Thermally reactive oligomers of aromatic poly(ether sulphone) containing poly(dimethylsiloxane): 2. Mechanical properties in the poly(ether sulphone) glass transition range

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The study of the mechanical properties of two-phase poly(ether sulphone)–poly(dimethylsiloxane)–poly(ether sulphone) (PSU–PDMS–PSU) 'triblock' networks in the PSU glass transition range shows strong dependence of both the T_g and the moduli on the molecular weight of the blocky components. By proper arrangement of the molecular weight of the composing PSU and PDMS, 'triblock' networks of desired mechanical properties are feasible. Kinetic interpretation of the pertaining WLF constants suggests polymer specific values and correlation with entropic and energetic contributions to the rheological properties. These entropic and energetic factors seem to show a 'compensation effect' like behaviour.

(Keywords: poly(ether sulphone); mechanical properties; glass transition)

INTRODUCTION

In the previous paper[1], we have presented the synthesis of thermally reactive oligomers of poly(ether sulphone) (PSU) containing poly(dimethylsiloxane) (PDMS) and their thermal characterization by d.s.c. and dynamic thermomechanometry in the torsion pendulum mode.

Thermal analysis data suggested not only the two-phase character of the PSU–PDMS–PSU 'triblock' networks, but also the molecular weight dependence of the glass transition and mechanical moduli. Consequently, as synthesis of 'triblock' networks with desired mechanical properties seems realizable, a more detailed characterization of their mechanical properties is the aim of this paper.

EXPERIMENTAL

Taking into account the suggested dependence of the moduli on the molecular weight of the components of the 'triblock' networks, the rheological study was concentrated mainly on the PSU glass transition region, using the isothermal oscillatory torsion bar geometry in the rheometer mode in the 0.025–7.5 Hz frequency range. The measurements were executed on an Instron 3250 rheometer using torsion bars of 35 × 3 × 3 mm. In the temperature range of the PSU T_g, the temperature was varied in steps of 5°C. The rheological data were then shifted to isotherm master curves using both the WLF relation[2] and the temperature-dependent activation energy $E(T)$ method suggested by Brekner *et al.*[3] The latter method was also applied for constructing isochrone master curves.

RESULTS AND DISCUSSION

Isotherm and isochrone master curves

In *Figure* 1 the isotherm master curves of the storage modulus for homo-PSU networks are shown, indicating dependence on molecular weight before cure. All master curves are shifted to the same reference temperature $T_g + 7$ K, thereby allowing the superposition of the curves in the PSU glass transition range. As expected, the smaller the molecular weight before cure (identical with the smaller length of the chain between network junctions after cure), the higher the modulus of the rubber plateau, G'_e. At the same time, the glass transition range itself is more and more enlarged, i.e. the master curves gradually become flatter. This latter effect and the parallel shift of the T_g range to higher temperatures with decreasing molecular weight of the PSU is much better shown in the respective isochrone master curves of the storage modulus, shown in *Figure 2.*

The corresponding isochrone master curves of the loss modulus, G'', in *Figure 3* indicate that in parallel with the shift of the master curves to higher temperatures with decreasing molecular weight of PSU, a spreading of the loss peak is also observed, suggesting an enlargement of the relaxation time spectrum, typical for increasing

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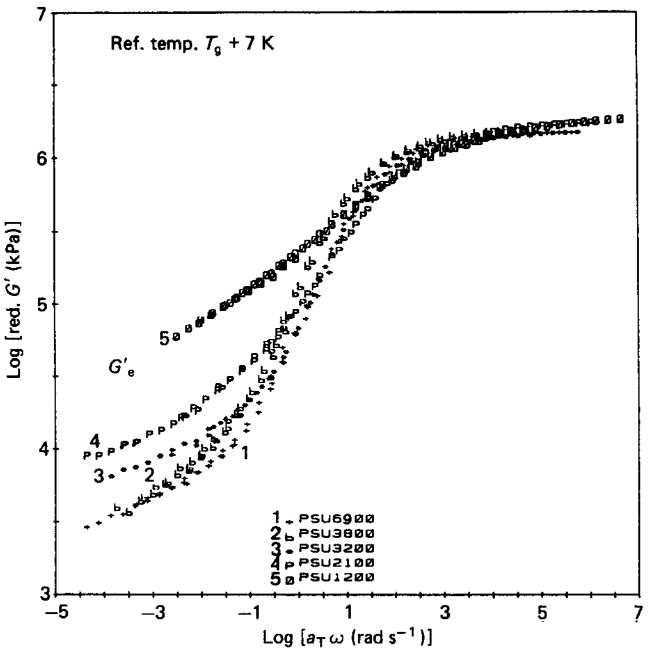

