STRUCTURE AND TRANSITIONS IN ATACTIC POLYSTYRENE

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ABSTRACT

WANS experiments were performed in order to investigate the liquid state of atactic polystyrene. It was found that PS undergoes both a reversible and an irreversible structural change at a temperature which corresponds to T_{ll}, the liquid-liquid transition. These results plus earlier results on birefringence are interpreted in terms of a structural model presented by Mitchell and Windle.

1. INTRODUCTION

Despite the fact that "over the years more studies have been made of polystyrene (PS) than of any other noncrystalline polymer"[1] much remains unclear about this material. There is just beginning to emerge a coherent picture of its structure, while the nature of the transitions which it undergoes, especially the liquid-liquid transition, may be described as controversial. In earlier work on the temperature dependence of the birefringence of atactic PS (at-PS),[2,3] we presented evidence that this transition is in some sense a structural change, and suggested[2] that it might represent a short range order transition. In order to study this possibility, we began a neutron diffraction study of atactic polystyrene, from room temperature through the glass transition temperature, T_g, and the liquid-liquid transition temperature, T_{ll}, to 190°C. In what follows, we present the first results of this study. These results will be interpreted in terms of the structural model recently presented by Mitchell and Windle[1] (referred to hereafter as M-W), rather than of short range order. The birefringence results can also be readily explained from the same point of view.

2. BIREFRINGENCE AND STRUCTURE OF ATACTIC POLYSTYRENE

It has been known for some time[4-7] that solvent cast at-PS films tend to be birefringent, with an anisotropy in the refractive indices of light polarized perpendicular and parallel to the plane of the film. Prest and Luca[6] showed that this is due to the orientation of the backbone chains in the plane of the film. The same authors[8] showed that this birefringence disappears if the films are cast at or above T_g. However, there was very clear evidence[7] that once the birefringence was established it could remain despite annealing above T_g. We have recently demonstrated[2,3] that a film which is birefringent remains so up to considerably above T_g, the birefringence disappearing at a temperature very close to T_{ll}. As all of our measurements were performed at room temperature, we could not obtain any quantitative information on the kinetics of the disappearance of birefringence. However, we found that holding a sample for three hours at a temperature one or two degrees below the temperature of disappearance did not make the birefringence disappear. Thus, if T_{ll} is not a phase transition temperature, but rather a relaxation temperature, the relaxation is very slow, and totally unrelated to the relaxations taking place at T_g.

Two recent wide angle x-ray scattering (WAXS) studies strongly support the picture of structural changes at T_{ll}. Hatakeyama[9] investigated the behavior of the first and second diffraction peaks of PS. The first peak is the so-called "polymerization peak"[10] while the second is a peak associated with styrene. He found that the ratio of the amplitude of these two peaks changes dramatically for high molecular weight at-PS between T_g and T_{ll}, and very little immediately above and below this range. In a remarkable study, M-W showed that the first peak in PS is in fact an "interchain" peak, related to the spacing between polymer chains. In order to explain the detailed diffraction patterns and their temperature dependence, they proposed a model of "superchains," bundles of roughly six chains in which the phenyl groups are stacked. Since the peak persists to above T_{ll}, (although M-W do not discuss this in their paper) it is clear that the superchains must persist as well. We shall return to the implications of these two publications later.

3. WIDE ANGLE NEUTRON SCATTERING

While there have been a great many WAXS studies of at-PS and a few small angle neutron scattering studies,[11] there appear to have been few if any studies of at-PS by wide angle neutron scattering (WANS). Since WAXS is sensitive to electron density, whereas WANS depends upon nuclear scattering, the two can give complementary information. We decided to perform WANS studies of at-PS from room temperature through T_g and T_{ll} to 190°C, to see if we could clarify the nature of the structural changes taking place in this temperature range. Preliminary studies with normal, hydrogenated material suggested that interesting changes might be taking place. However, the large incoherent scattering background from the protons precluded any detailed analysis of these results. In order to overcome this difficulty, we have performed WANS studies on deuterated polystyrene. We present here the first results of this work.

