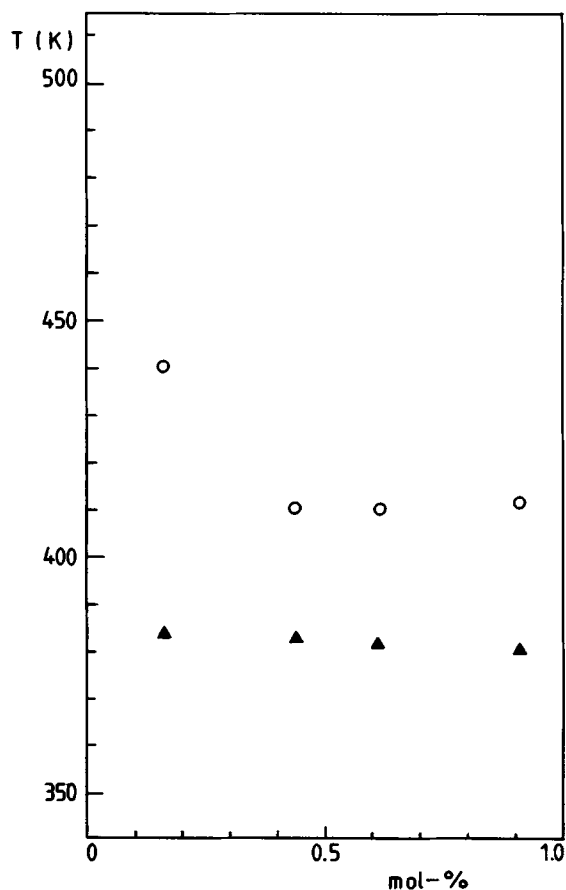
Heating thermograms of the sample series PSX 200 are shown in Figure 1. The thermograms change



**Figure 4** Dynamic viscosity ( $\circ \bullet$ ),  $G'$  ( $\triangle \blacktriangle$ ) and  $G''$  ( $\circ \bullet$ ) for samples 1 (filled symbols) and 2 (open symbols) of the series PSX 200.

abruptly with increasing degree of crosslinking; a very large exotherm becomes apparent in insoluble samples. This is the case also with the series PSX 400 and PSX 2000. The exotherm detected in thermograms 1 and 2 (Fig. 1) is of the order of magnitude of  $-5$  J/g or less, but in thermograms 3–5, of about  $-100$  J/g. Only the order of magnitude can be given because the enthalpy change was observed to vary strongly with the physical form of the sample. However, the onset of the exotherm,  $T_{\text{exo}}$ , did not change considerably when the mesh size of the sample was varied.

It is evident that the exotherms in curves 3–5 (Fig. 1) cannot be due to the flowing or sintering of the polymer because they are detected only with tightly crosslinked samples, i.e., with those that do not change their form, at least visually detectably, during heating. It is suggested that the exotherm is in this case mainly due to the elasticity of the sample, and it indicates a stress relaxation occurring at  $T > T_g$ . Thus, in the present study " $T_{\text{exo}}$ " is used in a



**Figure 5** Transition temperatures for the insoluble part of the samples of the series PSX 400. Symbols as in Figure 3.

**Table II** Glass Transition Temperatures for the Samples

Polymer	Sample	$T_g$ (sol + gel)	$T_g$ (gel)
PSX 200	1	382	382
	2	382	382
	3	384	386
	4	385	385
	5	383	384
PSX 400	1		384
	2		383
	3		381
	4		380
PSX 2000	1	378	
	2	376	
	3	375	
	4	374	
	5	370	
PSX 35000	1	381	
	2	381	
	3	382	
	4	381	
	5	381	
	6	382	

fairly broad sense, and it indicates the onset temperature of any exothermic process observed above  $T_g$ .

