Chain Conformation of Isotactic Polystyrene in the Bulk Amorphous State as Revealed by Small-Angle Neutron Scattering

J. M. Guenet,* C. Picot, and H. Benoit

Centre de recherche sur les Macromolecules (C.N.R.S.), 67083 Strasbourg Cedex, France.
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ABSTRACT: The conformation of labeled isotactic polystyrene (IPSD) in the bulk amorphous state has been investigated using the technique of small-angle neutron scattering (SANS) for two kinds of matrices: IPS matrices and atactic polystyrene (APS) matrices. The experiments have shown in the case of IPS matrices that the chain presents Gaussian behavior for samples molded above melting temperature T_m and rapidly quenched to room temperature. For APS matrices two phenomena have been observed. At first, the isotactic tagged chains exhibit Gaussian character when they are dispersed in APS matrices having the same or higher molecular weight. In this case the radius of gyration decreases drastically with temperature. In return, IPSD chains behavior diverges from Gaussian state in a certain range of temperature by using APS matrices of lower molecular weight. This is particularly shown by the variation of the scattered intensity in the intermediate range which is proportional to $q^{-1.66}$ [$q = (4\pi/\lambda) \sin(\theta/2)$] for samples molded at 180 °C and $q^{-2.5}$ for samples molded at 200 °C instead of q^{-2} for Gaussian coil. However, these abnormal effects vanish when the samples are prepared above melting temperature T_m. All the results are discussed in terms of conformational models.

Some years ago[1] the solution properties of isotactic polystyrene (IPS) were studied in order to determine the unperturbed chain dimensions and to compare them with the equivalent parameters of atactic polystyrene (APS). These values have been obtained from good solvent measurements using the Krigbaum method[2] since the θ conditions are difficult to realize for IPS. It was then interesting to study the conformation of IPS in bulk matrices in the glassy state for which the chain should be Gaussian. Recent experiments of small-angle neutron scattering (SANS) and light scattering have shown that indeed unperturbed dimensions of APS[3] in bulk and polyethylene[4] in the molten state are almost the same as in θ solvents. Nevertheless, some particular attention has to be taken by considering the amorphous state. It has been recently demonstrated[5] using the "scaling" theory that bulk amorphous state and θ point conditions do not correspond rigourously to the same phenomenon. By considering the same unperturbed dimensions, the θ point has been interpreted as a tricritical point involving compensation between polymer–polymer and polymer–solvent interactions. On the other hand, in bulk, the Gaussian character of the chain results from contacts and strong interpretation between macromolecules. In the case of IPS the influence of tacticity on the conformational behaviors is not well known. It is the purpose of this paper to present some investigations by SANS on the conformation of labeled IPS chains dispersed in an amorphous matrix. The labeling of chains of IPS with deuterium (IPSD) provides a neutronic contrast without changing significantly the physicochemical properties. For example, in the case of IPS a difference in melting point of 5.5 °C has been found for samples crystallized at 180 °C ($T_{m\ IPSD}$ = 209.5 °C, $T_{m\ IPSH}$ = 215 °C).

As for measurements on APS, two domains of transfer momentum [$q = (4\pi/\lambda) \sin(\theta/2)$] can be considered: the Guinier range $qR_g \ll 1$, where the scattered intensity can be written

$$I(q) \sim \exp\frac{-q^2R_g^2}{3} \sim 1 - \frac{q^2R_g^2}{3} \qquad (1)$$

R_g being the radius of gyration of the labeled chain, and the intermediate range $1/R_g \ll q \ll 1/l$, the domain of asymptotical behavior of the form factor of the chain conformation of statistical unit l. Then $I(q)$ can be expressed as

$$I(q) \sim 1/q^{1/\nu} \qquad (2)$$

Table I

fraction	M_w	M_w/M_n
1	1 100 000	1.5
2	700 000	1.32
3	500 000	1.2
4	300 000	1.2
5	254 000	1.15
6	154 000	1.13
7	95 000	1.13
8	27 000	1.25

where ν is a classical excluded volume exponent (for a Gaussian coil $\nu = 0.5$, for a three dimensional excluded volume $\nu = 0.6$, for a rod $\nu = 1. . .$).

Measurements have been carried out taking into account the different experimental parameters like preparation temperature of the sample and molecular weight of the tagged chains and the matrix. Both situations of labeled IPS in APS and in IPS amorphous matrices have been considered in order to investigate the influence of the surrounding tacticity on the conformation.