Experimental

Deuterated at-PS (at-dPS) of M_n = 239,000 and M_w = 338,000 was synthesized, and characterized by gel permeation chromatography. It was dissolved in cyclohexane, precipitated in the form of a powder in methanol, and dried at 90°C. The resulting powder was loaded into a 1/4 inch diameter cylindrical vanadium cell. Vanadium was chosen in order to avoid an overlap between the diffraction pattern of the sample and that of the container. A series of WANS experiments were performed on the 2XD powder diffractometer[12] at the Missouri University Research Reactor:

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(1) A powder scan was run of at-dPS at room temperature, and compared with that of deuterated styrene monomer (dSM).

(2) The sample was annealed in a sand bath for 15 minutes at a series of temperatures, spaced 10°C apart, from 80°C to 200°C, and measured at room temperature after each annealing step.

(3) The sample was re-annealed at temperatures covering the same range, but spaced 20°C apart, for an hour at each temperature, and remeasured at room temperature.

(4) The sample was measured at temperatures between 100°C and 200°C, during which time the temperature was held to within 2°C. Measurements were taken every 10°C over this range.

All of the above experiments were performed at a wavelength of 1.3 Å. Experiments (1) to (3) were performed with an open collimator, so that counting times were 7.5 hours each. Experiment (4) was performed with a Soller collimator, so that the total counting time at each temperature was 12 hours.

4. RESULTS

The powder scans for the at-dPS and dSM samples are shown in Figure 1. To each dSM peak there corresponds a peak in the at-dPS pattern, shifted to slightly lower Q (= $4\pi \sin\theta/\lambda$) due to the free volume in the polymer. In addition, there is a shoulder on the second peak, at approximately 1.9 Å^{-1}. All of the positions of these peaks and the shoulder are in good agreement with the positions reported from WAXS measurements.[11] Finally, there is a peak in the at-dPS scan, at lower Q, at approximately 0.6 Å^{-1}, which does not correspond to a dSM peak. This is the so-called "polymerization peak."[10] (In what follows, we shall call this Peak 1, the following, Peak 2, etc.) Peak 1 is stronger here than the succeeding peaks, whereas in WAXS Peak 1 is considerably weaker than Peak 2. We were unable to observe Peak 1 in WANS on hydrogenated polymer. These differences can be readily understood. In WAXS the only contribution to this peak is from C-C correlations, whereas in WANS, D-D and C-D correlations also contribute to the total amplitude. Since the proton scattering amplitude is negative, the various contributions can cancel each other for
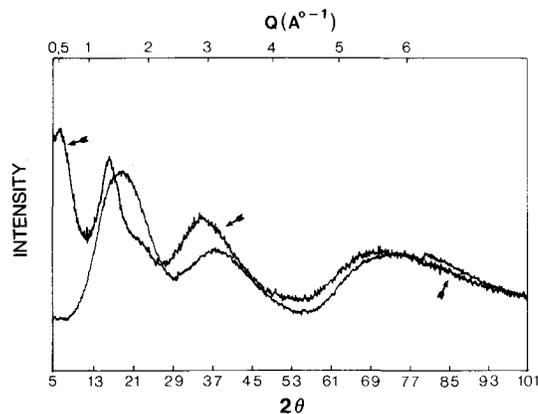

Fig. 1. WANS spectra of deuterated at-PS (arrows) and deuterated styrene monomer.

Table I. Ratio of WANS intensity measured at room temperature of Peak 1 compared with other peaks as a function of annealing temperature (15 min at each temperature). The entries 180/1 and 180/2 indicate the results of first and second annealings (see text).

Temp. (°C)	Peak 1/Peak 2	Peak 1/Peak 3	Peak 1/Peak 4
room temp.	1.095	1.357	1.615
80	1.075	1.361	1.597
90	1.084	1.342	1.600
100	1.059	1.317	1.572
110	1.085	1.318	1.601
120	1.059	1.312	1.555
130	1.052	1.304	1.554
140	1.050	1.285	1.531
150	1.036	1.284	1.513
160	1.023	1.248	1.493
170	1.019	1.256	1.487
180/1	1.012	1.231	1.449
180/2	1.016	1.253	1.456
190	1.031	1.277	1.510
200	1.036	1.274	1.462

ordinary *at*-PS, explaining the lack of this peak in that case. The slight difference in the position of this peak in WANS and WAXS can probably also be explained by the presence of additional scattering centers in the first case.

