# Block copolymers with a polyvinyl and a polypeptide block: factors governing the folding of the polypeptide chains

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AB block copolymers polystyrene–poly(γ-benzyl-L-glutamate) (SG) of various molecular weights and compositions were synthesized and studied by X-ray diffraction and infra-red spectroscopy. They exhibit lamellar mesophases in the solid state and in dioxane concentrated solution. Each sheet of the lamellar structure results from the superposition of two layers: one formed by the polyvinyl chains in a disordered conformation, the other formed by the polypeptide chains in an α-helix conformation arranged in a hexagonal array and generally folded. The comparison of the lamellar structure of copolymers polystyrene–poly(γ-benzyl-L-glutamate) (SG), polybutadiene–poly(γ-benzyl-L-glutamate) (BG) and polystyrene–poly(ε-carbobenzoxy-L-lysine) (SCK) showed that: (1) for the three types of copolymers (copolymers SG or BG or SCK) the number of folds of the polypeptide chains increases with the molecular weight of both the polyvinyl and the polypeptide blocks; (2) for copolymers of fixed molecular weight of the polyvinyl block and fixed degree of polymerization of the polypeptide block the number of folds of the polypeptide chains depends upon the nature of both the polyvinyl and the polypeptide blocks: a polypeptide chain is more folded when it is linked to a polystyrene chain than to a polybutadiene chain but a poly(ε-carbobenzoxy-L-lysine) chain is more rigid than a poly(γ-benzyl-L-glutamate) chain.

**Keywords** Block copolymers; polypeptides; structure; conformation; chain folding; X-ray diffraction

## INTRODUCTION

Some years ago, we undertook the synthesis and the structural study of AB block copolymers with a vinyl and a peptide block[1-4] because of their practical and biological interest. The technological interest of vinyl–peptide block copolymers results from the ability of polypeptide chains to exhibit numerous conformations (helices of various types, parallel or antiparallel β chains, coiled chains...) with varying properties. The biological interest of vinyl–peptide block copolymers is related both to the possibility of preparing model membranes where the copolymers play the part of 'amphipatic integral proteins'[3], and to the improvement of compatibility with blood resulting from the introduction of a peptide block in copolymers[5].

We showed that AB vinyl–peptide block copolymers exhibit an original lamellar structure both in the solid state and in concentrated solution in different solvents. Each sheet of the lamellar structure results from the superposition of two layers, one formed by the polyvinyl chains in a disordered conformation, the other formed by the polypeptide chains in an α-helix conformation, arranged hexagonally and generally folded[2,4].

In this paper we describe the structure of block copolymers polystyrene–poly(γ-benzyl-L-glutamate) (SG) of different molecular weights and compositions and we compare them with copolymers polybutadiene–poly(γ-benzyl-L-glutamate) (BG)[1,2] and polystyrene–poly(ε-carbobenzoxy-L-lysine) (SCK)[4] in order to show the respective influence of the different factors that govern the folding of the polypeptide chains.

## EXPERIMENTAL

### *Materials*

*Solvents.* Tetrahydrofuran (THF), benzene, dioxane, *N,N*-dimethylformamide (DMF) were purified as already described[1,6].

*Monomers.* Styrene was purified under high vacuum[6], γ-benzyl-L-glutamate was prepared by action of benzylic alcohol on glutamic acid[7] and the γ-benzyl-L-glutamate-*N*-carboxyanhydride (NCA) was obtained from the amino acid by the phosgene method as improved by Fuller *et al.*[8].

*Carbon dioxide, thionyl chloride ($SOCl_2$) and hexamethylenediamine.* These were purified as described elsewhere.

*Initiator:* Cumyl potassium was prepared under high vacuum[9].

### *Synthesis of block copolymers*

*Polymerization of the first block.* The first block, polystyrene (PS) was prepared by anionic polymerization in an all glass apparatus under high vacuum in dilute THF solution (less than 5%) at low temperature (−70°C) with cumyl potassium as initiator[6,9].

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*Carboxylation of the polystyrene block.* A large excess of dired and purified carbon dioxide was added under vacuum to the vigorously stirred THF solution of the living PS, an immediate decoloration of the solution occurred and a carboxylated PS was obtained. After addition of HCl the polymer was precipitated, washed and dried under vacuum. Carboxylation was verified by Rhodamine G[10] and titrated with sodium methoxide[11] and found to be higher than 95%.