Experimental Section

1. Synthesis of IPS. The hydrogenated and deuterated isotactic polystyrenes (IPSH and IPSD) have been synthetized by the classical Natta method.[6] The complete methods of synthesis, purification, and fractionation have been already described in a previous paper.[7]

The hydrogenated polymer used only as solid solvent contributes mainly to the incoherent scattered intensity and has then been roughly fractionated. Only the extreme molecular weights of the distribution have been extracted. The GPC chromatogram in THF of this product is represented in Figure 1a. The deuterated polymer has been fractionated more carefully. The values of the molecular weights as well as the polydispersities of the fractions are listed in Table I. An example of the GPC chromatogram in THF is drawn in Figure 1b for fraction 7.

2. Preparation of the Samples for SANS Experiments. Two kinds of blends have been prepared: (i) blends of IPSD + IPSH in the respective weight proportions of C_D = 1% and C_H = 99%, and (ii) blends of IPSD + APSH in the same proportions as given previously. APSH has been synthetized by the classical anionic method.

Molecular dispersions of deuterated species in the protonated medium have been achieved in chlorobenzene solutions at 130 °C. The blends have been recovered by precipitation in methanol. Disk-shaped samples of 1 mm thickness and 15 mm diameter have been used for SANS measurements. They have been obtained by molding at high temperatures under vacuum in order to avoid oxydative degradations and to eliminate microvoids. To reach the relaxed state of macromolecules, molding times of 20 mm have

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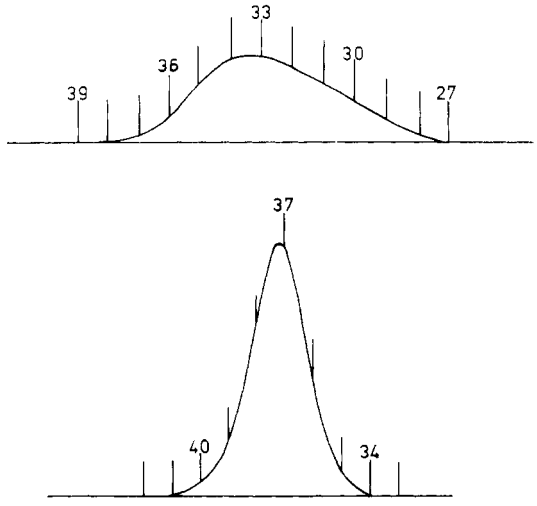

Figure 1. GPC chromatogram of the fractionated IPSH (a) and of a fraction (M_w = 95 000) of IPSD (b).

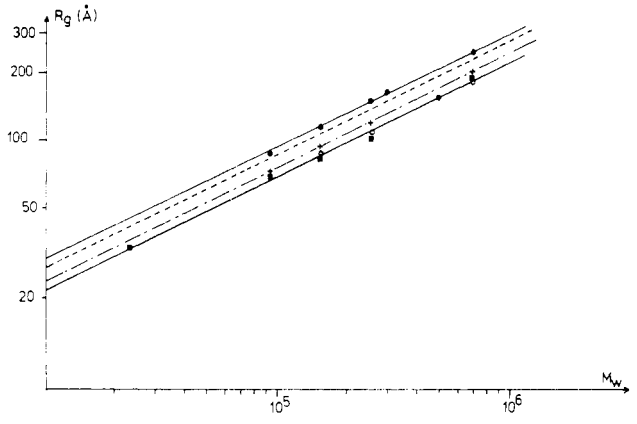

Figure 2. Log R_g plotted vs. log M_w: (●) C series; (- - -) atactic polystyrene;[3] (+) D series; (■) B series; (○) A series.

been used. The system has then been rapidly quenched to room temperature to freeze in the conformation. On the other hand solid samples with APSH matrices have been prepared by evaporation at room temperature from concentrated solutions in THF. All the characteristics of the blends (molecular weight of IPSD and corresponding matrices, preparation, temperature, . . .) are listed in Table II.

3. SANS Measurements. All the measurements have been carried out at the "Institut Laue-Langevin" (Grenoble, France) on a D11 small-angle camera described in ref 3. The neutrons available from a cold source have wavelengths ranging from 5 to 10 Å. For the investigated molecular weights and depending on the sample detector distance (20 m and 5 m) the available transfer momentum domain was: $3.10^{-3} \leq q < 5.8 \times 10^{-2}$ Å^{-1}.