When the sample was annealed [experiment (2)], the position of Peak 1 remained constant until 150°C, after which it shifted by about 0.4° to a slightly higher angle. All the other peak positions remained constant, within experimental error. Changes in peak heights were considerably more important. As the amount of polymer in the neutron beam could change with temperature, we present the changes in the form of ratios. In Table I we show the change of the ratios Peak 1/Peak n, where n may be 2, 3, or 4, as a function of annealing temperature. It is clear that all of these ratios decrease. In order to assure that this was not due to a change in the background, we also calculated the ratios Peak 1/Dip n, where n is 1, 2, or 3. These are given in Table II. In Figure 2 we plot the data for the Peak 1/Peak 2 ratio. The data show clearly that the ratio changes little until the annealing temperature reaches 90°C, the temperature at which the powder was dried and also near the T_g, drops until about 180°C, and then increases and seems to stabilize at 200°C (this is confirmed by comparison with other peaks and dips).

The second annealing study [experiment (3)] showed no further changes in these ratios, within experimental error. That is, the first run results in irreversible changes in the polymer configuration in the temperature range studied, after which the material is relatively stable.

Once the material was stable, measurements were made at various temperatures [experiment (4)]. The results are shown in Table III and Figure 3. The results in Table III are equivalent in nature to those contained in Table II; and the information shown in Fig. 3 is analogous to that of Fig. 2. Again, there are substantial changes between 100°C and 180°C, with the intensity ratio Peak

Peak 1 compared with other
each temperature). The entries
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k 3	Peak 1/Peak 4
7	1.615
1	1.597
2	1.600
7	1.572
8	1.601
2	1.555
4	1.554
5	1.531
24	1.513
248	1.493
256	1.487
231	1.449
253	1.456
277	1.510
274	1.462

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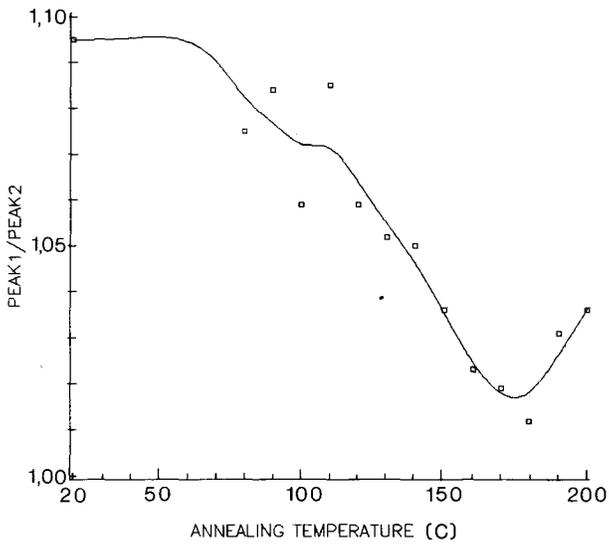| Temp. (°C)	Peak 1/Dip 1	Peak 1/Dip 2	Peak 1/Dip 3
room temp.	1.493	1.708	2.115
80	1.458	1.700	2.137
90	1.463	1.725	2.113
100	1.459	1.695	2.099
110	1.464	1.694	2.124
120	1.448	1.689	2.100
130	1.441	1.692	2.087
140	1.435	1.696	2.119
150	1.431	1.655	2.085
160	1.429	1.652	2.055
170	1.429	1.658	2.061
180/1	1.420	1.623	2.021
180/2	1.441	1.637	2.042
190	1.430	1.667	2.072
200	1.420	1.657	2.055

Fig. 2. Intensity ratio of the polymerization peak (Peak 1) over the second peak (Peak 2) as a function of annealing temperature. All measurements were made at room temperature. The curve is the result of a computer smooth and fit routine.

1/Peak n increasing with increasing temperature in this range. The ratios change relatively little above and below those limits. Qualitatively, this is in agreement with the WAXS measurements reported by Hatakeyama[9] for the first two peaks. While M-W did not specifically investigate the temperature range discussed here, the general behavior is also in qualitative agreement with their results.

5. DISCUSSION AND CONCLUSIONS

As we have noted above, M-W have shown that the first peak in PS is in fact an "interchain" peak, related to the spacing between polymer chains, whereas the other peaks are related to distances within the monomer. Thus, the changes reported here show that in the temperature range described above, the interchain configurations change substantially and irreversibly on the first run, as the structure which was built in by precipitation from solution is removed and replaced by an annealed structure. In addition, there is a reversible change with temperature, which M-W associate with a small change in interchain spacing.

