of the terminal groups in PCDG side chain, both CH_3 and Cz, are presumably attributed to the bulkiness of the Cz groups which are introduced into the side chain of the polyglutamate. The reason why the bulkiness of the side chain reduces the mobility is not clear at present, although two plausible mechanism, side chain–side chain interactions and/or side chain–solvent interactions, can be imagined.

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Some optical and mechanical properties of an ABC triblock copolymer, styrene/butadiene/2-vinylpyridine, and its hydrochloride salt

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INTRODUCTION

In a previous publication[1] on the optical and mechanical properties of the ABC triblock copolymer styrene/butadiene/α-methylstyrene (S/B/α-MS), we suggest that the presence of the third component C offers a further method of adjusting physical properties without necessarily altering the block molecular weights or rubber-to-glass ratio. In this paper an alternative method for modifying properties is considered: the inclusion of ionic or ionizable groups which confer ionomer character to the triblock copolymer system. Meyer and Pineri[2] have modified the viscoelastic properties of a butadiene/styrene/4-vinylpyridine random copolymer by complexing the pyridyl nitrogen with nickel chloride. This paper reports some optical and mechanical properties of a styrene/butadiene/2-vinylpyridine triblock copolymer (S/B/2-VP) and its hydrochloride salt (S/B/2-VP·HCl).

EXPERIMENTAL

The copolymer and its salt were prepared in our laboratories by Prudence[3]. The copolymer composition and block molecular weights are listed in *Table 1*. The butadiene microstructure is reported as 89.3% 1,4 and 10.3% 1,2 (vinyl).

Details of the light scattering apparatus have been given[4]; it is sufficient to note that a He–Ne laser (λ = 632.8 nm) was used as the light source. Dynamic mechanical data, on strain-free, benzene-cast and compression-moulded samples, were taken over the frequency and temperature ranges of 1 to 10^2 Hz and −120° to +120°C, respectively, using a Rheovibron. Tensile data were taken on ring samples at a test speed of 8.5×10^{-3} m/sec using an Instron tester.

Table 1 Copolymer and salt compositions and block molecular weights

Block	Percentage	Molecular weight $\times 10^{-3}$
S	20	12.5
B	64	40
2-VP	16	10
2-VP·HCl	20	13.5

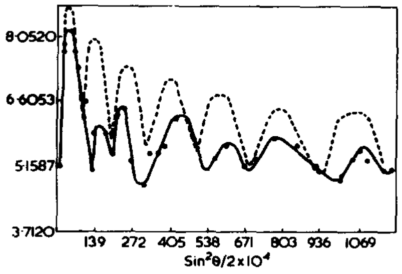

Figure 1 Logarithm of intensity *I* as a function of scattering angle θ. ——, Experimental data; – – –, theoretical data displaced vertically by an arbitrary distance

Table 2 Comparison of scattering dimensions of triblock copolymers

	S/B/2-VP	S/B/S*	S/B/α-MS*
Radius of scattering domain (μm)	2.5	$0.4^{5,8}$	0.4^{1}
Interdomain separation distance (μm)		1.0^{5}	$0.7–1.3^{1}$