Results and Discussion

1. Variation of R_g as a Function of Molecular Weight. The values of the radii of gyration calculated from Guinier plots are listed in Table II with the preparation characteristics of the samples. Figure 2 represents log R_g vs. log M_w for each series of samples. Actually the z-average molecular weight M_z should be used for a Gaussian coil. Nevertheless, the narrow molecular weights distribution of IPSD fractions allows us to use the weight average molecular weight M_w. This will only result in a small shift of the curves along the M_w axis. As it appears from both Table II and Figure 2, experimental results for A and B series are the same for identical IPSD molecular weights showing the noninfluence of the surroundings above the melting point. Consequently these values have been associated to calculate by the mean least-squares method the two constants ν and b of the law $R_g = bM\nu$.

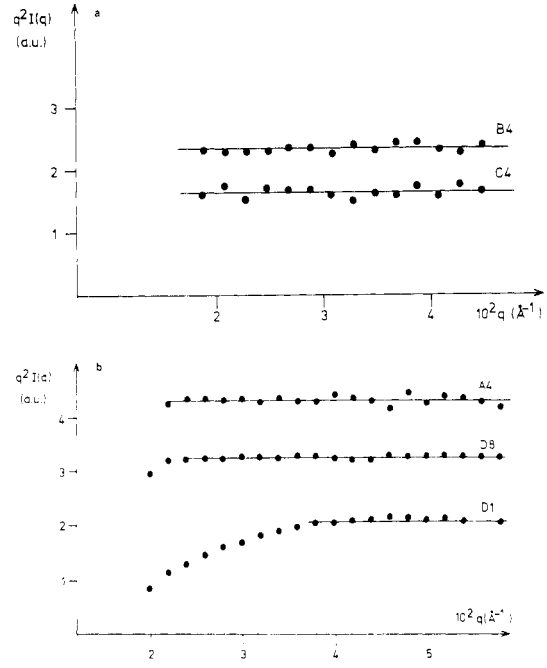

Figure 3. (a) $q^2I(q)$ in arbitrary units plotted vs. q for the same IPSD + APSH blend but prepared at room temperature (C4) and molded above the melting point of IPS (B4). (b) $q^2I(q)$ in arbitrary units vs. q for A4 (IPSD + IPSH), D8, and D1 (IPSD + APSH at 180 °C).

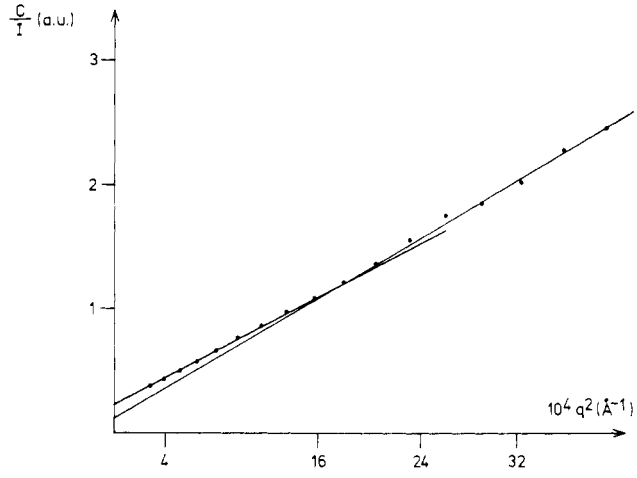

Figure 4. Debye plot $C/I(q)$ in arbitrary units vs. q^2. One can remark that the ratio of the intercepts of the initial and asymptotical tangents is close to 2.

From Table II it can be seen that the value of ν is very close to 0.5 in all the cases. This is a typical Gaussian exponent. However, a study of asymptotical behaviors of the scattered intensity should confirm this result. These studies have been carried out on samples A4, B4, C4, D8, and D1. These samples of high molecular weight (except D1) have been chosen in order to rapidly reach asymptotical behavior. Plots of the SANS experiments of $q^2I(q)$ against q are drawn in Figure 3a,b. The existence of a plateau in this representation confirms the Gaussian character of the chains in all cases. No deviation from this behavior as mentioned by Yoon and Flory[8] can be detected since one would have to perform scattering measurements at much higher q values to observe a significant influence of the short and non-Gaussian sequences. In the special case of D1 the two ranges of transfer momentum ($qR_g < 1$ and $qR_g > 1$) can be investigated. By plotting $I^{-1}(q)$ against q^2 one can obtain a typical Debye curve for Gaussian coil.[9] In Figure 4 such a plot is drawn for D1 and shows the good