For at-PS of reasonably high molecular weight, T_g occurs somewhat above 100°C. For example, in our birefringence study we found that the T_g of a sample with $M_n = 70,000$ was 106°C, or 379 K, and that the birefringence disappeared at 163°C, or 436 K. We identified this latter temperature as T_{ll}, in agreement with the empirical rule[13]

$$T_{ll}/T_g = 1.20 \pm 0.05 \tag{1}$$

The molecular weight of the polymer studied here is considerably higher. We may expect (but have not yet measured) that the corresponding temperatures would be slightly higher in this case. We therefore arrive at the conclusion that in the range roughly between T_g and T_{ll} the interchain structure of at-PS changes both, irreversibly with the annealing out of unstable configurations, and reversibly. One might have expected such irreversible changes from the DSC work of Gillham and Boyer,[14] which showed an endothermic peak for the first run (their Fig. 20).

Table III. Ratio of WANS intensity of Peak 1 compared with other peaks as a function of measurement temperature for a fully annealed sample.

Temp. (°C)	Peak 1/Peak 2	Peak 1/Peak 3	Peak 1/Peak 4
20	0.987	1.213	1.424
100	1.037	1.299	1.538
110	1.016	1.322	1.515
130	1.074	1.354	1.610
140	1.082	1.377	1.594
150	1.090	1.380	1.648
160	1.120	1.454	1.730
170	1.151	1.473	1.745
180	1.177	1.513	1.760
190	1.185	1.490	1.705

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354	1.610
377	1.594
380	1.648
454	1.730
473	1.745
513	1.760
490	1.705
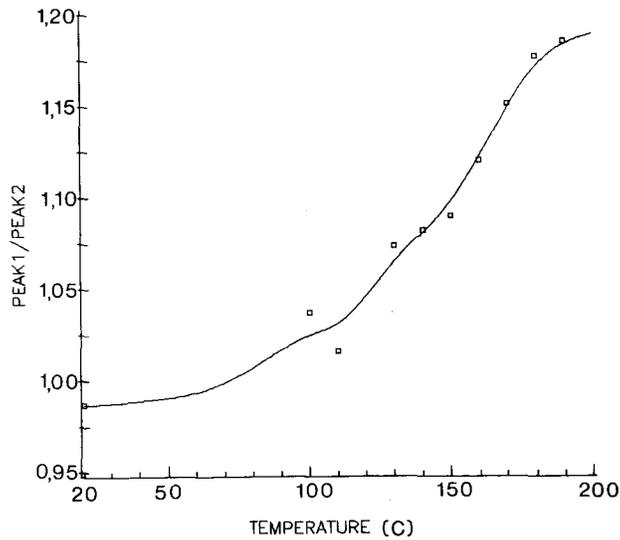
3. Intensity ratio of the polymerization peak (Peak 1) over the second peak (Peak 2) as a function of temperature. The curve is the result of a computer smooth and fit routine.

The interchain correlation persists however, to considerably higher temperature. M-W report that the interchain peak is still very intense at 250°C.

Building on these results, and making use of the superchain model proposed by M-W, we can speculate on the thermodynamics of at-PS. For this purpose, we shall take Fig. 21 of ref. 1, in which they show correlations between superchains crosslinked by skeletal bonds of the PS molecules, more seriously than those authors seem to have intended. We insist that our proposal is consistent with, but not required by, the current experimental situation.

It is clear that the superchains are stable from well below T_g to well above T_{ll}. We suggest that, at least for thin layers in the presence of a surface which tends to align the backbones parallel to it, the birefringent, long range ordered configuration is stable below T_g. In this state, the distinction between one superchain and its neighbor becomes blurred. The fact that films are no longer birefringent when cast above T_g[8] shows that this order is no longer stable above this temperature. However, its persistence in films which have already been cast[2] suggests that short range order between superchains is stable, and that the long range order is metastable, up to T_{ll}. Thus, T_{ll} would represent an order-disorder transition between superchains, at least for at-PS.