Figure 1 Isotherm master curves of the storage modulus, G', of PSU networks in the PSU glass transition range

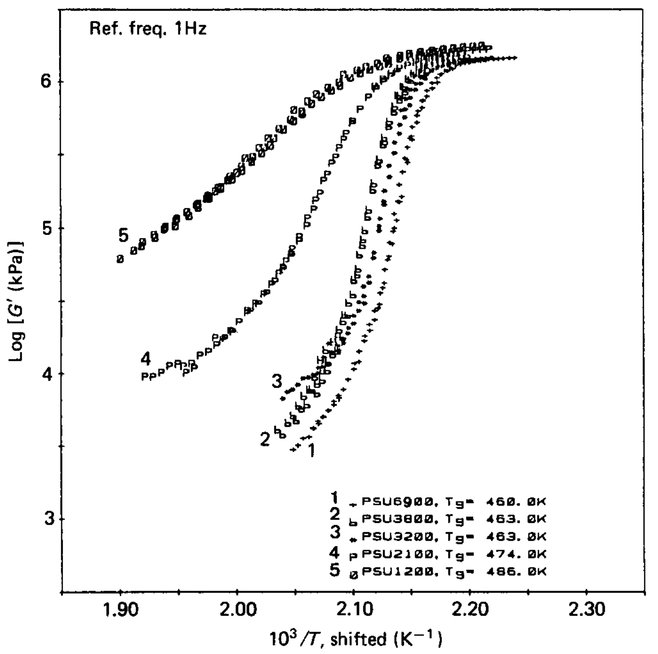

Figure 2 Isochrone master curves of the storage modulus, G', of PSU networks in the PSU glass transition range

polydispersity of the system. This broadening of the loss peak is, at the same time, accompanied by a decrease in the attained maximum value of the loss modulus, G''_{max}. The latter then also indicates changes in system polydispersity.

The molecular weight dependence of the characteristic moduli G'_e and G''_{max} of homo-PSU networks is illustrated in *Figure 4*. The aforementioned influences on the rubber plateau storage modulus, G'_e, and on the maximum value of the loss modulus peak, G''_{max}, are quite evident. At the same time, it is seen that both values level off for increasing molecular weight of the PSU.

Whereas the molecular weight before cure of the PSU is mainly responsible for the value of the storage modulus in the rubber plateau, G'_e, the molecular weight of the soft PDMS middle block in 'triblock' networks determines the height of the storage modulus below the PSU glass transition temperature, G'_{gl}. This is clearly shown by the isotherm master curves in *Figure 5* for the storage modulus of 'triblock' networks with increasing molecular weight of the PDMS and constant molecular weight of the PSU ($M_n = 3800$). Owong to the chosen reference temperature, $T_g + 7$ K, all curves are again superimposed in the PSU glass transition region. Since all curves tend to

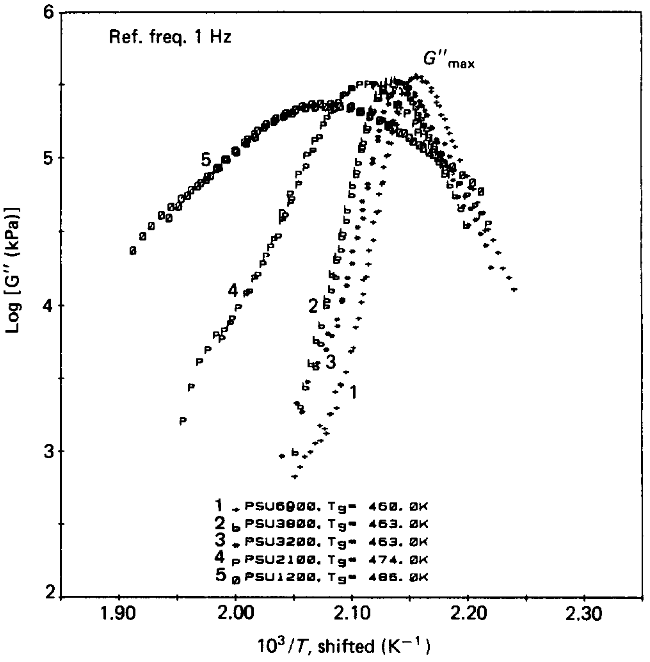

Figure 3 Isochrone master curves of the loss modulus, G'', of PSU networks in the PSU glass transition range