Table II

sample	M_w IPSD	M_w IPSH	M_w APSH	T_{prep}, °C	R_g, A	b	ν
A4	7×10^5				185		
A3	5×10^5	5×10^5		240	153		
A2	2.54×10^5				108		
A1	1.54×10^5				88		
B4	7×10^5				188	0.2	0.506
B2	2.54×10^5				103		
B1	1.54×10^5		2.9×10^5	240	83		
B5	9.5×10^4				69		
B6	2.7×10^4				35		
C4	7×10^5				245		
C2	2.54×10^5				155		
C7	3×10^5		2.9×10^5	25	165	0.28	0.5
C1	1.54×10^5				115		
C5	9.5×10^4				90		
D8	7×10^5		7.5×10^5		200		
D2	2.54×10^5		2.9×10^5	180	120	0.23	0.503
D1	1.54×10^5		2.9×10^5		94		
D5	9.5×10^5		2.9×10^5		73		

Table III

sample	T, °C	R_g, Å	$C_M = \langle r_0^2 \rangle / nl^2$
E1	140	135	9.33
E2	160	126	8.13
E3	180	118	7.13
E4	200	111	6.31
E5	220	104	5.54
E6	250	101	5.22

agreement with the calculation. Nevertheless, the ratio between the slopes of the initial and asymptotical curves is close to 0.82 instead of 2/3 expected for monodispersed macromolecules. Since this ratio is equal to $2M_z/3M_n$ a small polydispersity could explain this descrepancy.

Looking at these results two comments can be made: (i) for C-series samples, the values of the unperturbed dimensions are of the same order of magnitude as those given by Krigbaum et al.,[1] i.e., 10 to 20% higher than these of the atactic one; and (ii) R_g diminishes drastically with increasing temperature.

In the following section of this study, the variation of R_g with the temperature for a given molecular weight of tagged chains will be considered in more detail.

2. R_g Variation with Temperature. In order to characterize the variation of R_g as a function of temperature, measurements in the Guinier range on IPSD molecular weight of 2.54×10^5 dispersed in an APSH matrix ($M_w = 2.9 \times 10^5$) have been performed (E series samples). It has been assumed in this kind of study that the fast quenching from molding to room temperature conserves the sample in the same conformational state.

The values of the radius of gyration for each molding temperature deduced from the Zimm plot (Figure 5) as well as the values of the characteristic ratio $C_M = \langle r_0 \rangle^2 / nl^2$ are listed in Table III. The C_M temperature dependence obeys a simple relation (Figure 6) which leads to d log $C_M/dT = -5.5 \times 10^{-3}$ K^{-1}. This value is somewhat larger than the value d log $C_M/dT = -10^{-4}$ K^{-1} measured from the change of dimension of an atactic polystyrene by Kuwahara et al.[10]

It would be tempting to explain such results by considering the progressive breaking of 3_1 helices which has been already proposed for other experiments.[11] The radius of gyration would then be expressed as:

$$R_g \sim M \exp\frac{-\Delta E}{RT} \qquad (3)$$

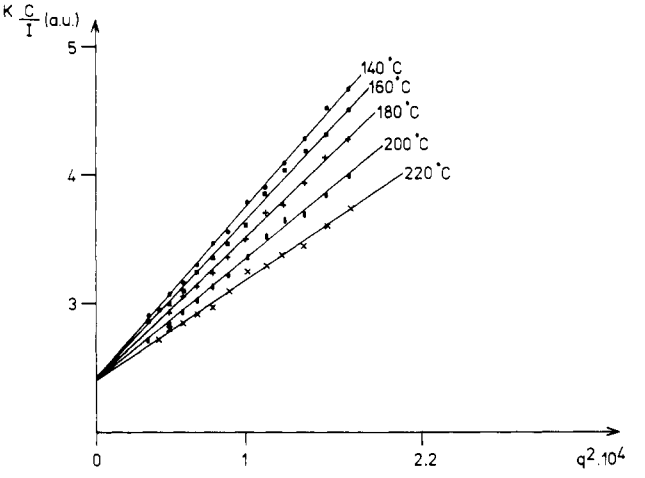

Figure 5. Zimm plots obtained from measurements on E series samples showing the decrease of R_g with temperature.