One would suspect that the superchains would disintegrate at a lower temperature than the PS molecule itself. Whether this happens or not remains to be verified. If it does, it cannot take place at the temperature called T_{ll} by Boyer and co-workers[15] (or $T_{l\rho}$ in their most recent publications[16]). This is reported to be at 40 to 50°C above T_{ll}, whereas the interchain peak is still strong at 20 or 30°C above that.[1] As our proposal depends very strongly on the existence of the "polymerization peak," and as this peak is observed only in PS and a few other polymers,[1] it is also not clear that our explanation of T_{ll}, should apply to other linear polymers.

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DISCUSSION

R.E. Robertson (University of Michigan, Ann Arbor, Michigan): I actually thought that you were going really well, that this was certainly a T_{ll} transition because it seemed to depend on the entire molecule and wasn't just short range order.

A. Yelon: Believing it doesn't depend on seeing a kink, when you're seeing something disappear entirely.

R.E. Robertson: If I'm not mistaken, the reason for birefringence on casting these films is basically because you have anisotropic drying. As the solvent evaporates you should reach the glass transition temperature for that mixture.

A. Yelon: That's at least one thing that's claimed.

P.M. Dreyfuss (Michigan Molecular Institute, Midland, Michigan): On what type of surface do you cast the films?

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A. Yelon: We've been casting them on glass but you can cast them on all kinds of surfaces ... can anneal them all kinds of ways. If it were just a question of anisotropic drying then it ... be hard to understand why it persists. If you look at the degree of birefringence, it is clear ... you make it up to a certain thickness the whole thing is birefringent, and if you make it ... that thickness the film is still birefringent but a smaller and smaller fraction is birefringent. ... words, it looks like the material close to the surface is birefringent and the material far ... the surface is not. It seems as though the surface is telling it to lie in a certain way. I don't ... it's due to anisotropic drying. I think it's due to the surface telling it which way to conform, ... obviously remains to be demonstrated.

G.R. Mitchell (University of Reading, Reading, United Kingdom): What solvent were ...cast from?

A. Yelon: In the birefringence work, we used xylene.

G.R. Mitchell: The first thing is that there are very, very strong solvent dependent ...gurations that can be generated, which people have studied in gels. Obviously, when you dry ... films you get quite close to a gelling point. Have you done any scattering studies on the ...?

A. Yelon: No, we have not done any scattering studies on the films.

G.R. Mitchell: The structure in your film may be completely different from the structure ... bulk.

A. Yelon: If we wanted to do neutron scattering experiments, in particular, we have to take ... deuterated material and cast films from it. We'd like to do this next, after we get permission ... the owners of the polymer to do it.

G.R. Mitchell: Is the T_g the same in these films? Have you measured the T_g of the films; is ... the same as the starting material?

A. Yelon: The only way we could really measure the T_g has been by thermal ...measurements, and in that case, yes, it is the same as the starting material.

R.E. Robertson: Wouldn't this whole phenomenon arise if there were anisotropic drying, drying from one surface? In this way the molecules get stretched and then clearly everything else would follow, and furthermore, it would be a long range effect as Dr. Boyer defines the T_{ll}.

A. Yelon: There is no question that the birefringence could be an artifact of the preparation; I don't deny that. But that's not the point. It may be, in fact, an artifact of the preparation technique and it just turns out that you get it because of the way it is dried or various other things that are going on while it is being made. In fact, when I started doing this, that's what I thought. The point is, if that's the case, one asks oneself, why is it that the temperature at which it no longer will work is T_g? That's a curious phenomenon because you'll keep on drying it well afterwards. There have been films that have been cast below T_g and have been dried above T_g very often, for example. That begins to say to me that perhaps it is not an artifact, but that the sample likes to be that way and that's what we're suggesting. I'm not saying that it's a clearly demonstrated ...ct by any means.

R.E. Robertson: It certainly is true that you can have surface effects. The surface does influence the way that molecules lie down and these effects would certainly extend in by one molecular diameter, not just the chain diameter but the molecular diameter; this is something like 100 nm. How thick are these films? They're quite a lot thicker than that, aren't they?

A. Yelon: I haven't done the studies but other people have reported that the material continues to develop birefringence up to several microns.

J.M.G. Cowie (University of Stirling, Stirling, Scotland): Wouldn't you be able to resolve this problem if you cooled the material from the melt on a glass surface and looked to see if you regenerated the birefringence?