*Amination of the carboxylated polystyrene.* A dilute (5%) benzene solution of carboxylated PS is refluxed for 4 h with 30 equivalents of $SOCl_2$ in excess. Solvent, $SOCl_2$ in excess and hydrogen chloride formed are evaporated under vacuum. The polymer is dissolved in dry benzene and evaporated again twice. Then the polymer in dilute dry benzene solution is poured into a vigorously stirred benzene solution of hexamethylene diamine in large excess. The aminated polystyrene is precipitated into methanol and purified by three further precipitations to eliminate any residual trace of hexamethylene diamine. The yield of amination (always higher than 80%) is measured by a potentiometric titration[12,13], by a conductimetric titration[11] and by dinitrophenylation[11].

*Polymerization of the polypeptide block.* The polymerization of the NCA of γ-benzyl-L-glutamate initiated by the primary amine function of the aminated polystyrene (PS–$NH_2$) was carried out in the absence of moisture, at room temperature in DMF solution using a total concentration of PS–$NH_2$ and NCA between 2 and 5%. The polymerization was followed by i.r. spectroscopy (disappearance of the bands at 1860 $cm^{-1}$ and 1790 $cm^{-1}$, characteristic of the NCA).

*Fractionation of block copolymers*

Eventual homopolystyrene corresponding to the PS which was not aminated was precipitated by formic acid and eventual homopoly(γ-benzyl-L-glutamate) was precipitated by cyclohexane. Then copolymers were fractionated using a ternary mixture DMF/ethyl acetate/cyclohexane (1/2/3 in volume) as a solvent mixture and methanol as a precipitant.

*Characterization of block copolymers*

The molecular weight of the polystyrene block was determined by osmometry in toluene at 37°C (Mechrolab 503) and gel permeation chromatography in THF at room temperature (Waters Associates); the ratio $\bar{M}_w/\bar{M}_n$ was always between 1.05 and 1.10. Determinations of $\bar{M}_n$ before and after amination of the polymer showed that no detectable coupling occurred during amination.

The composition in polypeptide of the copolymers polystyrene–poly(γ-benzyl-L-glutamate) (SG) was determined by analysis of the nitrogen content of the polymer and by $^1H$ n.m.r. spectroscopy at 250 MHz (Cameca TSN.250) in $CDCl_3$ by comparing benzyl $CH_2$ and styryl $CH_2$ peak areas.

*Determination of the structure of block copolymers*

The structure of the fractionated copolymers and the conformation of their polypeptide chains were studied in dioxane solution and in the dry state by X-ray diffraction and infra-red spectroscopy. X-ray diffraction studies were performed with a Guinier type focusing camera using monochromatic X-rays (Cu $K_{\alpha 1}$) and operating under vacuum[15,16].

## RESULTS AND DISCUSSION

*Structure of copolymers polystyrene–poly(γ-benzyl-L-glutamate) (SG)*

The study by X-ray diffraction and infra-red spectroscopy of block copolymers SG with compositions between 18 and 84% of polypeptide has shown that they exhibit a periodic lamellar structure in concentrated solution of dioxane (less than about 50% of solvent) and in the dry state (after evaporation of dioxane at a slow rate). This is similar to that of copolymers polybutadiene–poly(γ-benzyl-L-glutamate) (BG)[2] and polystyrene–poly(ε-carbobenzoxy-L-lysine) (SCK)[4].

(1) *Description of the structure*

This lamellar structure consists of plane, parallel, equidistant sheets; each elementary sheet of thickness $d$ results from the superposition of two layers, one of thickness $d_A$ formed by the polystyrene blocks in a more or less random coil conformation; the other, of thickness $d_B$, formed by the poly(γ-benzyl-L-glutamate) chains in an α-helix conformation perpendicular to the interface, assembled hexagonally and generally folded (*Figure 1*).

The characteristic parameters of the lamellar structure are:

(i) the total thickness $d$ of a sheet and the lattice parameter $D$ of the hexagonal array formed by the polypeptide chains, both directly deduced from X-ray patterns.

(ii) the thickness $d_A$ and $d_B$ of the polystyrene and polypeptide layers and the average surface $S$ available for a molecule at the interface between the two layers, calculated using formulae (1), (2) and (3) based on simple geometrical considerations.

(iii) the surface $\Sigma$ available to a polypeptide helix and derived from $D$ using formula (4).