* Dimensions are dependent on block molecular weight and casting solvent

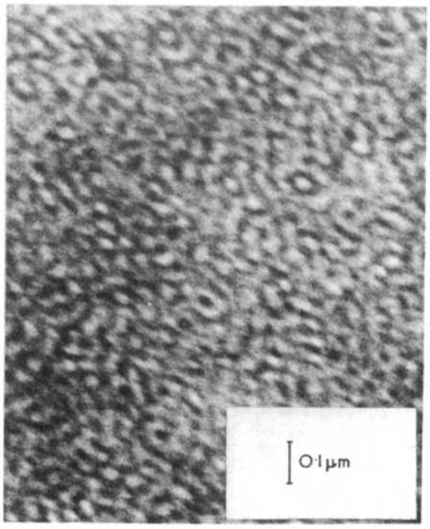

Figure 2 Electron micrograph of S/B/2-VP; magnification × 125 000

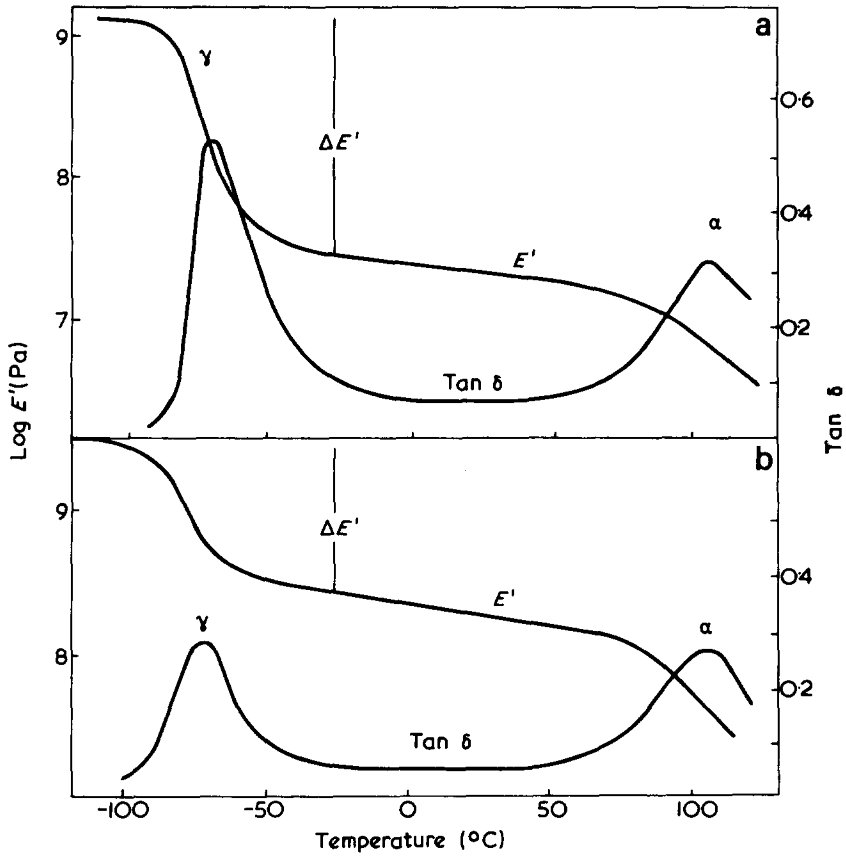

Figure 3 (a) Dynamic mechanical properties of compression-moulded S/B/2-VP at 110 Hz as a function of temperature. (b) Dynamic mechanical properties of compression-moulded S/B/2-VP·HCl at 110 Hz as a function of temperature

RESULTS AND DISCUSSION

In contrast to our previous work with ABA[4,5] and ABC[1] triblock copolymers the Debye–Beuche analysis of light scattering[6] did not explain the scattering behaviour of S/B/2-VP, as the scattering intensity I passed through a number of maxima and minima when plotted as a function of the scattering angle θ (*Figure 1*). The S/B/2-VP scattering data could be fitted to the Rayleigh–Gans expression for spherical particle scattering[7]:

$$I = K[3(\sin x - x\cos x)x^{-3}]^2$$

with a scattering radius r equal to 2.5 μm (*Figure 1*). K and x in the above expression are a constant and $(4\pi/\lambda)r \sin(\theta/2)$, respectively. This fit indicates that large (compared to other triblock domain sizes, *Table 2*) spherical, monodisperse particles occur in this system.

Figure 2 shows a relatively high magnification (× 125 000) electron micrograph of an osmium tetroxide stained, benzene-cast film of S/B/2-VP. At this magnification the interior of a particle, rather than a group of scattering particles, is seen. The scattering particle appears to be an aggregate of small (light, unstained) domains of end blocks dispersed in a (dark, stained) matrix of butadiene. Price *et al.*[9] have shown from selectively stained electron micrographs of a similar ABC triblock copolymer, styrene/isoprene/2-vinylpyridine, that the scattering particles there consist of aggregates of *both* end blocks.

The composition of the two phases might have been deduced from the copolymer composition and solubility parameters δ of the constituents. The almost 2 to 1 excess of butadiene and its relatively low solubility parameter[10] ($\delta = 17.5 \times 10^{-3}\ \mathrm{J^{1/2}/m^{3/2}}$) compared to those of the end blocks[9,10] ($\delta^S = 20.0 \times 10^{-3}\mathrm{J^{1/2}/m^{3/2}}$ and $\delta^{2\text{-VP}} = 21.7 \times 10^{-3}\ \mathrm{J^{1/2}/m^{3/2}}$) probably ensures that the scattering phase is a mixture of end blocks dispersed in a butadiene matrix.

The dynamic mechanical properties at 110 Hz of moulded S/B/2-VP are shown in *Figure 3a* where two relaxation processes are evident: a low temperature γ-process and a high temperature α-process. (The dynamic properties of benzene-cast S/B/2-VP are similar to those of the moulded polymer and are not shown. For the sake of brevity dynamic data taken at 3, 10 and 50 Hz, which were used to calculate the activation enthalpies ΔH of the loss processes, using a plot of log frequency vs. $1/T$ (K) $\tan \delta_{\max}$, are also presented.) The low temperature γ-loss process at –70°C is due to the butadiene glass–rubber transition T_g, and the single high temperature α-loss process at 102°C is due to the glass–rubber transitions of the end blocks, which are similar[10]; $T_g^S = 100°\mathrm{C}$ and $T_g^{2\text{-VP}} = 104°\mathrm{C}$.