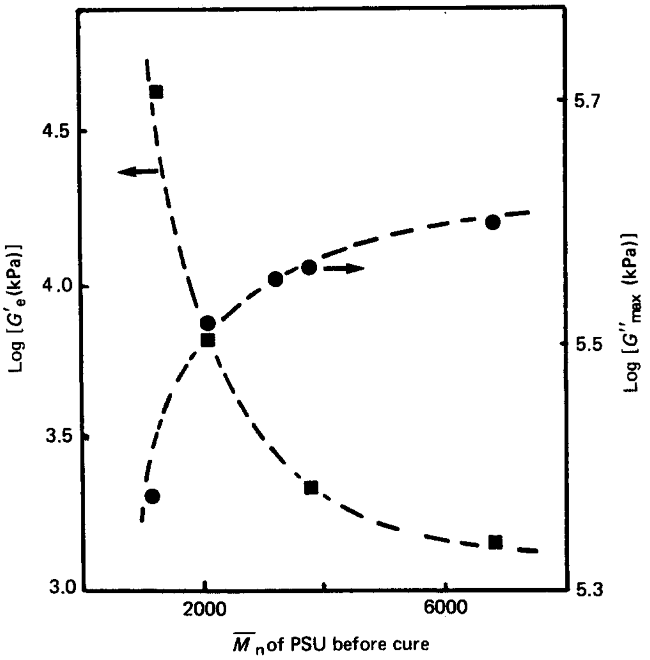

Figure 4 Dependence of the characteristic moduli of PSU networks in the rubber plateau, G'_e, and of the maximum of loss modulus peak, G''_{max}, on the molecular weight of PSU before cure

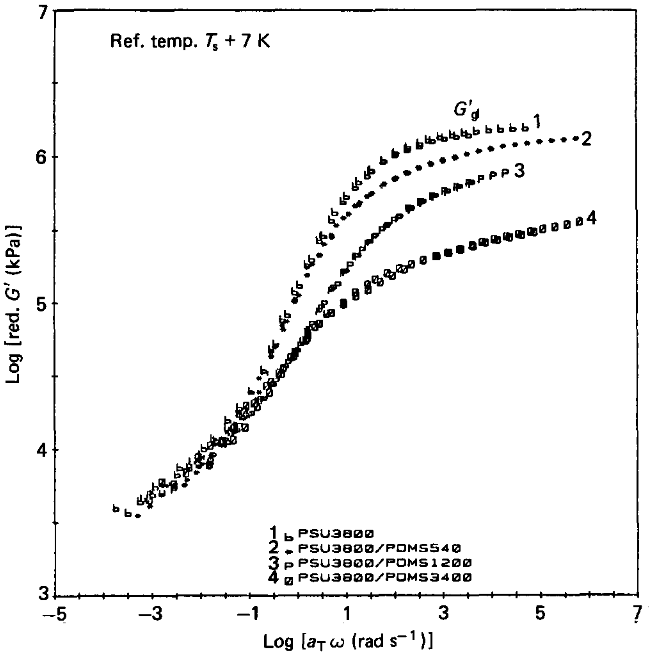

Figure 5 Isotherm master curves of the storage modulus, G', in the PSU glass transition range of 'triblock' networks of PSU-3800 with increasing molecular weight of the PDMS middle block

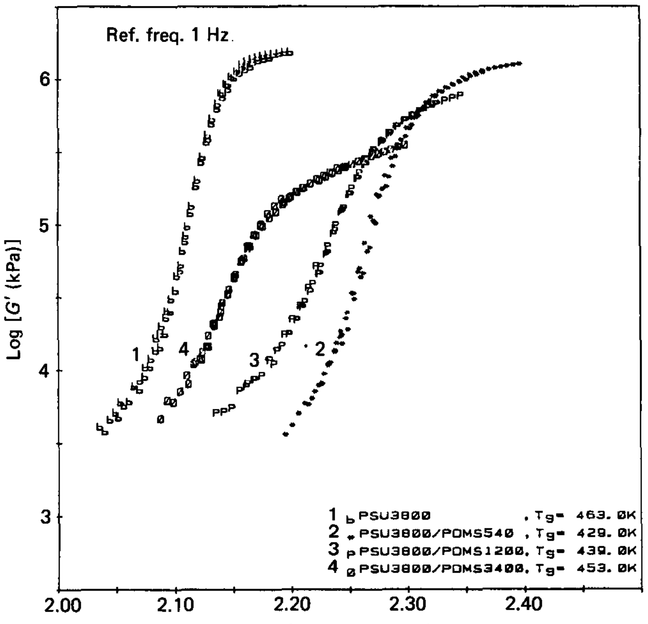

Figure 6 Isochrone master curves of the storage modulus, G', in the PSU glass transition range of the 'triblock' networks as in *Figure 5*

the same rubber plateau value, G'_e, the dependence of this value only on the molecular weight of PSU is confirmed.

