PII: S0032-3861(97)10313-5

Structure of freeze-dried atactic polystyrene from dilute solutions

Takashi Sasaki*, Mitsuhiro Tanaka and Toshisada Takahashi
Department of Materials Science and Engineering, Fukui University, 3-9-1 Bunkyo, Fukui 910, Japan

The structure of freeze-dried atactic polystyrene (a-PS) prepared from dilute benzene and cyclohexane solutions was examined by using Fourier transform infra-red spectroscopy, wide-angle X-ray scattering and differential scanning calorimetry (d.s.c.). The phenyl–phenyl correlation in the freeze-dried a-PS is weak compared with that in the reference sample cast from a 5 wt% solution in tetrahydrofuran. The data suggest an expanded chain conformation for the specific structure of freeze-dried a-PS, which can easily be formed from a good solvent at high temperature, and with high-molecular-weight a-PS. The d.s.c. data of freeze-dried a-PS showed an endothermic peak just below the glass transition temperature, indicating an enthalpy difference between the freeze-dried and melt states. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: amorphous polymer; structure; freeze-dried atactic polystyrene)

INTRODUCTION

In general, the structure of an amorphous polymer glass, which is essentially in a non-equilibrium state, depends on the history of sample preparation. Among various methods, the freeze-drying technique, which has frequently been employed as an excellent drying technique, is unique for the treatment of samples of polymer materials[1]. When a very dilute polymer solution in the absence of any polymer–polymer interactions is freeze-dried, a specific structure may be obtained: i.e. the individual polymer chain is isolated without chain entanglement and overlapping. The freeze-drying method was applied in studies on the crystallization of isotactic polystyrene[2,3] and polycarbonate[4], and the results showed higher crystallinity and very rapid crystallization compared with the usual crystallization from the melt. Such results, however, suggest that a certain structural change occurs rapidly during the freezing and drying processes, and the conformational structure in the solution may not necessarily be preserved.

We have already investigated freeze-dried atactic polystyrene (a-PS) by Fourier transform infra-red spectroscopy (*FT*i.r.), and have found some absorption bands characteristic to the specific structure of freeze-dried a-PS[5]. In this study, we examined further the structure of freeze-dried a-PS under different preparation conditions by *FT*i.r., wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (d.s.c.) to clarify how the conformational structure in the preparation solution influences the resultant freeze-dried structure.

EXPERIMENTAL

The a-PS samples used in this study were the same as those in a previous study[5]. *Table 1* shows the characteristics of these a-PS samples. Benzene and cyclohexane were used as

good and poor (theta) solvent, respectively, and these were distilled just before use. The sample polymers were dissolved in the solvents, these 0.02–5.0 wt% solutions were rapidly (almost instantaneously) frozen by pouring them directly into liquid nitrogen, and then the frozen solvents were sublimated in a freeze-drying apparatus (Yamato DC-55A). The solution temperature just before pouring into liquid nitrogen was varied from 10 to 50°C for the benzene solutions. As for the cyclohexane solution, the solution temperature was kept at 34.5°C (theta condition for a-PS). The reference samples were also prepared by casting from 5 wt% solution in tetrahydrofuran (THF) at room temperature.

The WAXS measurements were performed with a 12 kW rotating-anode X-ray generator (JEOL JDX-8750) as a source of Cu K_α radiation ($\lambda = 1.54$ Å) and a diffractometer (slit collimation) equipped with a monochrometer [graphite (0002)] before a scintillation counter. The scattering intensity data thus collected were analysed in order to calculate the radial difference distribution function (RDDF) relevant to the atomic density difference, $\rho(r)$, at a distance r, defined as[6]

$$\mathrm{RDDF}(r) = 4\pi r^2 \Delta\rho(r) = \frac{2r}{\pi} \int_0^\infty si(s) \sin(sr)\,\mathrm{d}r \quad (1)$$

with

$$i(s) = \left[I_{\mathrm{coh}}(s) - \sum a_i f_i^2(s) \right] \Big/ \sum a_i f_i^2(s) \equiv I(s) / \sum a_i f_i^2(s)$$

and

$$s = \frac{4\pi}{\lambda} \sin\theta$$

where I_{coh} is the coherent scattering intensity on an absolute scale, and a_i and $f_i(s)$ are the fraction and atomic scattering factor of each atom, respectively. To obtain experimental I_{coh}, we corrected the raw data by accounting for the background scattering, the polarization effect and the incoherent scattering, and then normalized them in electron units.

