area under the melting curve with phase indices. The peak areas have been measured as shown in *Figure 1* for a sample of draw ratio 5.0. Appropriate correction factors have been used for melting peak areas due to crystallization before melting. This was carried out with the help of standard samples whose heat of fusions are known. The peak area thus measured is plotted as a function of crystalline plus intermediate and crystalline phase indices and are shown in *Figures 2* and *3* respectively. It is found that peak area is directly related to crystalline plus intermediate phase index. It is likely that the oriented amorphous regions of the samples attain a higher order of perfection with increasing temperature at a heating rate of 20°C/min here and finally melt, explaining the linear relationship. The relationship between peak area and crystalline phase index is found to give a continuous curve as shown in *Figure 3*. This can be used for the determination of crystalline phase index of an unknown sample. Thus the experimental relationships shown in *Figures 2* and *3* provide a procedure for the determination of crystalline, intermediate and amorphous phase indices of PET fibres from d.t.a. thermograms directly.

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^{13}C spin-lattice relaxation study of molecular motions of sidechains in α-helical polyglutamates

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A spin–lattice relaxation time T_1 from ^{13}C n.m.r. is useful for elucidating molecular motions of polypeptides containing the ring groups such as phenyl[1,2] and pyrrolidinyl[3]. A ^{13}C T_1 of a protonated carbon in macromolecules is governed mainly by dipole–dipole interactions with the directly attached protons[4]. It is demonstrated that the correlation times of carbons in a side chain attached to α-helical polyglutamates satisfy the extreme narrowing condition, and therefore one can simply interpret observed ^{13}C T_1s under this condition[2].

In a previous paper[5] it was shown that there is no internal rotation of the pendant carbazolyl (Cz) group in poly(*N*-vinylcarbazole) (PVCz) on the basis of the T_1 measurements. The hindrance of the side chain motion in PVCz arises presumably from the bulkiness of the Cz group[5,6]. It is interesting to find out how much the motion of a polyglutamate molecule is influenced when a bulky group such as Cz is introduced at the end of the side chain.

^{13}C n.m.r. spectra of the α-helical polyglutamates generally show no apparent peak corresponding to the α-carbon in the backbone. This is a result of line-broadening caused probably by polymer aggregation, if no solvent to prevent the aggregation (non-aggregate solvent) was added. In such non-aggregate solvents as dichloroacetic acid and trifluoroacetic acid (TFA), it is found that charge-transfer complexes form between the Cz group and the solvents*, and the molecular motions of the side chain are drastically disturbed by the complex formation. Thus, it is hard in such a case to distinguish the internal rotation of the side chain from the overall reorientations of the backbone. In order to overcome this difficulty, we prepared a modified poly(γ-methyl-D-glutamate) (PCDG) in which CH_3 groups are partly substituted by the Cz-ethyl groups so that we can compare T_1 values of the different terminal groups on the side chain attached to the identical backbone and obtain some information on the molecular motions of the side chains.

For comparison among the molecular motions of the different side chains in the α-helical polyglutamates ^{13}C T_1 of the terminal groups in the polymers, such as PCDG, poly(γ-methyl-D-glutamate) (PMDG) and poly(γ-benzyl-L-glutamate) (PBLG), dissolved in the neat helicogenic solvents were measured by the partly relaxed Fourier transform (*PRFT*) method. PMDG (degree of polymerization; *DP* = 85) and PBLG (*DP* = 1320) were supplied by Ajinomoto Co. PCDG (*DP* = 85), the partly ester-interchanged PMDG, which consists of 78.8% of β-*N*-carbazolylethyl-D-glutamate units and 21.2% of methyl-D-glutamate units was prepared from PMDG using a previously published method[7]. ^{13}C T_1 was measured by the PRFT method at 30°C employing either a Varian CFT-20 n.m.r. spectrometer (operating at 20 MHz) or a JEOL JNM-FX100 n.m.r. spectrometer (25.15 MHz). The sample solution was contained in a 10 mm o.d. n.m.r. tube, and no degassing was carried out as no appreciable effect of oxygen molecules to the ^{13}C relaxation in polymer solution has been reported[8]. Either $CDCl_3$ or $CDCl_2CDCl_2$ was used as the solvent, and TMS as the internal reference.

A set of PRFT spectra of PCDG in $CDCl_3$ is shown in *Figure 1*. The assignment of each peak was carried out by comparing the peaks with the ^{13}C spectra of poly(*N*-vinylcarbazole)[5] and of the other polyglutamates[1,2], and are given in *Figure 1*. The T_1 values of the resolved peak were determined by the semilog plot of the peak height against time[9], which lies fairly well on a straight line. In *Figure 2* the obtained T_1 values are shown as $N{\cdot}T_1$, where N is the number of the attached protons, for the several carbons in the side chains.

