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Extended and Threefold Helical Conformations in Gels of Isotactic Polystyrene

Effect of Solvent

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Summary

Gels of isotactic polystyrene (iPS) were prepared, using solvents of different molecular geometries, by rapid quenching of the solutions formed at high temperatures. The extended conformation was observed in gels prepared with bulky, cyclic hydrocarbon solvents, whereas the aromatic solvents promoted the threefold helical structure. The gels containing the threefold helix were more elastic compared to those with the extended conformation. The effect of the solvent geometry is explained qualitatively,

Introduction

The accessibility of the non-staggered tt conformation to the skeletal bonds was detected in the stereochemical calculations on isotactic PMMA (SUNDARARAJAN and FLORY, 1974). Subsequent analysis of a series of such vinyl chains (SUNDARARAJAN, 1979, 1980) showed this to be a common feature for chains bearing planar substituents. Although the perfectly staggered tt conformation of the skeletal bonds incurs severe repulsive overlap of the side groups attached to the adjacent C^{α} atoms, a rotation of about 20° around the skeletal bonds relieves the repulsion and the non-staggered tt state becomes comparable in energy to the tg state. The latter, when perpetuated, generates the familiar threefold helical structure with a repeat distance of 6.65A.

The x-ray diffraction pattern recorded by Girolamo et al (1976) from gels of iPS, prepared by rapid quenching of the solution in decalin, was different from that of the threefold helical structure. Stereochemical calculations showed (SUNDARARAJAN, 1979) that such a diffraction pattern could be accounted for by an iPS chain containing 12 monomers in a repeat distance of 30.6A, with the non-staggered tt disposition of the skeletal bonds. This conformation (called the extended conformation) is shown in projections in Figure 1. Subsequent publications (ATKINS et al, 1980; LOVELL and WINDLE, 1980; CORRADINI et al, 1980) confirmed the possibility of such a conformation.

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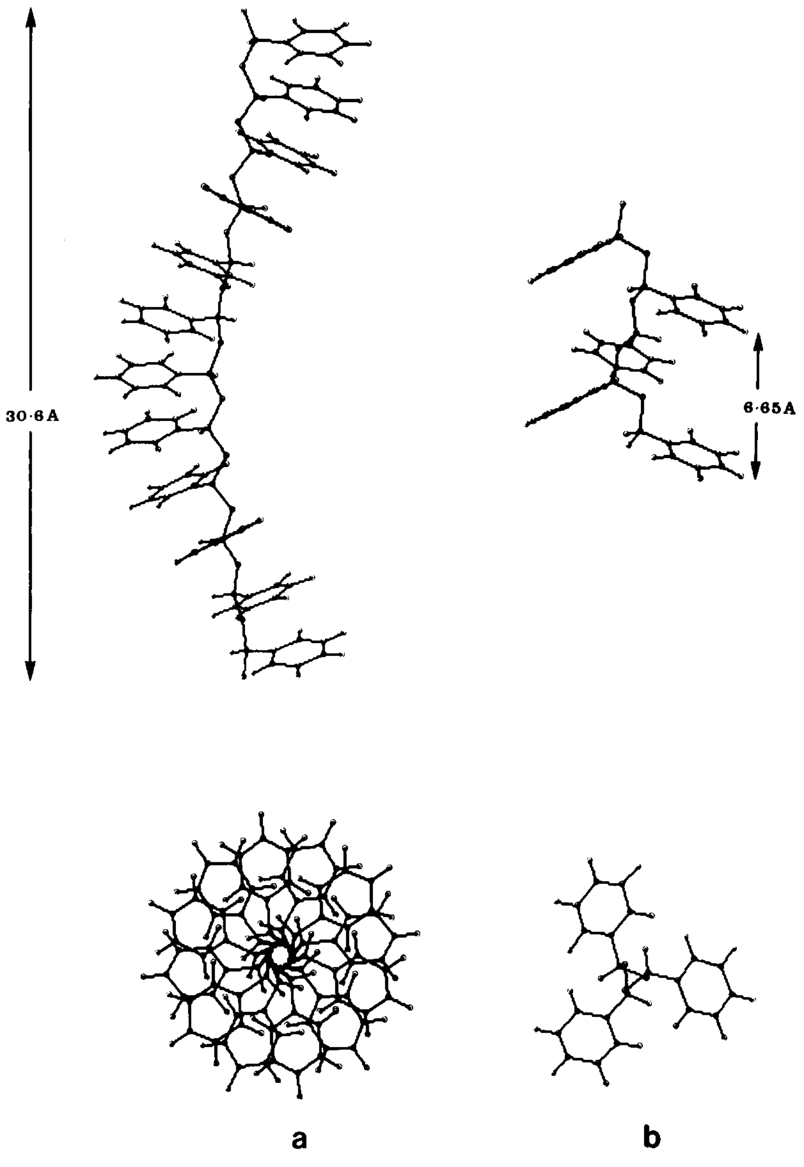