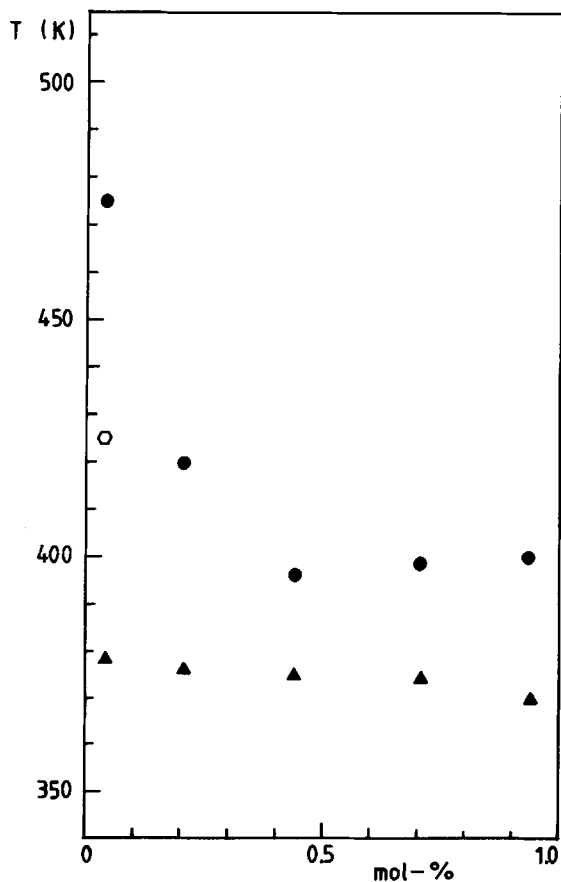
The thermograms of the series PSX 35000 are shown in Figure 2. In this series the strong exotherm at  $T > T_g$  is not detected. This finding is in accordance with the previously suggested origin of the exotherm, i.e., stress relaxation due to the elasticity of the sample. All the polymers PSX 35000 form turbid solutions when mixed with chloroform and thus they are either not crosslinked but branched polymers or just slightly crosslinked polymers, soluble due to the length of the crosslinker. It can be seen from Figure 2 that with increasing content of polysiloxane the shape of the thermogram changes to a fairly complex one, distinctly different from that of polystyrene.

Figure 3 summarizes the results of the DSC measurements on the sample series PSX 200. With increasing concentration of the crosslinker,  $T_{\text{exo}}$  can be seen first to increase and then to decrease considerably. Two first samples with the crosslinker concentration  $< 0.2$  mol % are soluble in chloroform; so, following the arguments by Boyer,<sup>13</sup> the increase in  $T_{\text{exo}}$  is evidently due to the increase of the size of the polymer, caused in this case by the increasing

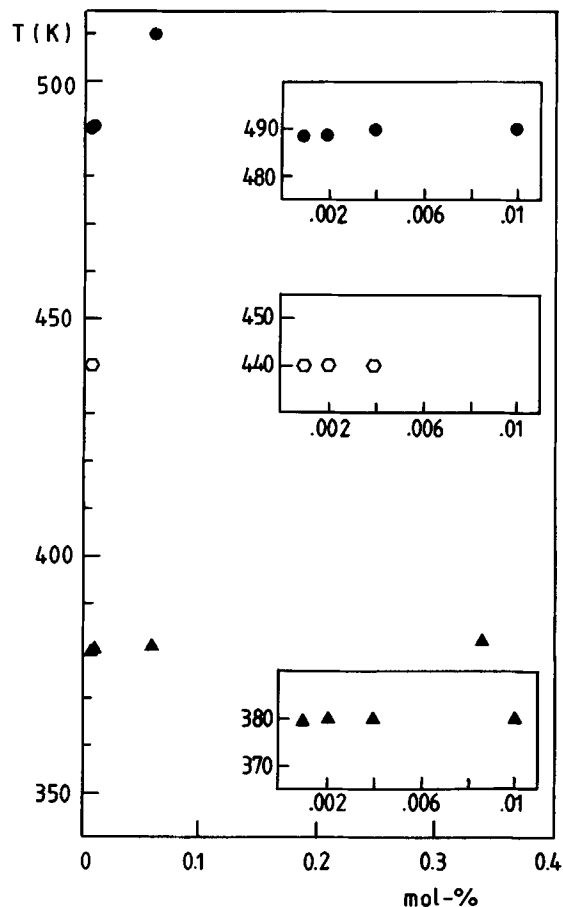
amount of the bifunctional monomer.  $T_{11}$  is detected only in the soluble samples, and it increases with increasing crosslinker concentration.