(iv) the projection $h$ on the helix axis of the distance between two polypeptide residues given by formula (5).

(v) the average length $\bar{L}$ of a helix given by formula (6).

(vi) the number of folds $v$ of the polypeptide chains and the number of times $\mu$ that a polypeptide chain crosses the polypeptide layer thickness $d_B$, given by formula (7).

$$d = d_A + d_B \tag{1}$$

$$d_B = d\left[1 + \frac{CX_A V_A + (1-C)\varphi_A V_S}{CX_B V_B + (1-C)\varphi_B V_S}\right]^{-1} \tag{2}$$

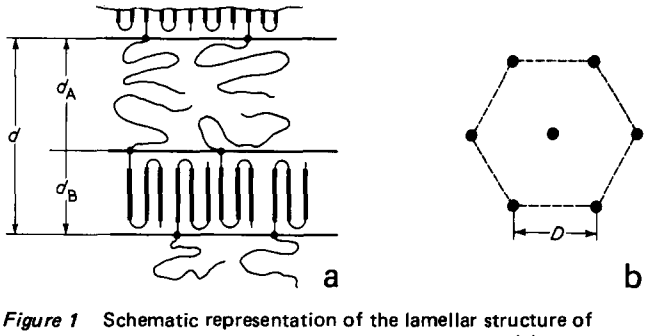


*Figure 1* Schematic representation of the lamellar structure of copolymers with a polyvinyl and a polypeptide block. (a) $d$ = inter-sheet spacing; $d_A$ = thickness of the layer containing the polyvinyl chains; $d_B$ = thickness of the layer containing the folded polypeptide helices; (b) hexagonal array of the polypeptide helices: $D$ = distance between two helices

*Table 1* Influence of the molecular weights of the polypeptide and polyvinyl blocks on the number of folds of the polypeptide chains in block copolymers polystyrene–poly(γ-benzyl-L-glutamate) (SG)

| Copolymer | $\bar{M}_n$ PS[a] | % PG[b] | $\bar{M}_n$ PG[b] | $\bar{P}_n$ PG[b] | $\bar{L}$ (Å) | $d_B$ (Å)[c] | $d_B/c$[d] | $\mu$[c] | $\nu$ |
|---|---|---|---|---|---|---|---|---|---|
| SG.11 | 25000 | 31 | 11200 | 51.3 | 77 | 79 | | 0.98 | 0 |
| SG.12 | 25000 | 39 | 16000 | 73 | 109.5 | 56 | 2.07 | 1.96 | 1 |
| SG.13 | 25000 | 41 | 17400 | 79.3 | 119 | 61 | 2.26 | 1.95 | 1 |
| SG.14 | 25000 | 47 | 22200 | 101.2 | 152 | 49 | 1.82 | 3.10 | 2 |
| SG.15 | 25000 | 50 | 25000 | 114 | 171 | 56 | 2.07 | 3.05 | 2 |
| SG.16 | 25000 | 58 | 34500 | 157.6 | 236.5 | 78 | 2.89 | 3.03 | 2 |
| SG.17 | 25000 | 64 | 44500 | 203 | 304.5 | 78 | 2.89 | 3.90 | 3 |
| SG.18 | 25000 | 71 | 61200 | 279.5 | 419.0 | 82 | 3.04 | 5.11 | 4 |
| SG.19 | 25000 | 94 | 131200 | 599.3 | 899 | 112 | 4.15 | 8.03 | 7 |
| SG.7 | 38700 | 18 | 8500 | 39 | 58.5 | 27.5 | 1.02 | 2.13 | 1 |

[a] PS: polystyrene block
[b] PG: poly(γ-benzyl-L-glutamate)
[c] $d_B$ and $\mu$ values correspond to dry copolymers
[d] The $d_B/c$ ratio has significance only when the polypeptide chains are folded. $c = 18h = 27$ Å = repeat unit along the helix axis

$$S=\frac{2M_BV_B}{Nd}\left[1+\frac{X_AV_A}{X_BV_B}+\frac{(1-C)}{C}\frac{V_S}{V_B}\frac{1}{X_B}\right] \quad (3)$$

$$\Sigma=\frac{\sqrt{3}}{2}D^2 \quad (4)$$

$$h=\frac{2}{\sqrt{3}}\frac{mV_B}{ND^2} \quad (5)$$

$$\bar{L}=h\,P_n=1.5\,P_n \quad (6)$$

$$\mu=\nu+1=\bar{L}/d_B \quad (7)$$

with:

$C$ copolymer concentration (in g per g in solution)
$X_A$ weight fraction of the polystyrene block in the copolymer
$X_B$ weight fraction of the polypeptide block in the copolymer
$V_A$ specific volume of the polystyrene block: $V_A=0.852$
$V_B$ specific volume of the polypeptide block: $V_B=0.785$
$V_S$ specific volume of the solvent, $V_S=0.967$ for dioxane
$\varphi_A$ and $\varphi_B$ partition coefficient of the solvent ($\varphi_A+\varphi_B=1$). From the study of respective intensities of the different orders on X-ray patterns we have found that $\varphi_A=0.80$ and $\varphi_B=0.20$
$M_B$ number average molecular weight of the polypeptide block
$N$ Avogadro's number
$m$ molecular weight of a benzyl glutamate unit $m=219$
$P_n$ number average degree of polymerization of the polypeptide block.

(2) *Justification of the structure*

The lamellar character of the structure is demonstrated by X-ray diffraction (presence in the region of very low angles on X-ray patterns of a set of 3–5 sharp lines with Bragg spacings in the ratio 1, 2, 3, 4, 5).

The hexagonal packing of the polypeptide chains is also established by X-ray diffraction (presence in the region of low angles on X-ray patterns of a set of 3 sharp lines with Bragg spacings in the ratio 1, $\sqrt{3}$, $\sqrt{4}$).

The α-helix conformation of the polypeptide chains is demonstrated by infra-red spectroscopy (bands Amide I and Amide II at 1655 and 1545 $cm^{-1}$ respectively) and by X-ray diffraction (the value deduced from the parameter $D$ of the hexagonal lattice and the molecular characteristics of the copolymers for the projection on the helix axis of the distance between two polypeptide residues: $h=1.50\pm0.02$ Å is in good agreement with an α-helix).

The folding of the polypeptide chains is deduced from the comparison of their average length $\bar{L}$ ($\bar{L}=h\,\bar{P}_n$) with the thickness $d_B$ of the polypeptide layer. *Table 1* shows that the polypeptide chains are folded from 1 to 7 times except for the copolymer SG.11 and that the polypeptide chains seem to fold after an integer number of repeat units ($d_B=nc$ with $c=27$ Å = the repeat unit along the helix axis). Folding of the polypeptide chains after crossing half the thickness of their layer and a tilt of the polypeptide chains on the plane of the lamellae are rejected for reasons already discussed[2,4,17].

(3) *Influence of the solvent concentration*

All the copolymers SG studied have a similar behaviour *versus* solvent concentration. When the dioxane concentration increases:

(i) the total thickness $d$ of a sheet and the thickness $d_A$ of the polystyrene layer both increase,

(ii) the thickness $d_B$ of the polypeptide layer remains nearly constant,

(iii) the specific surface $S$ at the interface and the surface $\Sigma$ occupied by a polypeptide helix both increase, but the ratio $S/\Sigma$ is independent of the solvent concentration and $S/\Sigma=2\,\mu$ for all copolymers in agreement with our model of the structure.

*Figures 2*, *3* and *4* illustrate this behaviour for 3 copolymers of different compositions: SG.11 (31% polypeptide and 0 fold), SG.13 (41% polypeptide and 1 fold) and SG.18 (71% polypeptide and 4 folds).

*Factors governing the folding of the polypeptide chains*

The principal factors governing the folding of the polypeptide chains in hydrophobic copolymers with a polyvinyl block and a polypeptide block are the solvent concentration, the molecular weight of the blocks and the nature of the blocks.

(1) *Influence of the solvent concentration*

For the tree types of copolymers studied, copolymers polystyrene–poly(γ-benzyl-L-glutamate) (SG) (this paper),