A. Yelon: No, you do not. Once the birefringence has gone away when you cool it down it does not come back.

J.M.G. Cowie: Even in contact with the surface?

A. Yelon: Yes. When we have the sample on the glass, we heat it up to above T_{ll} and the birefringence goes away and when we bring it back down to room temperature it's not there anymore. So, no, it does not come back. That means that either it wasn't the stable state in the first place or that in cooling it down, the relaxation effects are such that it doesn't get back to what would be the equilibrium condition.

J.M.G. Cowie: It would suggest to me that it isn't a surface effect. If you're casting it, it has nothing to do with the orientation of the surface and that's not what is controlling it.

A. Yelon: That's quite possible. You can take your choice of which of these two treatments is getting it closer to the equilibrium structure, as clearly one or the other of them is not. What I've said here is that if we accept that birefringence is preferred in the presence of a surface, and if we accept that T_{ll} is a kind of short range order transition, all of our observations are easily explained. The point is, if the other interpretations are correct, then I have a hard time explaining it; that's where we are.

G.R. Mitchell: Following my preferred method of resolving these issues, have people tried making these films using solvents other than xylene?

A. Yelon: Yes, xylene is by no means the only solvent that will work.

G.R. Mitchell: What sort of solvents are these particular solvents? Are they aromatic? Do they fall into different types of classes?

A. Yelon: There are several solvents that will give it to you. Other workers have observed birefringence in films cast from benzene and from methylene chloride.

G.R. Mitchell: I know that you're working with atactic polystyrene, but people have found that if you make gels from different sorts of solvents you get quite different conformations which is not surprising if you consider the rather open nature of the polystyrene chain. You can get some solvents in and they won't come out, so you can stabilize an all *trans* conformation, whereas perhaps the normal crystalline conformation in isotactic polystyrene would be a helix. If you can get that difference from solvents, I wonder whether you're just getting a different sort of structure.

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[...] a hard time explaining it; that's

[...]olving these issues, have people

[...] will work.

[...] solvents? Are they aromatic?

[...] Other workers have observed
[...]

[...] polystyrene, but people have
[...] quite different conformations
[...] polystyrene chain. You can get
[...] trans conformation, whereas
[...] would be a helix. If you can
[...] a different sort of structure.

A. Yelon: The first point I can answer, the second point I cannot. The first point is that you [...]cast the material from several different solvents and it becomes birefringent. We haven't, and I [...]'t think anyone else has done a study of whether the temperature at which it stops being [...]fringent, either when you're making it or when you're annealing it, is a function of the solvent [...] which you cast it. That would be an interesting subject and also a lot of work.

J.K. Kruger (Universitat des Saarlandes, Saarbrucken, Federal Republic of Germany): I [...] not completely understand the differences between the film made from solution and that from the [...]lt. If you go down from the melt to the glass transition on a glass slide, in general, because of the [...]ference in expansion coefficients, you will immediately get some birefringence.

A. Yelon: My thought on the subject is that if you cast it from solution the molecules will [...]ve enough mobility so that they can get to align in the plane, whereas once they're in the melt, they [...] longer have the mobility to align in the plane.

J.K. Kruger: In general, is the T_{ll} transition also observed in material which has not been prepared from solution?

A. Yelon: Yes. All of these neutron scattering measurements are not on birefringent films. This is a material that is a powder that has been treated. What I said is that the T_{ll} transition is a short range order transition, and if you put in this longer range order below a temperature where its stability disappears, then it remains metastable because of the fact that you have this short range order. In other words, the fact that superchains are communicating with each other saying "stay aligned with me" causes this material to stay aligned in the plane of the film beyond the temperature at which it would stay aligned in the plane of the film when you were making it.

J.K. Kruger: So, what you want to state is that polystyrene film made from solution has another different short range order than that of a film which has been cooled down from the melt?

A. Yelon: No. I assume that the short range order is the same; but superimposed upon the short range order in the one case is a long range order, and in the other case not. Because of the fact that in solution the molecules can move much more easily, I assume that they can get closer to the equilibrium configuration and that the answer to the question, which one is choosing the best one, would be the solution rather than the melt.

R.E. Robertson: Well, that's only true when it's real dilute.

A. Yelon: Yes, it's more true when it's more dilute.