The complex temperature dependence of the PSU glass transition on the length of the incorporated PDMS block, suggested by d.s.c.^{1}, is confirmed by the isochrone master curves of the storage modulus of the 'triblock' networks shown in *Figure 6*. Independent of the length of the PSU block, the PSU T_g shift to lower temperatures is maximum for the 'triblock' with the shortest PDMS middle block; but then with increasing molecular weight of PDMS, the PSU glass transition again approaches gradually the T_g of the parent homo-PSU network.

Similar to those of homo-PSU, the changes in T_g are accompanied by a broadening of the loss modulus peak. This broadening increases with increasing molecular weight of the PDMS (*Figure 7*).

The dependence of the moduli of the 'triblock' networks on the molecular weight of the PSU block for constant molecular weight of the PDMS middle block is illustrated by the isochrone master curves of the storage modulus in *Figure 8*. Owing to the fact that the PSU-1200/PDMS-3400/PSU-1200 'triblock' was too soft in the temperature range of the PSU glass transition, it was not possible to study this sample by the torsion bar rheometry method applied for all other samples.

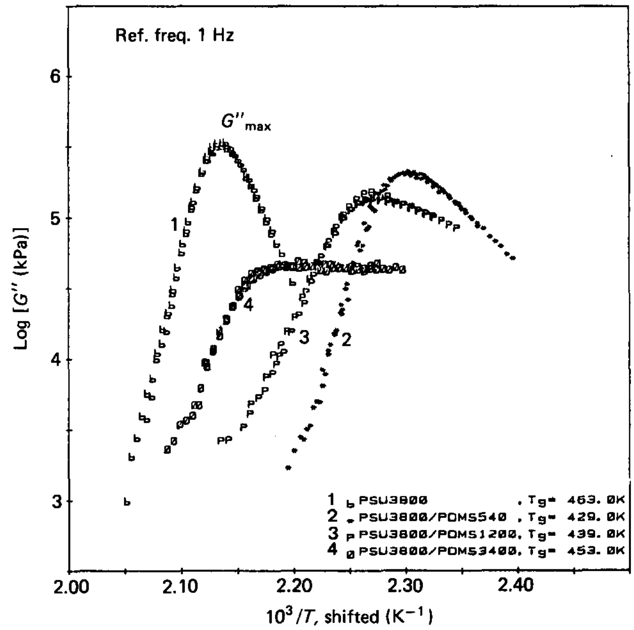

Figure 7 Isochrone master curves of the loss modulus, G'', in the PSU glass transition range of the 'triblock' networks as in *Figure 5*

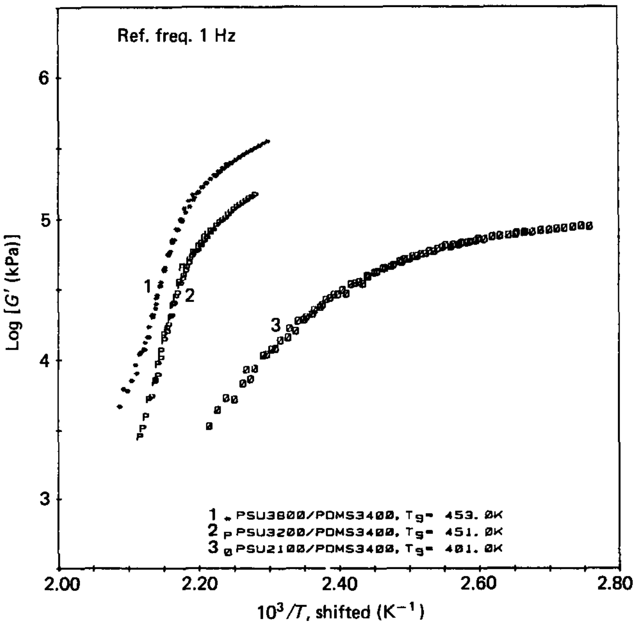

Figure 8 Isochrone master curves of the storage modulus, G', in the PSU glass transition range in 'triblock' networks with constant PDMS-3400 middle block length and different molecular weights of PSU before cure