Figure 3b shows the dynamic mechanical properties at 110 Hz of S/B/2-VP following quaternization of the pyridyl nitrogen to give the pyridinium salt S/B/2-VP·HCl. The polymer salt is also characterized by α- and γ-relaxation processes. The high temperature α-process has a slightly lower magnitude (tan δ peak height) and activation enthalpy than that for S/B/2-VP, and is located some 6°C higher. The low temperature γ-process, which is located at –70°C, is about one half the magnitude (tan δ peak height and modulus step height $\Delta E'$) of the S/B/2-VP γ-process, but its activation enthalpy is about 20% higher.

The effect of quaternization is also apparent in the height of the dynamic modulus plateau (*Figures 3a* and *3b*) and in the tensile properties shown in *Figure 4*. The modulus plateau of S/B/2-VP·HCl is approximately an order of magnitude higher than that of S/B/2-VP. The stress–strain curve of S/B/2-VP·HCl resembles that of a tightly crosslinked elastomer, whereas those of benzene-cast and compression-moulded S/B/2-VP are more typical of

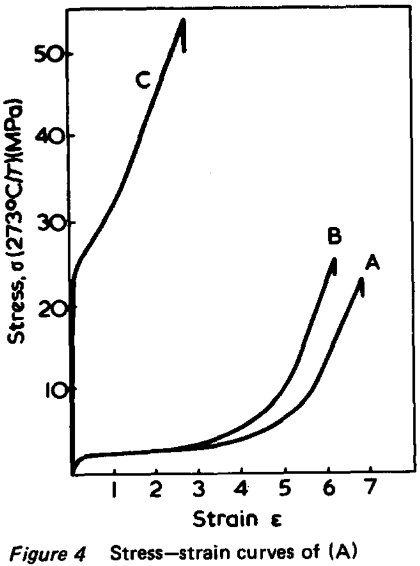

Figure 4 Stress–strain curves of (A) compression-moulded S/B/2-VP; (B) benzene-cast S/B/2-VP; and (C) compression-moulded S/B/2-VP·HCl

Table 3 A summary of the mechanical properties of S/B/2-VP and S/B/2-VP·HC1 and a comparison with those of other triblock copolymers

Mechanical property	S/B/2-VP (moulded)	S/B/2-VP·HCl (moulded)	S/B/S^{8,12,13}	S/B/α-MS^1
Modulus E' 25°C 110Hz (Pa)	2.5×10^7	2.1×10^8	1.0×10^7	2.0×10^8
α-Relaxation process:				
Tan δ, temperature location (°C)	102	108	95	150
Tan δ, peak height	0.31	0.27	0.50	0.90
ΔH (kJ/mol)	374	376	–	–
γ-Relaxation process:				
Modulus step height, $\Delta E'$	~2 decades	~1 decade		
Tan δ, temperature location (°C)	–70	–70	–70	–60
Tan δ, peak height	0.52	0.28	0.60	0.35
ΔH (kJ/mol)	105	122	–	–
Reduced stress (273/T) at 100% strain (MPa)	2	31	2	5
Shore 'A' Hardness	64	94	41–63	80

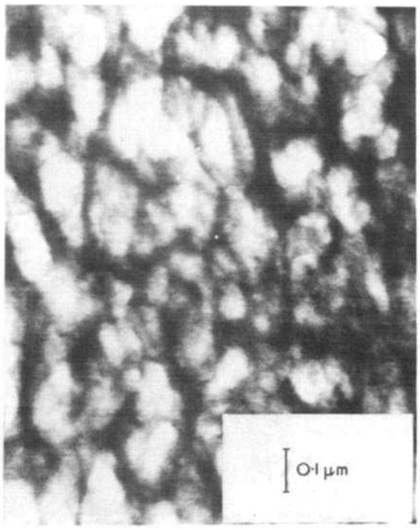

Figure 5 Electron micrograph of S/B/2-VP·HCl; magnification X 125 000

triblock copolymers. A summary and comparison of the mechanical behaviour of unquaternized and quaternized S/B/2-VP and two other triblock copolymers having a butadiene matrix is given in *Table 3.*

Ion clustering, i.e. ionomeric behaviour[2,14], is a possible explanation for the observed changes in physical properties following quaternization: increases in α-process temperature location and rubbery modulus plateau height; decreases in α-process intensity and solubility in organic solvents; and tensile behaviour resembling that of a tightly crosslinked elastomer. A high magnification (x 125 000) electron micrograph of the inside of a S/B/2-VP·HC1 scattering particle (*Figure 5*) also shows that the scattering particles consist of aggregates of domains. These inner domains are much larger, almost by a factor of five, than those of S/B/2-VP.

The reason for the pronounced effect of quaternization on the γ-relaxation process may be the larger domain size of the S/B/2-VP·HC1 polymer salt. In order to form the larger domains the butadiene matrix chains become strained and lose some of their mobility. This is reflected in the reduction in tan δ peak height and the increased activation enthalpy of the S/B/2-VP·HC1 γ-process. A slight increase in the temperature location of this γ-process might have been expected. The lack of matrix mobility is consistent with the enhanced tensile strength and reduced elongation at break of the copolymer salt.

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