* To whom correspondence should be addressed

Table 1 Molecular weight and tacticity of the a-PS samples

	a-PS1	a-PS2	a-PS3
M_n	12 400	109 900	2 276 000
M_w	13 200	114 200	2 316 000
M_w/M_n	1.06	1.04	1.02
Racemic fraction	0.49	0.49	0.49
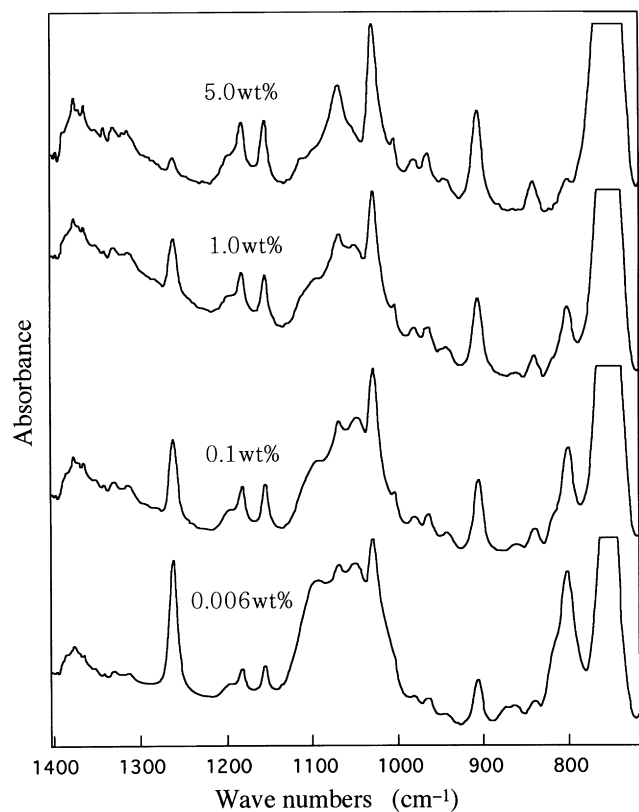
Figure 1 Infra-red absorption spectra of freeze-dried a-PS2 ($M_n = 109\,900$) from benzene solutions of different concentrations at 25°C

Table 2 Relative peak intensity of the 1262 cm^{-1} i.r. band for freeze-dried a-PS2

Solvent	Temperature (°C)	Relative intensity at 1262 cm^{-1}
Benzene	10	1.50
	30	1.89
	50	2.42
Cyclohexane	34.5 (theta state)	1.00

Calculations of the RDDFs were performed by the method of Schubach *et al.*[6] with a damping function to eliminate the termination error[7].

The *FT*i.r. measurements were carried out at room temperature by using JASCO FT/IR-8000 and Nicolet Magna 560 instruments. The resolution was 2 cm^{-1}. The d.s.c. measurements were done at a heating rate of 10°C min^{-1} in air with a Perkin–Elmer DSC7. The temperature readings were calibrated with an indium standard.

RESULTS AND DISCUSSION

*FT*i.r. spectra

We have already reported that freeze-dried a-PS prepared from a dilute solution exhibits characteristic i.r. bands at 1047, 1098 and 1262 cm^{-1}, which correspond to a certain structure specific to the freeze-dried sample[5]. In this study, we found a fourth characteristic i.r. band at 803 cm^{-1} in addition to the above three. *Figure 1* shows the *FT*i.r. spectra for the freeze-dried a-PS2 ($M_n = 109\,900$) prepared from benzene solutions of different concentrations. We can see that all of the four specific absorption peaks increase with decreasing concentration. This fact indicates that the specific structure of the freeze-dried a-PS can be formed easily when chain entanglement (or chain overlapping) is absent. In other words, the freeze-dried specific structure contains fewer chain entanglements.