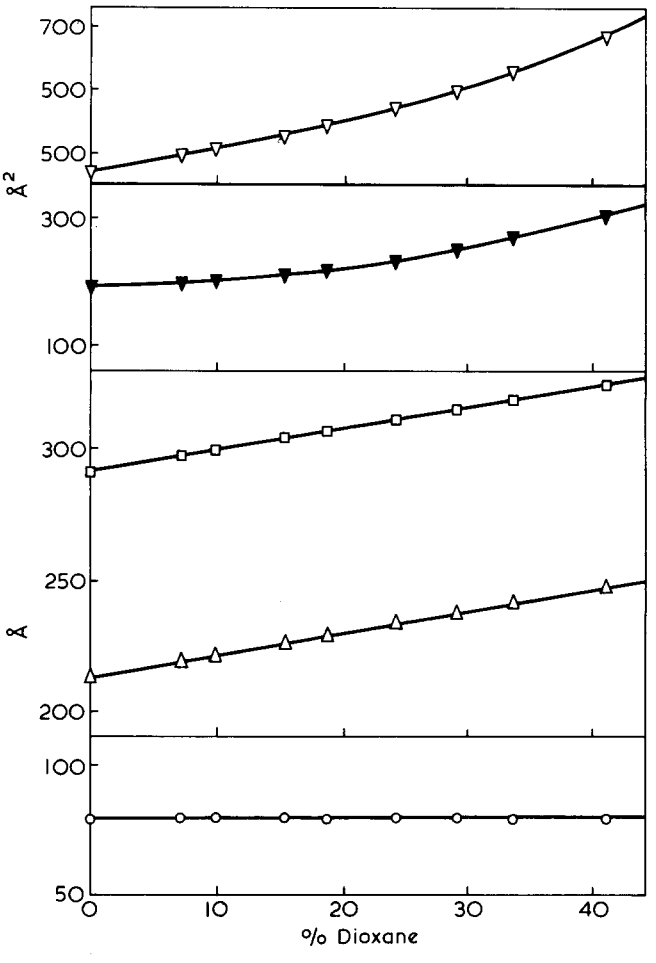


*Figure 2* Variation of the structural parameters of the lamellar structure with dioxane concentration in the case of the copolymer SG.11 containing 31% of polypeptide. □: $d$ = intersheet spacing; △: $d_A$ = thickness of the polystyrene layer; ○: $d_B$ = thickness of the polypeptide layer; ▽: $S$ = specific surface; ▼: $\Sigma$ = surface per polypeptide helix

copolymers polybutadiene–poly(γ-benzyl-L-glutamate) (BG)[2] and copolymers polystyrene–poly(ε-carbobenzoxy-L-lysine) (SCK[4], the thickness $d_B$ of the polypeptide layer is nearly independent of the solvent concentration and the number of folds of the polypeptide chains is independent of the solvent concentration. This independence of the number of folds from the solvent concentration is illustrated in *Figure 5* where we have plotted the evolution of $\mu = \nu + 1$ as a function of dioxane concentration for 3 copolymers SG of different compositions.

(2) *Influence of the molecular weight of the polypeptide block*

For a given type of copolymer and for a fixed value of the molecular weight of the polyvinyl block, the number of folds of the polypeptide chains increases with the molecular weight of the polypeptide block. For copolymers polystyrene–poly(γ-benzyl-L-glutamate) with a polystyrene molecular weight of 25 000 the number of folds of the polypeptide chains increases from 0 to 7 when the molecular weight of the poly(γ-benzyl-L-glutamate) block increases from 11 200 to 131 200 (*Table 1*). For copolymers polybutadiene–poly(γ-benzyl-L-glutamate) the number of folds of the polypeptide chains increases from 0 to 1 when the molecular weight of the poly(γ-benzyl-L-glutamate) block increases from 6 800 to 23 700 (*Table 2*). For copolymers polystyrene–poly(ε-carbobenzoxy-L-lysine) the number of folds of the polypeptide block increases from 1 to 2 when the molecular weight of the poly(ε-carbobenzoxy-L-lysine) increases from 20 800 to 49 000 (*Table 3*).

The increase in the number of folds of the polypeptide chains with increase in molecular weight of the polypeptide block occurs discontinuously; the number of folds taking integer values in the limits of accuracy of their determination (*Table 1*). Furthermore the number $n = d_B/c$ of repeat units $c$ after which the polypeptide chains fold tends to increase with the number of folds (*Table 1*).