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* The solution changes from colourless to blue on addition of the non-aggregate solvents

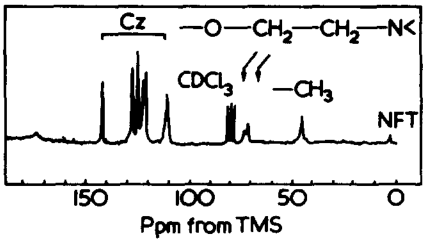

Figure 1 ^{13}C spectrum of PCDG (280 mg) in $CDCl_3$ (1 ml)

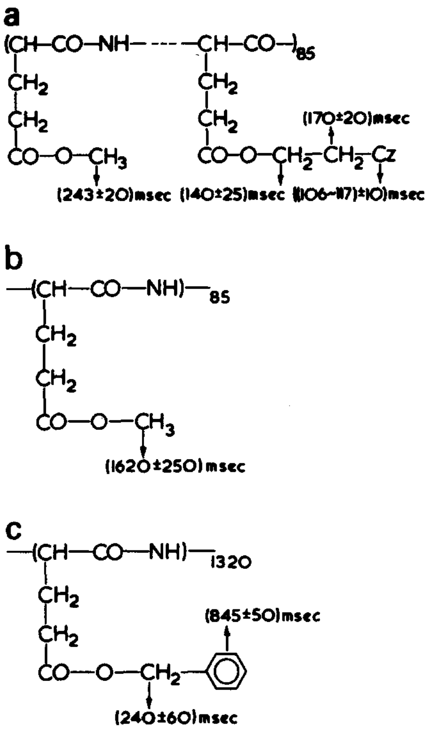

Figure 2 ^{13}C T_1 values of (a) PCDG; (b) PMDG; (c) PBLG, in $N \cdot T_1$ in msec. Each value was obtained by the *PRFT* method. PCDG, by CFT-20 in $CDCl_3$; PMDG, by CFT-20 in $CDCl_2CDCl_2$; and PBLG by FX100 in $CDCl_3$

In the extreme narrowing condition, which holds for such a system, the T_1 is inversely proportional to the correlation time, τ_c, provided that the relaxation process is mainly determined by the dipole–dipole interactions[10]. Therefore, shorter T_1 means longer correlation time in the systems. The observed value of $N \cdot T_1$ for the CH_3 in PCDG is nearly twice as large as those of the Cz ring-carbons, in spite of the fact that both groups are pending on the identical backbone. A molecular motion of a side chain is, in general, a superposition of the two modes of the motions, one of the main chain and the other of the side chain itself. Thus the observed correlation time τ_c, which characterizes the molecular motion, can be split into the two τ_cs corresponding to the two modes, and expressed as follows[11]:

$$\left(\frac{1}{\tau_c}\right)_{\text{obs}} = \left(\frac{1}{\tau_c}\right)_R + \left(\frac{1}{\tau_c}\right)_I$$

where $(\tau_c)_{\text{obs}}$, $(\tau_c)_R$ and $(\tau_c)_I$ represent τ_c derived from the observed T_1, τ_c for the backbone reorientation and τ_c for the internal rotation of the side chain, respectively. If the carbons of the different species of the side chains, which are attached to the same backbone, have different $N \cdot T_1$ values, this difference indicates some disparity in the internal rotation of the side chain provided that the local molecular motions of the polymer backbone are not affected by the species of end-groups in the side chain. It was found that this is the case for PCDG as shown in *Figure 2*. A smaller observed value of $N \cdot T_1$ for the Cz group than for the CH_3 implies a longer correlation time $(\tau_c)_I$ of the Cz group, which means more restricted motion of the Cz group than the CH_3, because the same $(\tau_c)_R$ is reasonably assumed for both the Cz and the CH_3 which are pendant from the identical backbone. It is interesting to note that the molecular motion of the Cz group is more hindered than that of the CH_3 in spite of the farther separation from the backbone.