Table 2 shows a comparison of the relative peak intensities of the 1262 cm^{-1} band for the freeze-dried a-PS2. Here, the relative peak intensity was estimated by taking the 1028 cm^{-1} band (C–H in-plane bending of the phenyl ring) as the reference peak. As we revealed in a previous paper[5], the 1262 cm^{-1} band is fairly sensitive to the specific structure of freeze-dried a-PS, although the detailed assignment for this band has still not been done[5,8–10]. We can see that the 1262 cm^{-1} peak is stronger for the sample from benzene solution than for the sample from the cyclohexane theta solution, despite the fact that the former solution is more favourable for forming chain overlapping. This indicates that the expanded chain conformation is rather preferable for forming the specific structure of the freeze-dried a-PS. *Table 2* also shows the results of the solution temperature dependence just before freezing for the benzene solution. It shows that the peak intensity is stronger for the higher solution temperature. Since the chain-expansion coefficient is generally an increasing function with respect to temperature above the theta temperature (perturbed state)[11], the present temperature dependence again suggests a strong relationship between the specific structure of the freeze-dried a-PS and an expanded chain conformation. Considering the almost instantaneous freezing process in our experiments, we can assume that the chain dimension of the freeze-dried a-PS from benzene solution is larger than at least the unperturbed chain dimension (Gaussian chain).

Figure 2 shows the *FT*i.r. spectra for the freeze-dried a-PS of different molecular weight from the 0.1 wt% benzene solutions at 25°C. We see that the four specific absorption bands increase with increasing molecular weight. For example, the relative absorption intensities, A, of the 1262 cm^{-1} band for the three samples in *Figure 2* were obtained as A(a-PS1):A(a-PS2):A(a-PS3) = 1:1.42:1.78. This result seems to be inconsistent with the above result (the concentration effect) that the chain overlapping disturbs the formation of the specific structure of freeze-dried a-PS. However, we consider here that the molecular weight dependence obtained is probably due to a structural relaxation which occurs either in the freezing or drying process. Since, in practice, the freezing process is not completely instantaneous, a certain relaxation process accompanied by the conformational rearrangements, which give rise to chain shrinkage, may occur during freezing to some extent. Such a structural relaxation is more difficult in the polymer with higher molecular weight owing to its lower chain mobility and, as a result, the expanded structure tends to remain in the higher-molecular-weight a-PS.

In a previous paper[5], we reported that the 1262 cm^{-1} band does not exist in the benzene solution itself, and this suggests the occurrence of a certain structural change during the freeze-drying process. Furthermore, crystallization of

the solvent may force the a-PS chain to take up other specific conformations. However, from the fact that the four specific i.r. bands appear at the same position for both benzene and cyclohexane, we can see that the detailed crystalline structure of the solvents does not strongly influence the structure of the freeze-dried a-PS.

WAXS and RDDF

The structure of a-PS in the glassy state has been studied
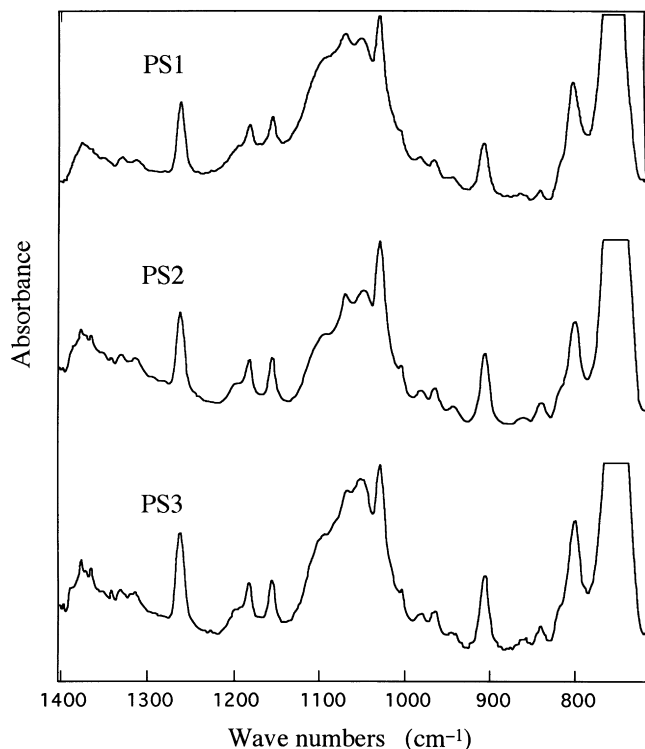
Figure 2 Infra-red absorption spectra of freeze-dried a-PS of different molecular weights prepared from a 0.1 wt% benzene solution at 25°C