For the PSX 200 samples containing  $> 0.2$  mol % crosslinker  $T_{exo}$  lies in the range 420–430 K. When the soluble part of the samples was extracted with chloroform, it was possible to repeat the measurements using the dried gel fraction;  $T_{exo}$  decreased to values between 370 and 390 K. In the crosslinked samples containing no soluble polymer the exothermic process begins instantaneously after passing the  $T_g$ .  $T_{exo}$  in the crosslinked polymers may evidently be used as an indicator of the efficiency of the network formation, and possibly also of the elasticity of the polymer.

The results of the rheological measurements on the samples 1 and 2 from the series PSX 200 are shown in Figure 4. Zero shear melt viscosity of the polymer is seen to increase with increasing amount of the crosslinking agent; this result is in accordance with the observed increase of  $T_{11}$  and  $T_{exo}$ . The shear thinning of sample 2 seen in Figure 4 indicates



**Figure 6** Transition temperatures for the series PSX 2000. Symbols as in Figure 3.



**Figure 7** Transition temperatures for the series PSX 35000. The overlapping points with crosslinker content  $< 0.01$  mol % are shown in the insets. Symbols as in Figure 3.

branching and incipient crosslinking of the polymer chains. The values of the storage and loss moduli increase with increasing amount of the PDMS derivative; simultaneously their frequency dependence is observed to decrease, which also indicates the beginning of the network formation. Sample 3 from the series PSX 200, as well as those crosslinked even more tightly, softened only partially and could not be measured in the rheometer. It is interesting to note that in the frequency range shown in Figure 4, sample 1 shows terminal behavior, i.e., curves for  $G'$  and  $G''$  cross over each other at a frequency around  $10^2$  rad/s. The crossover point for the sample 2 is approximately 1.8 rad/s. Lowering of the crossover frequency is, at least in some cases, indicative of an increase in the molar mass of the polymer. Further, lowering of the crossover modulus, observed in Figure 4 with increasing crosslink density may be due to the broadening of the molar mass distribution.<sup>16,17</sup>

The samples of the series PSX 400 contained, as

already noted, only the insoluble polymer fraction. The results of the DSC measurements on this series are shown in Figure 5.  $T_{\text{exo}}$  decreases with increasing crosslinking to about 410 K, a value considerably higher than the corresponding one for the insoluble samples of the PSX 200 series. The value of  $T_{\text{exo}}$  is thus affected by the increasing length of the siloxane crosslinker. It should be noted that the glass transition temperature slightly decreases with increasing crosslink density:  $T_g$  is 384 K for sample 1 and 380 K for sample 4. Lowering of  $T_g$  indicates that the PDMS units in PSX 400 are certainly long enough to soften the crosslinked polystyrene.