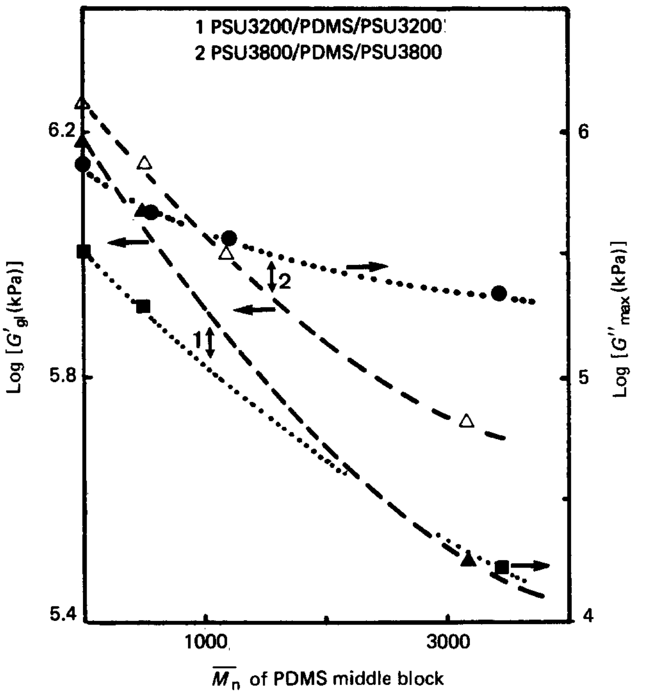

Figure 9 Characteristic moduli of PSU–PDMS–PSU 'triblock' networks. Storage modulus in temperature range below the T_g of PSU, G'_{gl}, and loss modulus at peak maximum, G''_{max}

The variation of the characteristic moduli below the PSU glass transition in 'triblock' networks due to the increasing molecular weight of the soft PDMS block is illustrated in *Figure 9*. Both the storage modulus below T_g of PSU, G'_{gl}, and the peak value of the loss modulus, G''_{max}, decrease with increasing molecular weight of the PDMS, the effect being more accentuated the smaller the molecular weight of the PSU before cure.

In conclusion, it seems that by proper choice of the block length of the components of the 'triblock' network, the mechanical properties are conveniently determinable.

WLF *constants and kinetic characteristics*

For better insight into the rheological behaviour, the data obtained were then used for evaluation of the constants of the WLF relation, the related 'Vogel' temperature, and the temperature-dependent activation energy of flow.

As has been shown in a recent publication by Schneider *et al.*[4], starting with the 'free volume' based WLF relation and the similar 'transition state energy barrier' based Eyring relation, the temperature dependence of the shift factor $\log a_T$ allows a correlation of the temperature-dependent activation energy of flow, $E(T)$, with the constants of the WLF relation, as outlined by the following set of relations:

'free volume'	'energy barrier'
$\eta = A'\exp(B_0 v_{0c}/v_f)$	$\eta = A\exp(E/RT)$
$\log a_T = -C_1 g\dfrac{(T-T_g)}{C_2^g+T-T_g)}$	$\log a_T = -\left(\dfrac{E}{2.3RT_g}\right)\dfrac{(T-T_g)}{T}$
$\dfrac{d\log a_T}{d(1/T)} = \dfrac{C_1^g C_2^g T^2}{(C_2^g+T-T_g)^2}$	$\dfrac{d\log a_T}{d(1/T)} = \dfrac{E}{2.3R}$

so that

$$C_1^g C_2^g\left(\frac{T}{(C_2^g+T-T_g)}\right)^2 = \frac{E(T)}{2.3R} \quad (1)$$

WLF and Arrhenius like dependences of the rheological behaviour are then distinguishable by the fact that the activation energy of flow is temperature-dependent in the WLF range and constant in the Arrhenius range.

The temperature-dependent activation energy of flow in the WLF range of rheological behaviour is related to the ratio at a given point of the slopes of the isochrone and isotherm viscoelastic curves[5] via:

$$\frac{E(T)}{2.3R} = \frac{[\partial(\log G')/\partial(1/T)]_\omega}{[\partial(\log G')/\partial\log\omega]_T} \quad (2)$$

On the other hand, the constants of the WLF relation are dependent on the chosen reference temperature, the correlation being given by the following expressions:

$$\begin{aligned} T_g - C_2^g &= T_0 - C_2^0 = T_V \\ C_1^g C_2^g &= C_1^0 C_2^0 = \text{constant} \end{aligned} \quad (3)$$

T_V is here the so-called 'Vogel' temperature. Rearranging equation (1), one obtains the equation of a straight line:

$$[2.3R/E(T)]^{0.5} = (1/C_1^g C_2^g)^{0.5}(1 - T_V/T)$$

which shows that

$$E \to \infty \qquad \text{for } T = T_V \text{, and } T_\infty = T_V$$

and as

$$T \to \infty \qquad (2.3R/E_\infty)^{0.5} = (1/C_1^g C_2^g)^{0.5}$$

i.e.

$$C_1^g C_2^g = E_\infty/2.3R$$

It follows that for $T = T_V$ the activation energy of flow $E(T) \to \infty$, supporting the idea that at this temperature any mobility in the system is definitely frozen in. The corresponding temperature, further called T_∞, is given by the intercept with the reciprocal temperature axis of the above straight line, obtained by plotting the temperature dependence of the $E(T)$ values in the respective coordinates. This temperature, in fact, has to be in relation with the 'Vogel' temperature obtained from the constants of the WLF equation, and may be compared with the T_2 temperature of the Gibbs–DiMarzio theory of the glass transition[6]. It can therefore be considered also characteristic of the entropic contribution to the viscoelastic flow.