extensively by WAXS to date[6,12–14]. Glassy a-PS usually shows a scattering peak appearing at $s \cong 0.75$ Å^{-1}, in addition to the main amorphous halo ($s \cong 1.4$ Å^{-1}). The former is called the 'polymerization peak' and appears strongly on the equator for an elongated (oriented) a-PS sample, which is thus considered to reflect the inter-main-chain (inter-molecular) correlation in the glassy state[14,15]. *Figure 3* shows WAXS profiles of the freeze-dried a-PS2 prepared from 0.1 wt% benzene (50°C) and cyclohexane (34.5°C) solutions, together with that for the reference cast sample. The profile for the cast sample obtained here is rather similar to that for bulk a-PS observed by other researchers[6,16]. As for the freeze-dried samples, we can see that the main amorphous peak is relatively weak compared with that for the cast sample. In addition, we can see that the peak at *ca.* 3 Å^{-1} is also reduced for the freeze-dried samples.

Figure 4 shows the RDDF curves derived from the $sI(s)$ data in *Figure 3*. The phenyl–phenyl distance correlation peaks, which appear at 5.0–6.3 Å [16–18], are weaker for the freeze-dried samples than for the cast sample. This indicates that the structural order formed between the phenyl groups is not well established for the freeze-dried structure. Considering that the i.r. data shown in the above section suggest a rather expanded chain conformation for the specific structure of the freeze-dried a-PS, we can say that the expanded chain conformation tends to prevent the formation of the phenyl–phenyl correlation which is observed strongly in the usual glassy state of a-PS[16–18].