(3) *Influence of the molecular weight of the polyvinyl block*

The number of folds of the polypeptide chains increases with the molecular weight of the polyvinyl block as illustrated by the comparison of 3 copolymers polystyrene–poly(γ-benzyl-L-glutamate): SG.7, SG.11 and SG.12 (*Table 1*). The polypeptide chains of the copolymer SG.7 with a molecular weight of 38 700 for its polystyrene block and a molecular weight of only 8 500 for its polypeptide block are folded once, while the polypeptide chains of the copolymer SG.11 with a smaller polystyrene block (25 000) but a higher polypeptide block (11 200) are

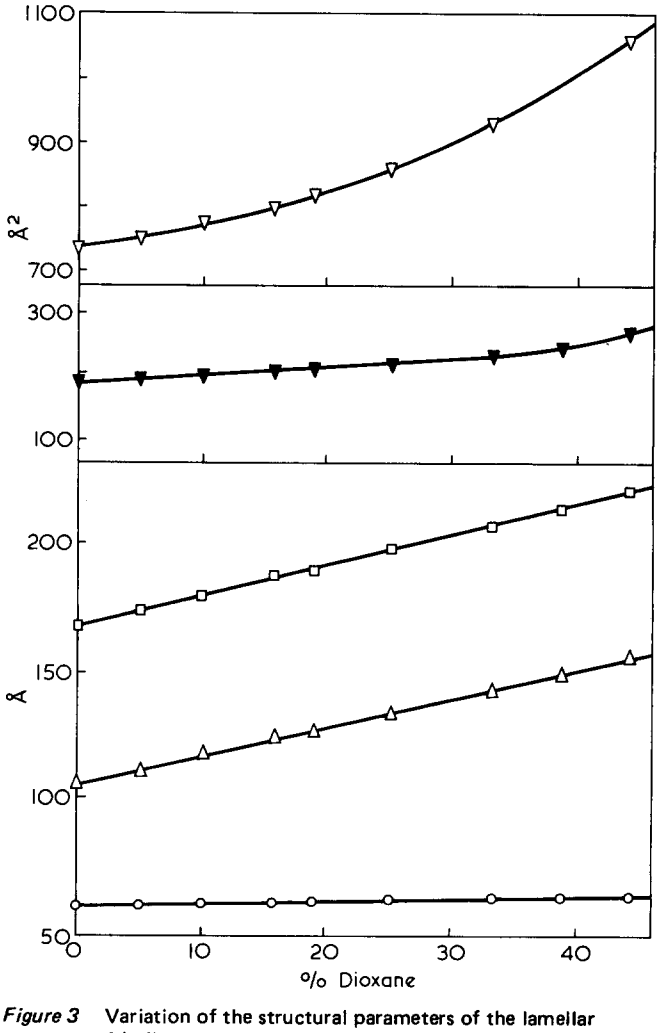


*Figure 3* Variation of the structural parameters of the lamellar structure with dioxane concentration in the case of the copolymer SG.13 containing 41% of polypeptide. □: $d$ = intersheet spacing; △: $d_A$ = thickness of the polystyrene layer; ○: $d_B$ = thickness of the polypeptide layer; ▽: $S$ = specific surface; ▼: $\Sigma$ = surface per polypeptide helix

not folded and for a molecular weight of polystyrene of 25 000 the folding of the polypeptide chains requires a molecular weight of the polypeptide block of 16 000 (SG.12).

(4) *Influence of the nature of the polyvinyl block*

Copolymers SG.14 (*Table 1*) and BG.32 (*Table 2*) have nearly the same molecular weight for their polyvinyl block: 25 000 for the polystyrene block of SG.14 and 25 600 for the polybutadiene block of BG.32 and nearly the same composition respectively 47 and 48% of poly(γ-benzyl-L-glutamate) but the number of folds of their polypeptide chains is different: they are folded twice in the copolymer SG.14 but only once in the copolymer BG.32. Therefore the number of folds of the polypeptide chains depends upon the nature of the polyvinyl block and the polypeptide chains are more folded when they are linked to polystyrene than when they are linked to polybutadiene.