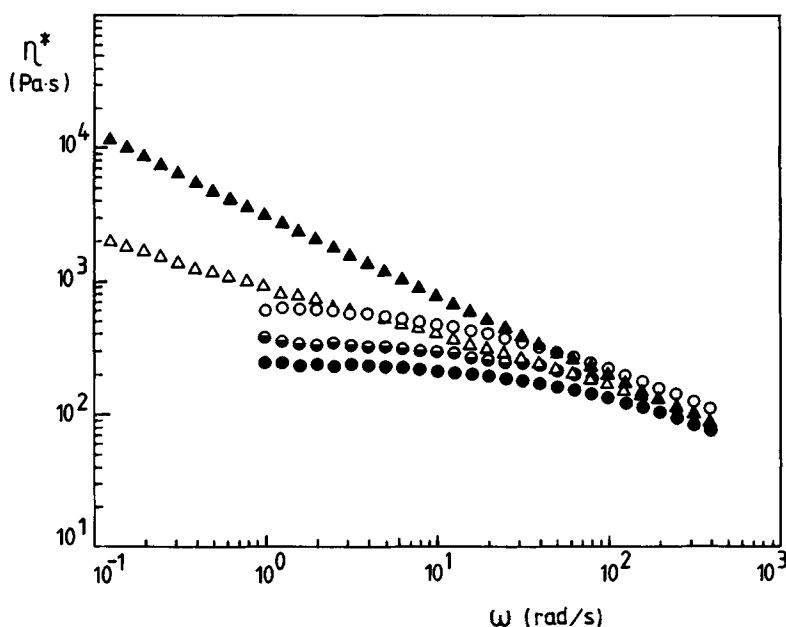
The glass transition temperatures for all the samples are shown in Table II. The thermograms were measured with a high heating rate in open sample pans. This probably affects the results, i.e., the  $T_g$ 's are slightly higher than they would be if the measurement had been conducted in a more conventional method. The measurement technique employed in this work makes it easier to detect  $T_{11}$  and  $T_{\text{exo}}$ , but the sensitivity of the observed  $T_g$  to small changes in molecular structure may not be the best possible. Repeated measurements with closed sample pans and varying heating rates have shown that the variation in the glass transition temperatures is in fact more pronounced than shown in Table II. The values reported here show the right tendencies, however; with these figures it is easy to see the differences between the different crosslinkers. More

detailed discussion on the glass transition will be given in the next report.

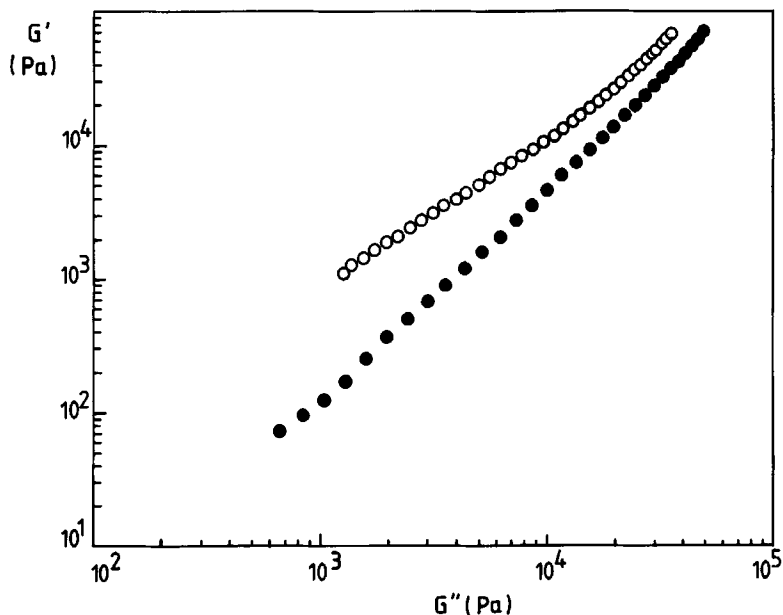
The transition temperatures of PSX 2000 series are shown in Figure 6.  $T_{\text{exo}}$  and  $T_{11}$  for sample 1 are approximately the same as for sample 1 of PSX 200 series, but  $T_g$  is slightly lower. With increasing crosslinker concentration  $T_{\text{exo}}$  falls down to values around 400 K,  $T_{11}$  vanishes, and  $T_g$  decreases.  $T_g$  for sample 1 is 378 K, and for the sample 5, 370 K. Note that of all the sample series studied, PSX 2000 has the lowest  $T_g$  values.

Polystyrenes reacted with the polymeric dimethylsiloxane crosslinker (PSX 35000) differ from the other polymers studied in this work. Of the six samples studied,  $T_{\text{exo}}$  could be detected for four, and a few times also for sample 5. The uncertainty concerning the fifth sample is due to heterogeneity of the samples with high PDMS content.  $T_{\text{exo}}$  is constant for samples 1–4 but increases with further increase of the crosslinker content, see Figure 7. The glass transition temperature is 381–382 K for all the PSX 35000 samples. The constancy of polystyrene  $T_g$  shows that PDMS with molar mass of 35,000 tends to demix from the PS phase; the same observation was made also during the polymerization experiments (see experimental section). The chemically different chains evidently behave almost independently of each other.