We can also recognize that the correlation peak observed at 2.5 Å for the cast sample, which corresponds to a distance between the second neighboring carbon atoms, tends to shift to a higher distance (2.9–3.0 Å) for the freeze-dried samples. However, if we assume that this is caused by a bond length or a bond angle deformation of the main-chain carbon atoms, a distortion of 1.53 Å → 1.77 Å for the bond length or 109.5° → 143° for the bond angle is needed, which is unrealistically large compared with the usual values for the all-*trans* conformation[19]. To solve this problem, further
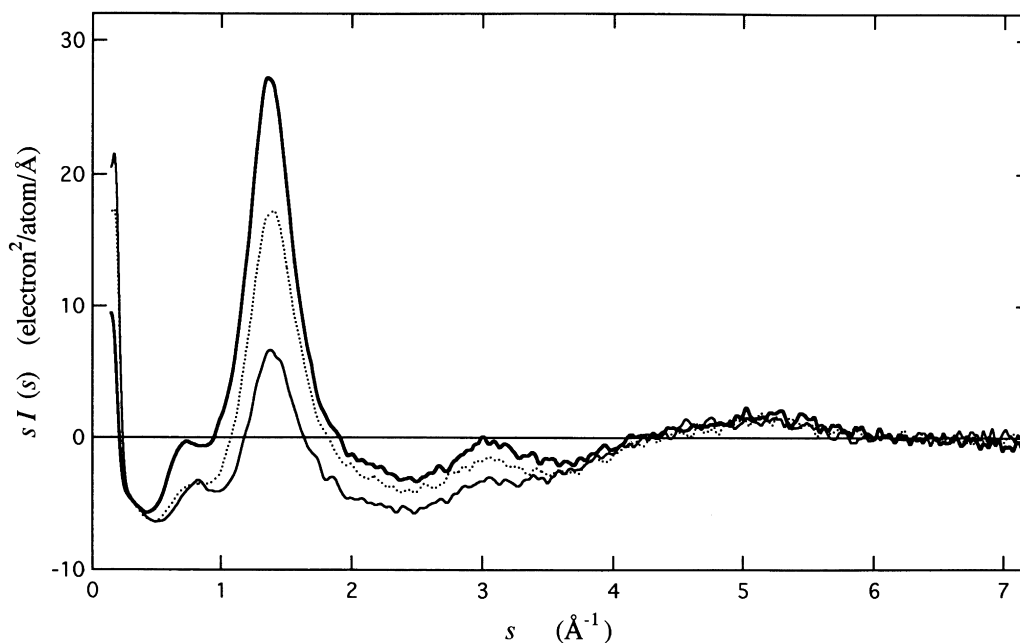
Figure 3 WAXS profiles of freeze-dried and cast a-PS2. The thin solid line indicates data for the sample freeze-dried from a 0.1 wt% benzene solution at 50°C, the dotted line the sample freeze-dried from a 0.1 wt% cyclohexane solution at 34.5°C, and the thick solid line the reference cast sample from a 5 wt% THF solution
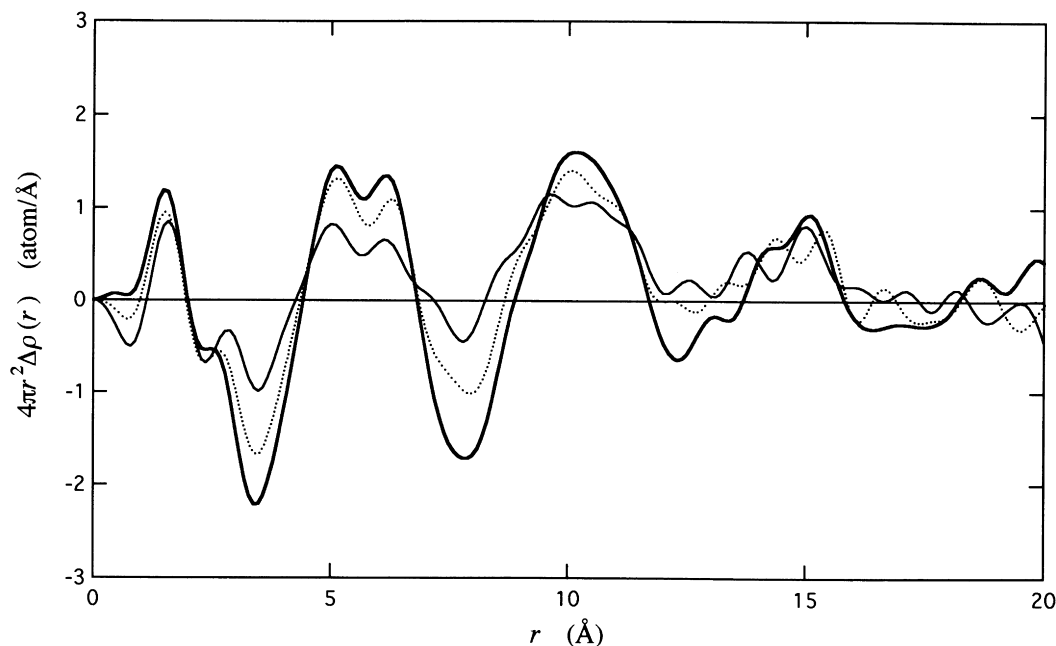
Figure 4 RDDFs calculated from the WAXS data in *Figure 3*. Each line corresponds to the same sample as in *Figure 3*
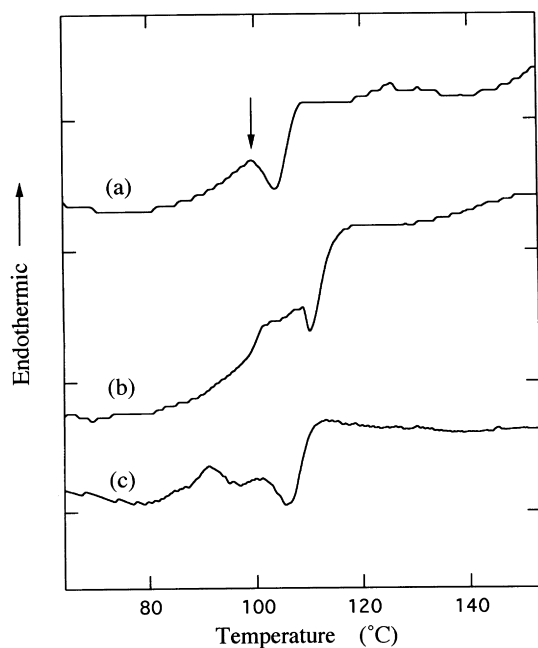

Figure 5 D.s.c. thermograms of the freeze-dried a-PS: (a) a-PS1 freeze-dried from a 0.1 wt% benzene solution at 25°C; (b) a-PS2 freeze-dried from a 0.1 wt% benzene solution at 25°C; and (c) a-PS2 freeze-dried from a 0.006 wt% benzene solution at 25°C

Table 3 T_g and ΔH estimated from the d.s.c. thermograms in *Figure 5*

	a-PS1	a-PS2	a-PS2
Concentration of the preparation solution (wt%)	0.1	0.1	0.006
T_g (°C)	107	113	109
ΔH (cal g^{-1})	0.343	0.489	1.90
Relative peak intensity of the 1262 cm^{-1} i.r. band	1.19	1.80	3.32

structural investigation should be done by other experimental techniques.