The extrapolation for $T \to \infty$ renders a high-temperature limit value of the activation energy of flow, E_∞, which is directly related with the product of the constants of the WLF equation. This limit E_∞ value may be assumed characteristic for the energetic contribution to the viscoelastic flow. Kinetic support of the WLF constants therefore results.

The representation of the experimental shift factors according to the WLF—and the related 'Vogel' relation (the expression for the latter is shown on the figure)—is illustrated in *Figure 10a*. From the changing slopes of the straight lines, it is evident that each system is characterized by its own WLF constants. The C_1 data thus obtained by the two different equations are compared in *Table 1*.

The temperature dependence of the $E(T)$ data computed in accordance with equation (2) from the ratio of the slopes of the isochrone and isotherm viscoelastic curves at a given point for the set of polymers listed in *Table 1* is presented in *Figure 11*. The levelling off of the $E(T)$ curves in the vicinity of T_g suggests the failure of the

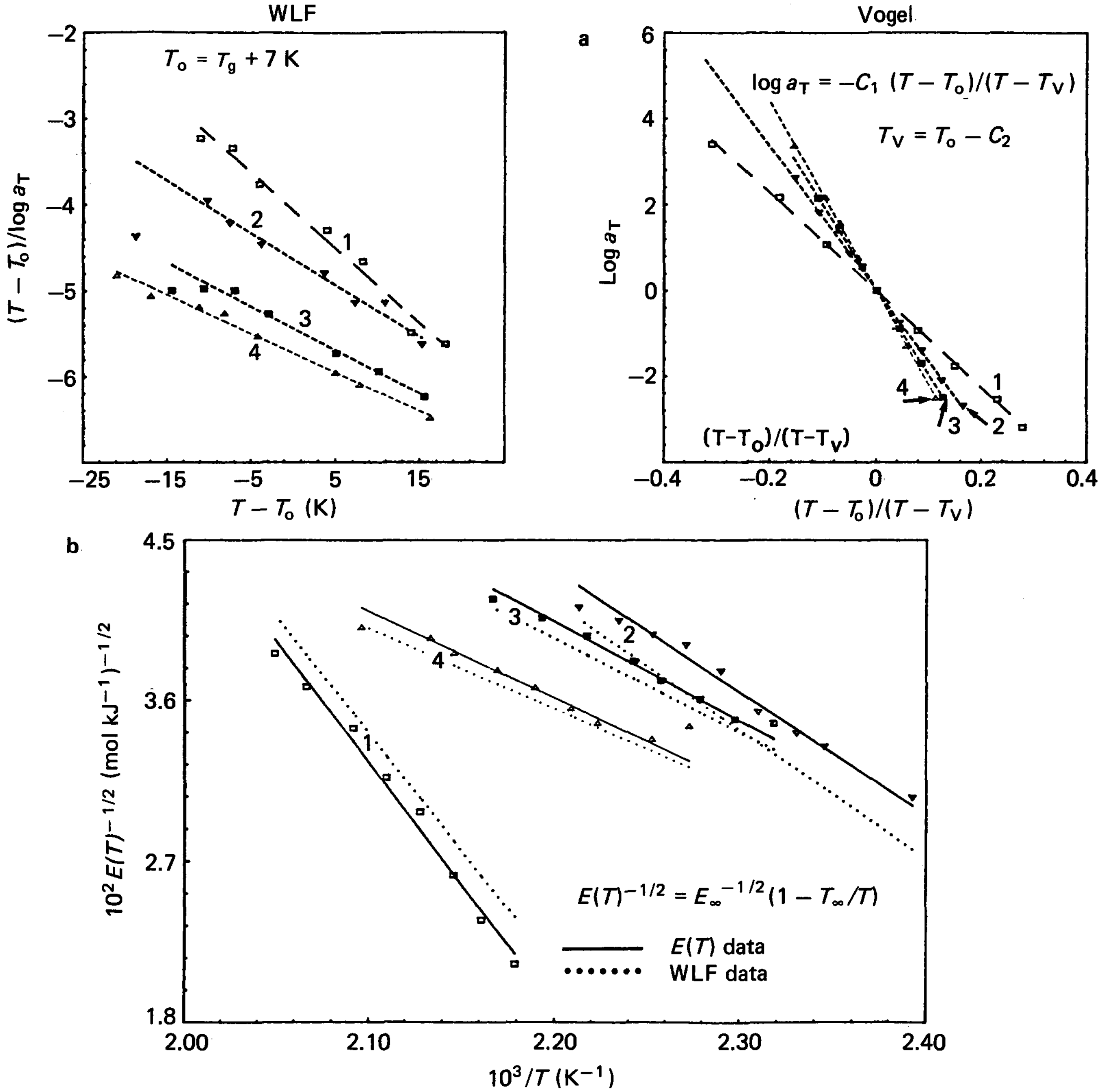

Figure 10 Log a_T and $E(T)$ data of 'triblock' networks. (a) Estimation of WLF constants according to the WLF and 'Vogel' relation (lines). (b) Representation of $E(T)$ data of *Figure 11* according to equation (4). Dotted lines obtained using the WLF constants; polymers numbered in the order given in *Table 1*