(5) *Influence of the nature of the polypeptide block*

Copolymers SG.13 (*Table 1*) and SCK.15 (*Table 3*) have the same degree of polymerization for their polypeptide blocks and the same length (119 Å) and the same number of folds ($\nu = 1$) for their polypeptide chains but very different molecular weight for their polystyrene blocks (25 000 and 37 000 respectively). As the number of folds increases with the molecular weight of the polyvinyl block, copolymers SG.13 and SCK.15 should present

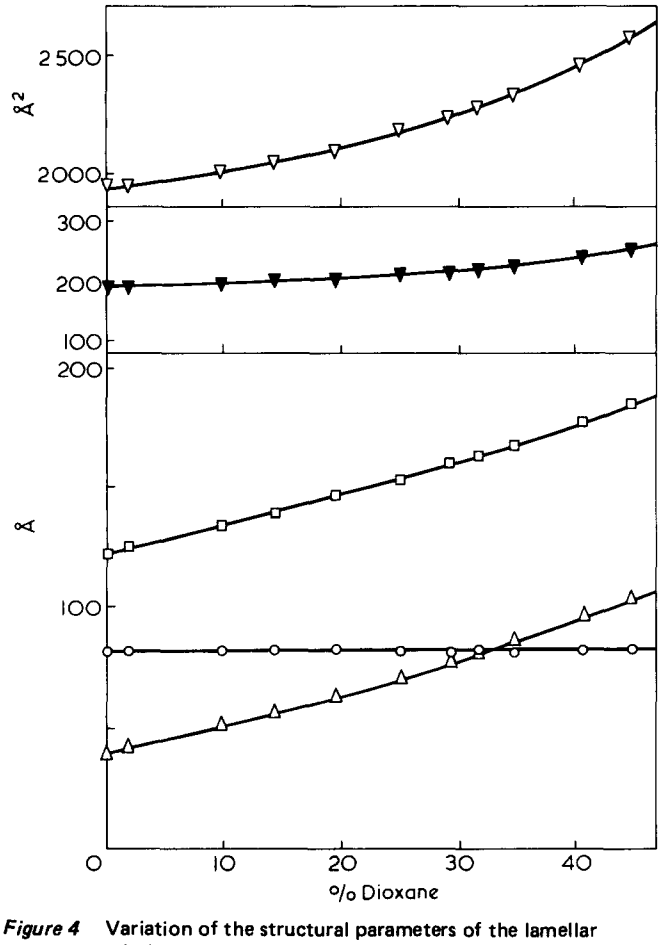


*Figure 4* Variation of the structural parameters of the lamellar structure with dioxane concentration in the case of the copolymer SG.18 containing 71% of polypeptide. □: $d$ = intersheet spacing; △: $d_A$ = thickness of the polystyrene layer; ○: $d_B$ = thickness of the polypeptide layer; ▽: $S$ = specific surface; ▼: Σ = surface per polypeptide helix

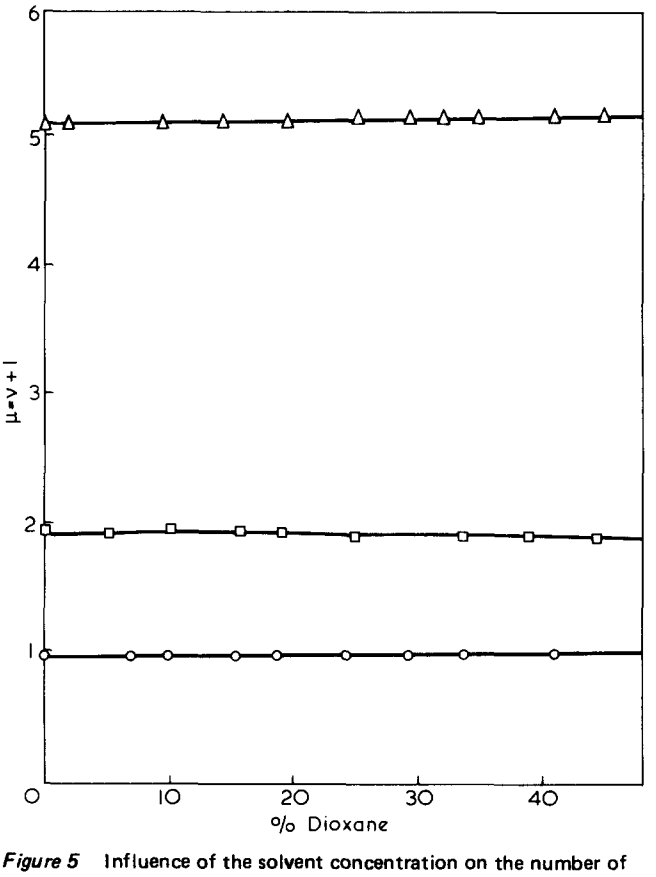


*Figure 5* Influence of the solvent concentration on the number of times $\mu = \nu + 1$ that a polypeptide chain crosses the thickness $d_B$; ○: copolymer SG.11 containing 31% of polypeptide; □: copolymer SG.13 containing 41% of polypeptide; △: copolymer SG.18 containing 71% of polypeptide