As for the freeze-dried a-PS prepared from cyclohexane solution in the theta state (34.5°C), we found the same features in RDDF as those from benzene solution, but the tendency is rather weak compared with that from benzene solution. For a-PS, the chain dimension in the theta solution is basically the same as that in the usual glassy state[20], but the different results of the i.r. and WAXS data between the freeze-dried a-PS from the theta solution and the cast sample principally show a remarkable aspect of molecular interaction in the freeze-dried state aside from the chain-expansion effect, i.e. a low contribution from the inter-molecular interaction. Indeed, most correlation peaks in the RDDFs of the freeze-dried samples are weaker than those of the reference cast sample (see *Figure 4*). This indicates that the correlated inter-molecular atomic pairs decrease drastically in the freeze-dried structure, and that the intra-molecular atomic pairs belonging to the same polymer chain mainly contribute to the WAXS data, resulting in a decrease of the atomic pair correlation strength as a whole.

Calorimetry

Figure 5 shows the d.s.c. thermograms for the freeze-dried a-PS. We can recognize an endothermic peak below the glass transition (indicated by the arrow in *Figure 5*). This peak corresponds to the enthalpy difference between the freeze-dried structure and a non-equilibrium glassy state (or at least the melt state in equilibrium), indicating that the enthalpy in the freeze-dried state is lower than that in the melt state. *Table 3* shows the glass transition temperature, T_g, and the area of the above enthalpy difference, ΔH, together with the relative absorbance of the 1262 cm^{-1} i.r. band characteristic of the specific freeze-dried structure. Here, we can see a qualitative correlation between the value of ΔH and the i.r. absorbance. The value of ΔH thus indicates the extent of formation of the specific freeze-dried structure.

Since the glass transition itself is accompanied by no

extra endothermic peak, just like in the quenched glass without the enthalpy relaxation, the structural change through the transition from the freeze-dried structure to the melt state in d.s.c. measurements probably occurs via the normal glassy state: i.e. the frozen non-equilibrium structure quenched from the melt. Considering the characteristic structural feature of the freeze-dried a-PS, we can consider that the present structural change should contain at least two processes: (1) shrinkage of the extended chains to the Gaussian state, and (2) establishment of the overlapping and entanglement between the chains. As for a-PS2, two (or more) endothermic peaks are discernible (*b* and *c* in *Figure 5*). The reason for this is not clear at the present time, but the above two processes of the structural change may be reflected in the multiple endothermic profile.

The glass transition temperatures of the freeze-dried samples are higher than that of the cast a-PS (*ca.* 100°C). This may be due to the fact that the above structural relaxation takes place prior to the glass transition. Actually, the scanning rate of the d.s.c. measurements ($10°C\,min^{-1}$) may not afford enough time for completion of the structural relaxation.

CONCLUSIONS

The present study showed that, in the specific structure of freeze-dried a-PS prepared from dilute solutions, the a-PS chain has an expanded conformation depending on both the solvent quality and temperature used for preparation. With such an expanded chain structure, the strong local structural order—especially the separation of 5–6 Å between the phenyl centres characteristic of the usual glassy a-PS—was found to become weak. In the freeze-dried samples, it is considered that the individual chains are separated from each other, and that the order between atoms with correlated distances is formed merely inside the isolated chain (intramolecular interaction) and in the small contacting region between them. Thus, the correlation strength of each atomic pair becomes weak for the freeze-dried a-PS as shown by the present results.

The difference observed between the good and the theta solvents used for sample preparation reflects a difference in the chain expansion in dilute solutions, although other unknown effects, such as the crystallization process of the solvent in the freezing process and the detailed local interactions between polymer and solvent in the frozen state, should be taken into account. Also, further investigation should be done to ascertain the validity of the present findings by direct measurement of the individual chain dimensions in the freeze-dried state. This is now under investigation.

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