Figure 8 shows the melt viscosities for some samples of PSX 2000 and PSX 35000 series. Of the series



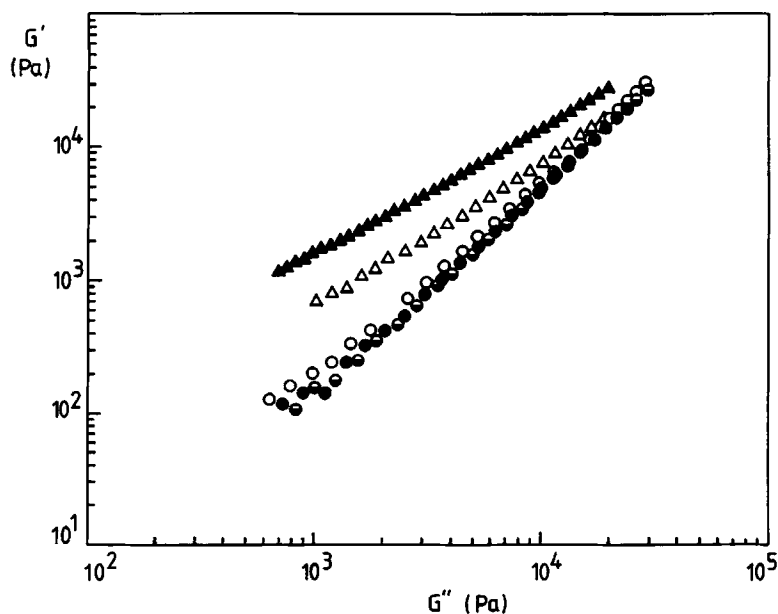
**Figure 8** Melt viscosity for PSX 2000 and PSX 35000 samples. PSX 2000: sample 1 ( $\blacktriangle$ ), sample 2 ( $\triangle$ ). PSX 35000: sample 1 ( $\bullet$ ), sample 3 ( $\ominus$ ), sample 5 ( $\circ$ ).



**Figure 9** Log  $G'$  vs. log  $G''$  for PSX 200: sample 1 (●), sample 2 (○).

PSX 2000 only two samples were soft enough to be measured with a plate-and-plate instrument. The melt viscosity of PSX 2000 *decreases* with increasing crosslinker concentration; this finding is very much in line with the observed decrease of  $T_g$  and  $T_{exo}$ . The decrease of  $T_g$  and melt viscosity, observed with increasing amount of crosslinker, shows that the siloxane derivative with an average molar mass of

2000 is long enough to increase the free volume around PS chains. The dynamic viscosity of the PSX 35000 samples is lower than that of the other sample series. Zero shear viscosity is seen to increase slightly with increasing amount of the PDMS derivative, indicating increasing molar mass, degree of branching, and/or crosslinking. For clarity, only three of the PSX 35000 samples are shown in Figure 8.



**Figure 10** Log  $G'$  vs. log  $G''$  for PSX 2000 and PSX 35000. PSX 2000: sample 1 (▲), sample 2 (△); PSX 35000: sample 1 (●), sample 3 (⊖), sample 5 (○).



The viscoelastic response of a polymeric fluid is considered to be more sensitive than its viscous response to variations in its molecular parameters.<sup>18</sup> The effect of various amounts of PDMS crosslinkers on the material characteristics of PS is demonstrated in Figures 9 and 10, where  $\log G'$  is plotted against  $\log G''$ . Several investigations have proved this kind of presentation of experimental data to be more sensitive to variations in the molecular architecture and the polymer morphology than  $\log G'$  versus  $\log \omega$  and  $\log G''$  versus  $\log \omega$ .<sup>16,19–21</sup> Interpretation of the data is based on the fact that when considering dynamic viscoelastic properties of a polymer,  $G'$  represents its elastic property and  $G''$  its viscous property.