Table 1 Thermal and rheological characterization of PSU–PDMS–PSU 'triblocks'

	T_g (K)		C_1			T_V	T_∞	E_∞ (kJ mol^{-1})	
Sample and M_n	Before	After cure	WLF	Vogel	C_2	(K)	(K)	From C_1C_2	$E(T)$
PSU(3800)	420	463	11.24	11.32	46.68	423.3	427.6	10.24	9.53
PSU(3800)/PDMS(540)	409	429	16.63	16.67	77.14	359.7	352.9	24.57	25.88
PSU(3800)/PDMS(1200)	409	439	19.67	19.62	107.02	338.9	341.5	40.32	36.72
PSU(3800)/PDMS(3400)	147/429	147/453	22.14	21.99	126.76	334.2	339.3	53.74	47.67

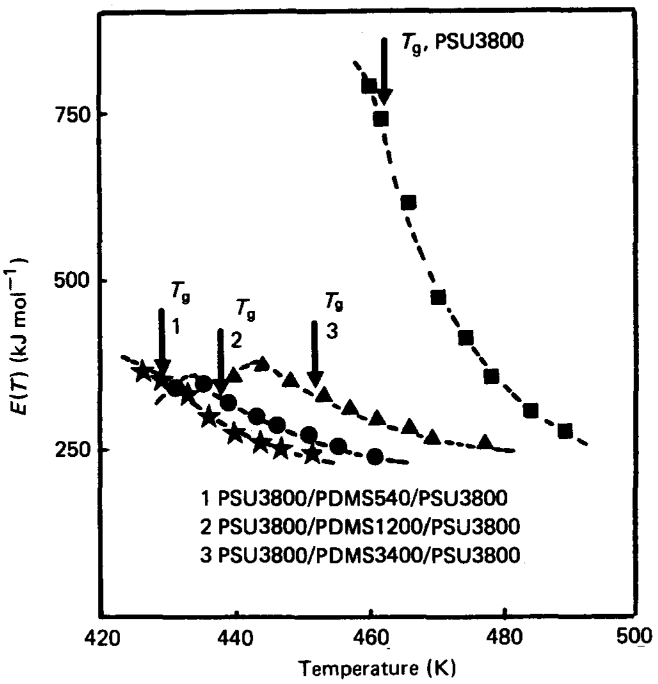

Figure 11 Temperature dependence of $E(T)$ data computed from the slopes of the isochrone and isotherm viscoelastic according to equation (2)

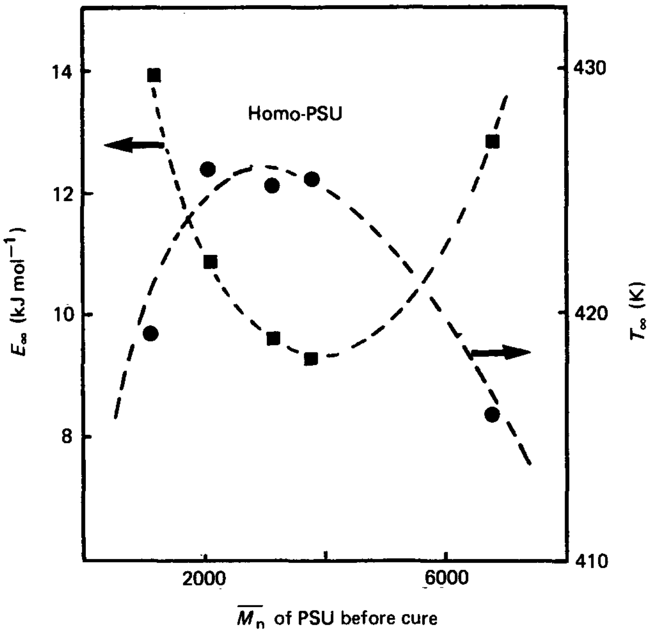

Figure 12 Variation of the characteristic E_∞ and T_∞ data in PSU networks

WLF relation in this temperature range. This is in accordance with the results of Schwarzl *et al.*[7], who observed a deviation in the experimental $\log a_T$ values from predicted WLF behaviour as T_g was approached.