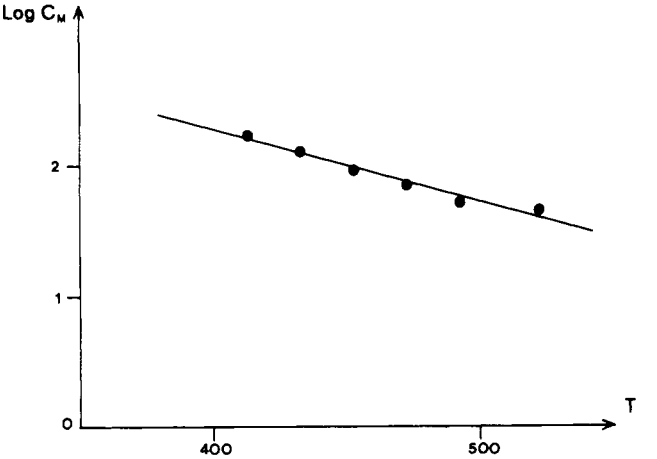

Figure 6. Log C_M vs. T (K) for E series samples.

where ΔE is the energy required for the formation of one break. By plotting log R_g vs. $1/T$ (Figure 7) one can deduce from the slope ΔE = 2.3 kcal which is very close to values obtained in other experiments.[11] However, Flory and co-workers[12] have shown by computing conformational energies as a function of skeletal bond rotations at 300 K that long sequences of (*tg*) dyads are essentially inexistant, their mean length representing approximatively one turn of a 3_1 helix. These calculations seem to be confirmed by

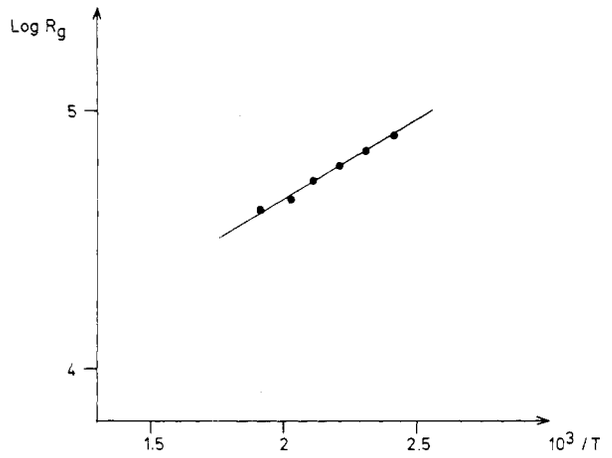

Figure 7. Log R_g vs. $1/T$ for E series samples.

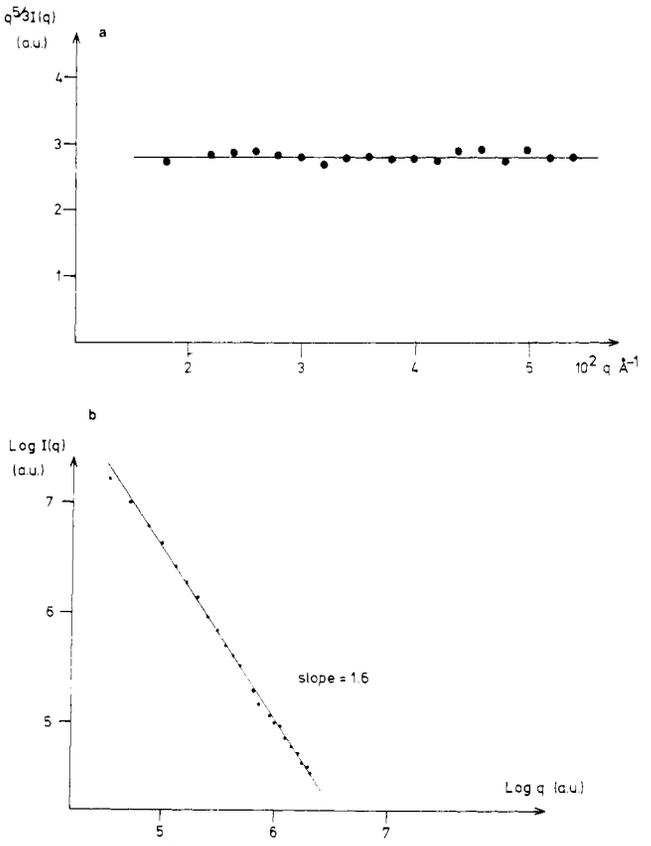

Figure 8. (a) $q^{5/3}I(q)$ in arbitrary units vs. q for the samples F11 where M_{IPSD} = 1 100 000 and M_{APSH} = 290 000. (b) Log $I(q)$ vs. log q for F4. From the slope, one deduces the exponent which is equal to 1.66.