There are several CH_2 carbons in PCDG; the β and γ CH_2 carbons and the CH_2 carbons in the Cz-ethyl. Little information is known on the dependence of the methylene carbon chemical shift on an adjacent group, and the assignment of the CH_2 carbons were made on the basis of the line-broadening of the peaks. It is generally believed that the line-widths of the β and γ methylene peaks are too broad to be detected without adding the non-aggregate solvent[1,2]. Thus, one can attribute the peaks observed in the range of the methylene chemical shift to the CH_2 carbons in the Cz-ethyl group. The broader peaks in the observed methylene band are assigned to the carbon attached to the ester oxygen atom, since this carbon is less mobile as it is closer to the backbone. T_1 measurements of these CH_2 carbons are less accurate than the others because of the smaller S/N ratio of these peaks. Taking account of this error, one can say that the $N \cdot T_1$ values of these carbons of the two CH_2 groups in the Cz ethyl were found to be approximately the same as each other and roughly one half of the methyl $N \cdot T_1$. Moreover, the $N \cdot T_1$ of the Cz carbons is closer to those of the two CH_2 carbons. It follows from these facts that the Cz-ethyl group in the side chain is more restricted than the methyl end, and also that the Cz-ethyl group moves as a solid unit in which no internal rotations about the C–C and C–N bonds occur.

The T_1 values of benzyl carbons of PBLG in neat $CDCl_3$ are very close to those reported in the literature[1], where T_1 were obtained from PBLG in a solvent different from our systems. This agreement suggests that the solvent plays no important role in the molecular motion of the side chain in the α-helical polyglutamates. The observed value of $N \cdot T_1$ from the phenyl carbons is larger than that of the CH_2 in the benzyl group in the case of PBLG. This means that the correlation time of the phenyl is shorter than the CH_2 and the phenyl ring rotates additionally in reference to the CH_2. The $N \cdot T_1$ value of the CH_3 carbon in PMDG is much larger than that of the same group in PCDG. Since the used samples of PCDG and PMDG have the same *DP* as well as a similar α-helical conformation, the skeletal reorientations of the polymers are assumed to be nearly the same, i.e. $(\tau_c)_R$ in equation (1) is taken to be equal for the two polymers. Therefore the above-mentioned difference in $N \cdot T_1$ can be ascribed to difference of $(\tau_c)_I$ in equation (1), namely of the internal rotation of the sidechain. Although different solvents are used in these two observations†, it is plausible to attribute the observed difference in T_1 to the variation in the side chain of these polymers, PCDG and PMDG, rather than difference in solvent species, because the solvent does not contribute to a side chain molecular motion responsible for the ^{13}C T_1, as mentioned above. Thus, one may say that the internal rotation of the CH_3 group in PCDG is much more hindered than that of the CH_3 in PMDG. From the above-mentioned comparison, one is lead to a conclusion that the terminal groups in PCDG side chains, even the CH_3 are not rotating so freely as in α-helical PMDG and PBLG. Furthermore, the internal rotation of Cz ring relative to CH_2 in the Cz-ethyl group is actually hindered and this part of the side chain in PCDG seems rather rigid. This restriction in the rotation in the Cz-ethyl presents an interesting contrast to the behaviour of the benzyl group in PBLG, which is freely rotating with respect to the CH_2 adjacent to the phenyl. No internal rotation of the Cz terminals and the decreased mobility

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† PMDG in $CDCl_3$ gave a ^{13}C *FT* spectrum with a very small S/N ratio, and T_1 was not successfully obtained

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

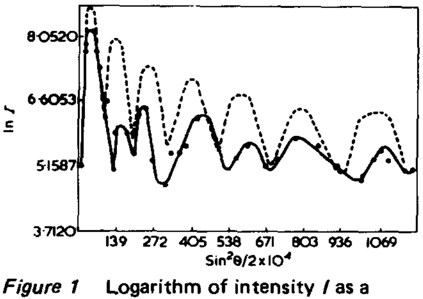

Figure 1 Logarithm of intensity *I* as a function of scattering angle θ. ———, Experimental data; – – –, theoretical data displaced vertically by an arbitrary distance

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

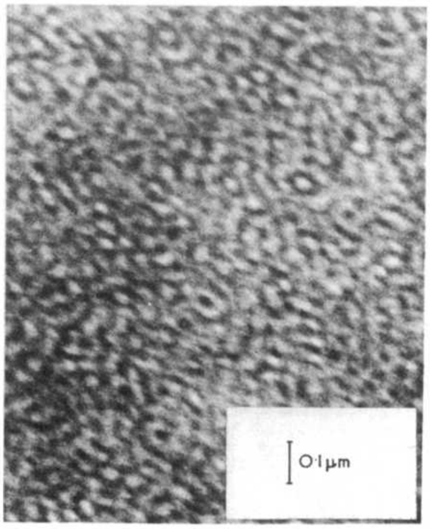

Figure 2 Electron micrograph of S/B/2-VP; magnification × 125 000