These E(T) values were used in *Figure 10b* for illustration of the temperature dependence according to equation (4) (full lines). In the same figure the representation of the same equation (4), but using the obtained WLF constants, is shown for comparison (dotted lines). The agreement is satisfactory and in *Table 1* both the thermal and the rheological characteristics of the 'triblock' networks presented in *Figure 10* are given.

The variation in the rheological characteristics in the PSU glass transition range for the homo-PSU networks is evidenced in *Figure 12.* It is interesting to note that a 'compensation' effect seems to be at work for the changes of the energetic and entropic contributions, taking into account the molecular weight dependence of those values. Similar change with the molecular weight of the PSU is observed in 'triblock' networks with a constant length of the PDMS soft middle block (*Figure 13*).

The effect on the 'kinetic' data with increasing length of the PDMS middle block is quite different. As expected, owing to the increased mobility of the PDMS chain, the characteristic temperature of entropic allowed onset of chain conformational mobility characteristic for the PSU glass transition range is more reduced the higher the molecular weight of the network forming PSU component. In parallel, the energetic contribution increases, again suggesting the supposed 'compensation' effect as it results from the data shown in *Figure 14*.

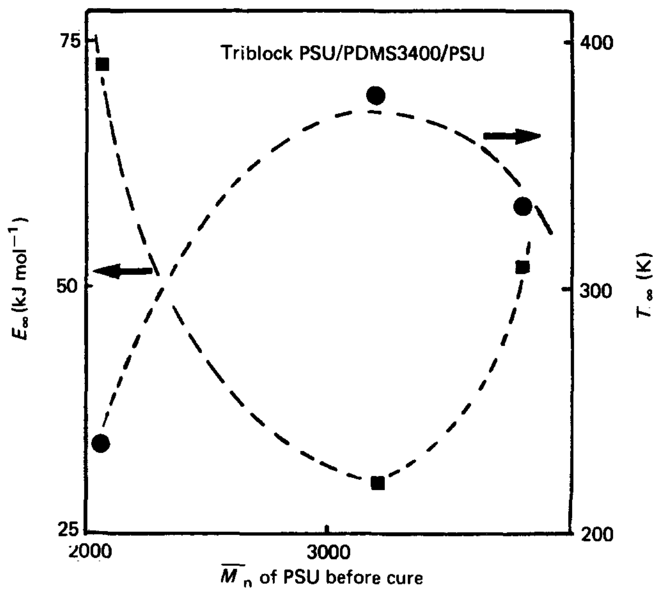

Figure 13 Dependence of the characteristic E_∞ and T_∞ data in 'triblock' networks on the length of the PSU block

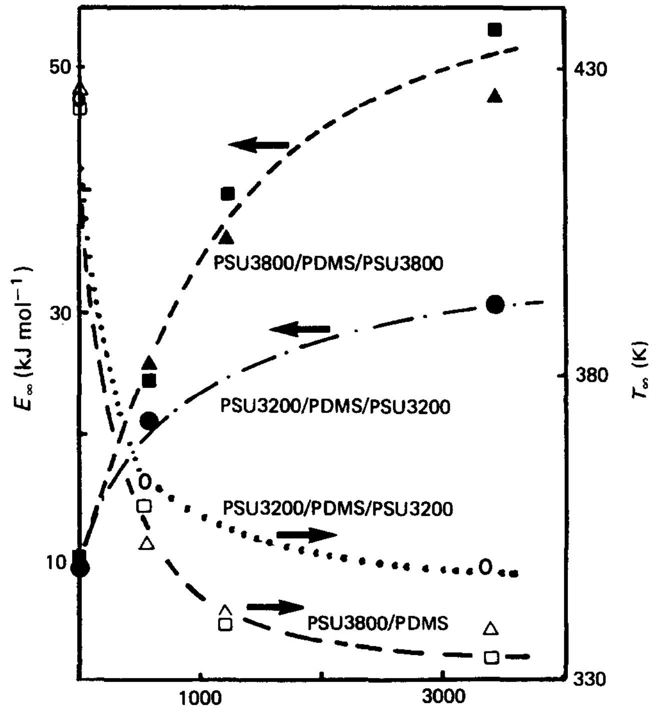

Figure 14 Dependence of the characteristic E_∞ and T_∞ data in 'triblock' networks on the length of the PDMS middle block

CONCLUSIONS

In conclusion, it may be stated that the mechanical properties of PSU–PDMS–PSU 'triblock' networks are determinable by the molecular weight of the component PSU and PDMS blocks. Concerning the rheological behaviour, entropic and energetic contributions are distinguishable. The contributions are related to the constants of the WLF relation. The changes in these contributions, as well as of the WLF constants, are block specific and seem to obey a 'compensation effect' law.

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