Table IV

sample	M_{IPSD}	M_{APSH}	T_{prep}, °C	R_g, Å	ν	$I(q)$
F11	1 100 000	290 000		235		
F4	700 000	290 000	180	200	0.5	$q^{-1.67}$
F9	500 000	100 000		165		
G11	1 100 000	290 000		295		
G4	700 000	290 000	200	200	0.7	$q^{-2.5}$
G9	500 000	100 000		152		
G10	300 000	100 000		113		

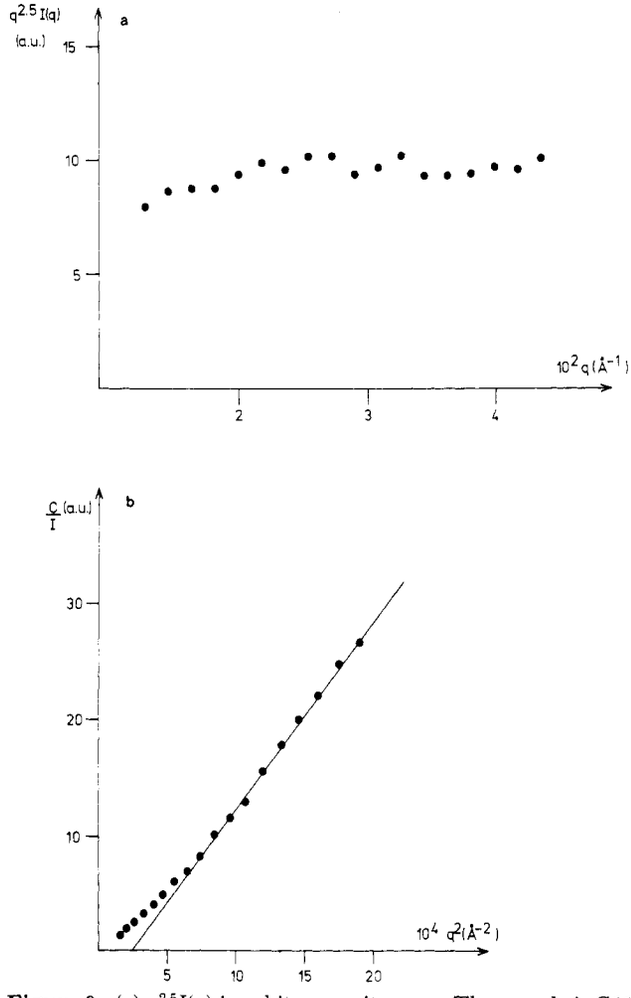

Figure 9. (a) $q^{2.5}I(q)$ in arbitrary units vs. q. The sample is G11 which differs from F11 only by the molding temperature. (b) $C/I(q)$ in arbitrary units vs. q^2 for G11. The curve exhibiting negative intercept (full line) differs significantly from a Debye function.

Kerr effect experiments[13] performed on poly(*p*-chlorostyrene) provided that the configurations are not perturbed by the presence of Cl atoms. The rotational isomeric results of Flory suggest nevertheless a decrease of C_M with temperature of the same order of magnitude as found in our experiments.[12] However, the solvent interaction energy taken into account in crude approximation in the calculation is adjusted with experimental results obtained at only one temperature and the case of a polymeric solvent (i.e., atactic polystyrene) has not been envisaged.

It seems difficult therefore to propose an unambiguous model for that thermal behavior.

3. Influence of APSH Matrix Molecular Weight. Previously described experiments have been carried out by using matrices of equivalent or higher molecular weight than the tagged IPSD chains in the range 120–220 °C. In these cases no particular conformational behavior of IPSD chains can be noticed. Now, using matrices of lower molecular weight, it has been observed that IPSD chains have no more pure Gaussian character. In Table IV are listed the characteristics of the investigated samples (F and G series) as well as the exponents of the asymptotical behavior of the scattered intensity (Figures 8a,b for F samples and 9a,b for G samples) and the R_g molecular weight dependence (Figure 10). The exponents measured in the intermediate range differ from the classical one (i.e., Gaussian exponent) obtained in the previous section. Such behavior has not been found for atactic polystyrene where the pure Gaussian statistic in the bulk is pointed out over a large range of matrix molecular weights. Nevertheless,