*Table 2* Influence of the molecular weight of the polypeptide block on the number of folds of the polypeptide chains in block copolymers polybutadiene–poly(γ-benzyl-L-glutamate) (BG)[2]

| Copolymer | $\bar{M}_n$ PB[a] | % PG[b] | $\bar{M}_n$ PG[b] | $\bar{P}_n$ PG[b] | $L$ (Å) | $d_B$ (Å)[c] | $d_B/c$[d] | $\mu$[c] | $\nu$ |
|---|---|---|---|---|---|---|---|---|---|
| BG.37 | 25 600 | 21 | 6800 | 31 | 46.5 | 48 | | 0.97 | 0 |
| BG.35 | 25 600 | 27.7 | 9800 | 45 | 67.5 | 65 | | 1.04 | 0 |
| BG.34 | 25 600 | 40 | 17 000 | 78 | 116 | 75 | 2.78 | 1.55 | 1 |
| BG.33 | 25 600 | 42.7 | 19 000 | 87 | 130 | 79 | 2.93 | 1.65 | 1 |
| BG.32 | 25 600 | 48.1 | 23 700 | 108 | 162 | 85 | 3.15 | 1.91 | 1 |

[a] PB: polybutadiene block (in 90% 1,2 linkage)
[b] PG: poly(γ-benzyl-L-glutamate)
[c] $d_B$ and $\mu$ values correspond to dry copolymers
[d] The ratio $d_B/c$ has significance only when the polypeptide chains are folded. $c = 18h = 27$ Å = repeat unit along the helix axis

*Table 3* Influence of the molecular weight of the polypeptide block on the number of folds of the polypeptide chains in block copolymers polystyrene–poly(ε-carbobenzoxy-L-lysine) (SCK)[4]

| Copolymer | $\bar{M}_n$ PS[a] | % PCK[b] | $\bar{M}_n$ PCK[b] | $\bar{P}_n$ PCK[b] | $L$ (Å) | $d_B$ (Å) | $\nu$ |
|---|---|---|---|---|---|---|---|
| SCK.15 | 37000 | 36 | 20800 | 79.5 | 119 | 66 | 1 |
| SCK.16 | 37000 | 57 | 49000 | 187 | 280.5 | 103 | 2 |

[a] PS: polystyrene block
[b] PCK: poly(ε-carbobenzoxy-L-lysine)

different numbers of folds if the rigidity of their polypeptide chains was the same; so the existence of an identical number of folds for the polypeptide chains of copolymers SG.13 and SCK.15 shows that the poly(ε-carbobenzoxy-L-lysine) chains are more rigid than the poly(γ-benzyl-L-glutamate) chains and will be less folded in copolymers with an identical molecular weight of the polyvinyl blocks and the same degree of polymerization of the polypeptide blocks. This result is confirmed by the comparison of copolymers SG.7 (*Table 1*) and SCK.15 (*Table 3*); for a similar molecular weight of the polystyrene block a number of folds $\nu$ of 1 requires only a degree of polymerization of 39 for a poly(γ-benzyl-L-glutamate) chain but of 79 for a poly(ε-carbobenzoxy-L-lysine) chain. These different rigidities of the α-helix of the two polypeptides are probably related to differences in the interactions between their lateral chains.

## CONCLUSION

It is interesting to compare block copolymers with an amorphous and a crystalline block[17,18] such as copolymers polystyrene–polyethylene oxide (PEO), polybutadiene–polyethylene oxide (BEO) and polystyrene–poly(ε-caprolactone) (SCL) with copolymers with a polyvinyl block of polystyrene or polybutadiene and a hydrophobic polypeptide block. The two types of copolymers exhibit for any composition only lamellar structure and in these lamellar structures the polypeptide chains as well as the crystalline polyethylene oxide or polycaprolactone chains are generally folded. Furthermore, in the two types of copolymers the number of folds increases with the molecular weight of the blocks and both the polyethylene oxide chains and the polypeptide chains are more folded when they are linked to polystyrene chains than to polybutadiene chains. However, the number of folds of the crystalline polyethylene oxide or polycaprolactone chains increases with the solvent concentration while the number of folds of the polypeptide chains is independent of solvent concentration.

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