Figure 9 shows the results from two PSX 200 samples.  $G'$  is seen to increase as the crosslinker content increases. In the low-frequency range the dynamic storage modulus is less than (sample 1) or nearly equal (sample 2) to the loss modulus. In the high-frequency regime the elastic response is higher than the viscous one. The curves are typical for branched polymers; almost equal values of  $G'$  and  $G''$  for sample 2 indicate incipient crosslinking. Similar changes have been reported to occur with increasing branching of polyolefin elastomers,<sup>16</sup> as well as with increasing concentration of rubber in ABS resins.<sup>20</sup>

Figure 10 shows  $\log G'$  versus  $\log G''$  for two samples of the series PSX 2000 and for three representative samples of the series PSX 35000. The PSX 2000 samples behave approximately as sample 2 of the PSX 200 series (Fig. 9). However, increasing the amount of PDMS crosslinker with molar mass about 2000 *decreases* the elastic contribution to the total response. In sample 1,  $G'$  is higher than in sample 2 over the whole frequency range. The decrease of elasticity with increasing crosslinking is somewhat surprising; evidently, an increase in free volume around PS chains is not the only effect caused by the PDMS derivatives. This point clearly needs to be clarified more thoroughly. It is tempting to suggest that the apparent number of elastically active crosslinks is lowered due to the association of the siloxane molecules, and due to clustering of the crosslinks. Spectroscopic studies on the phase separation are under progress.

There are two remarkable features in the  $\log G'$ – $\log G''$  curves for the sample series PSX 35000. First, all of the samples behave like sample 1 from the PSX 200 series; polymeric dimethyl siloxane crosslinker does not considerably increase the elasticity of the polymer. Second, there is only a slight variation of the viscoelastic properties of the product

polymer with increasing amount of PDMS derivative. In fact, commercial radical polymerized polystyrene has a  $\log G'$ – $\log G''$  plot very close to those measured for sample 1 from the PSX 200 series and for all samples of the PSX 35000 series. This shows that in PSX 35000 samples, viscoelasticity is governed by the properties of the polystyrene phase, due to the demixing of PS and PDMS phases. This conclusion is supported by the constant glass transition temperature measured for various samples of PSX 35000. Also, in those cases where  $T_{11}$  and  $T_{\text{exo}}$  are detected, the transition temperatures keep constant, with one exception already noted.

## CONCLUSIONS

Radical copolymerization of appropriate amounts of bifunctional PDMS derivatives with styrene produces insoluble polymers, when the average molar mass of the crosslinker is in the range 200–2000. Copolymers containing PDMS with molar mass of approximately 35,000 form turbid solutions in chloroform.

PDMS crosslinker with molar mass of 2000 has been shown to differ from the lower molar mass reagents. With increasing amount of the crosslinker,  $T_g$  of PS decreases considerably, as does also the melt viscosity and elasticity of the product polymers. On the other hand, in the series PSX 35000,  $T_g$  of PS keeps constant with varying amounts of the siloxane. Based on the calorimetric and rheological measurements, it is concluded that PSX 35000 samples are macroscopically phase-separated polymers.

Studying the copolymers by DSC, the network formation is detected as the disappearance of  $T_{11}$  and as a considerable decrease in  $T_{\text{exo}}$ . And  $T_{\text{exo}}$  in crosslinked samples is supposed to be due to the stress relaxation occurring above  $T_g$ .

In the chloroform-soluble samples of PSX 200 and PSX 2000,  $T_{11}$  and  $T_{\text{exo}}$  have been shown to be very sensitive to changes in the polymer structure. Both  $T_{11}$  and  $T_{\text{exo}}$  correlate with changes in dynamic viscosity of the polymer melt.  $T_{\text{exo}}$  seems to be related to the elasticity of the sample; this supports our suggestion about the elastic origin of the exothermic process detected in crosslinked samples above  $T_g$ . In this regard it is interesting to note that when crosslinker content of PS approaches 1.0 mol %,  $T_{\text{exo}}$  approaches 425 K for PSX 200, 410 K for PSX 400, and 400 K for PSX 2000.  $T_{\text{exo}}$  for PSX 35000 is 490 K or even higher, showing that the phase-separated samples with the high polymeric crosslinker belong to their own category.

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