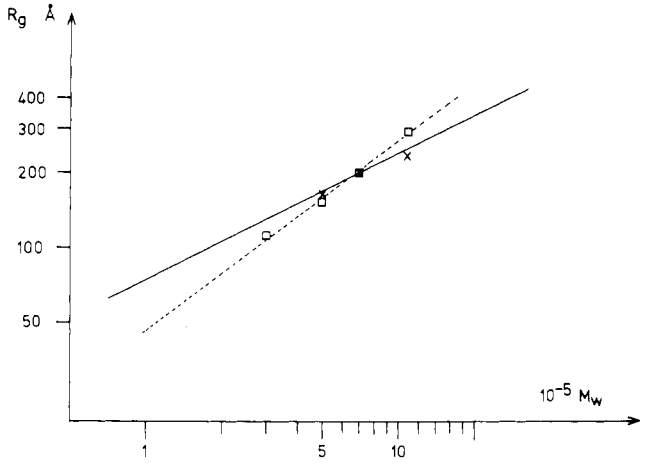

Figure 10. Log R_g vs. log M_w. Full line represents the D series with the exponent close to 0.5 (see Table II): x represent F samples and □ G samples. The dotted line gives an exponent close to 0.74.

Kirste and Lehnen[14] have shown that very high molecular weights of poly(dimethylsiloxane) (PDMS) dispersed in a very small molecular weights matrix of the same polymer exhibit expansed chain behavior. These latter results have been interpreted in terms of virial coefficient which depends on the ratio of the molecular weights of the labeled chains and the matrix. In our case such argument is irrelevant since the abnormal behaviors vanish at 240 °C (see samples B4 and C4) which is above the melting temperature of IPSD (T_m = 209.5 °C).

The q asymptotical exponent 1.66 for samples prepared at 180 °C is very close to the three-dimensional excluded volume exponent (5/3). However, such value could be fortuitous. For example, the intensity scattered by a chain globaly Gaussian having Gaussian and rodlike sequences could lead to a similar result. Then the radius of gyration would not differ significantly from that of a pure Gaussian coil. On the other hand, the value of the exponent of 2.5 observed for samples prepared at 200 °C could correspond to an intermediate conformation between a two-density system and a Gaussian chain. The R_g molecular weight variation $\sim M^{0.74}$ could suggest the existence of prolate scattering objects whose principal axis increases preferentially with molecular weight.

It would then be tempting to associate the previous abnormal exponents as a tendency toward crystallization of IPSD chains in the investigated temperature range. However, at this stage of the experimental results any reasonable model may be proposed to interpret clearly such behavior.

Nevertheless, it must be remembered that these kind of effects arise only for matrices of molecular weights lower than those of IPSD chains. Does this effect result from the degree of interchain penetration which could be different in such situations? Recently SANS experiments have been performed on atactic polystyrenes, the center of which has been labeled by deuteration.[15] The measurements of the scattered intensity $I(q)$ vs. q for molded solid samples have revealed diffraction peaks which lead to a reappraisal of the generally admitted concept of total chain interpenetration in bulk amorphous polymers.

This points out that the amorphous state for polymers is not so simple. Then it would be irrelevant to give further and clearer interpretations of the observed effects at the moment.

Conclusion

From solid samples prepared at room temperature by evaporation of concentrated solutions, we have confirmed the unperturbed values of IPS obtained by Krigbaum et al.[1] with other techniques. However, these unperturbed dimensions depend strongly on the temperature contrarily to those of APS or polyethylene. It would then be interesting to compute conformational energies taking into account the measured values of the characteristic ratio C_M in order to determine the most probable configuration of the dyads as a function of temperature. One has to notice that SANS experiments provide us unperturbed dimensions of IPS in a large range of temperature which was not directly available from other experimental methods.

On the other hand, the experiments have shown that the tacticity of the matrix has no effect on the chain conformation provided that the samples are molded above the melting temperature of IPS. Nevertheless, below this melting point, IPSD chains behave differently according to the molecular weight of the APS matrix being lower or higher. The divergence from Gaussian state has not been described by any theories which consider mostly flexible polymers only. Such unexpected results cannot unfortunately be cross-checked by other experimental techniques. It would be interesting to confirm this phenomenon by SANS experiments with other polymers having isotactic and atactic homologues.

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