Figure 1: The projections of (a) the extended conformation with non-staggered tt state of the skeletal bonds and (b) the threefold helix with tg conformation.

Examination of Figure 1 shows that in the threefold helix, the phenyl groups are in a suitable disposition for interaction with the solvent molecules or other chains. Since the intramolecular phenyl-phenyl interaction is negligible, this conformation would occur in profusion in good solvents. In the extended conformation, the interaction between the adjacent phenyls is predominant and as such the interaction with the solvent molecules is unfavorable. The intramolecular stacking of the phenyl groups here is similar to that in small molecule crystal structures of aromatic systems. Hence, such a conformation can be expected to be predominant in solvents with bulky geometries, i.e., the molecules which cannot interact stereochemically favorably with the phenyls. Thus, the conformation of the iPS in gels can be expected to be solvent dependent. Hence, iPS gels were prepared using solvents of different molecular geometries to determine the conformation of the chain in the crystalline domains.

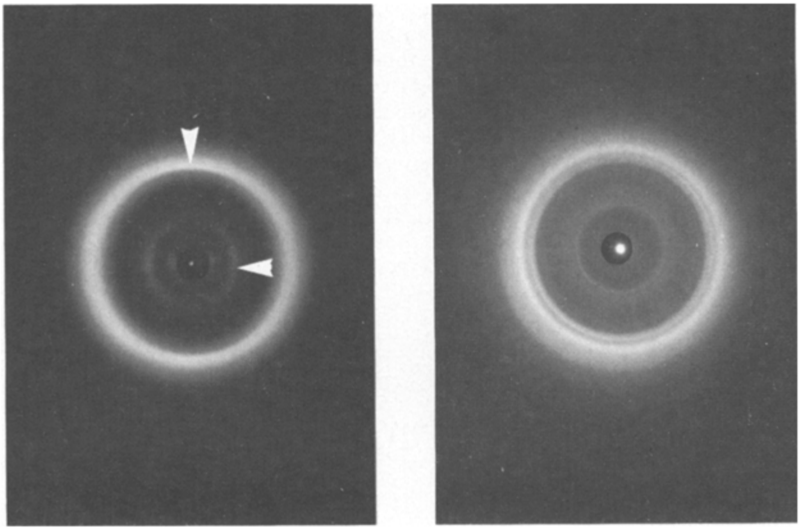
Experimental

Two samples of iPS were used: one (A) was from Polysciences and the other (B) was courtesy of Professor R.W. Lenz. Both samples were crystalline powder as received. Proton NMR analysis, using a Bruker WM250 spectrometer showed the isotactic dyad contents of the samples A and B to be 60-65% and 75-80%, respectively (G.K. Hamer, personal communication). Trans decalin (165,0), commercial cis/trans decalin (165,0), hexahydroindan (160,0), cyclooctane (145,0), cyclodecane (165,0), nitrobenzene (150,10), benzaldehyde (145,0), ethyl benzene (130,-90), *n*-butyl benzene (160,-80), and *t*-butyl benzene (160,-40), were used in this study. The first number in the brackets denotes the temperature (°C) at which the solution was prepared and the second is the temperature to which it was rapidly quenched. A concentration of 10% by weight was used throughout.

The conformation of the chains in the crystalline domains was determined mainly by x-ray diffraction and in a few cases, by DSC. A box-type camera (W. Warhus Co., Wilmington, DE) was used to record the diffraction patterns on films. Copper K_α radiation ($\lambda = 1.5418A$) was used. The patterns for the gels from benzaldehyde and ethyl benzene were recorded at temperatures of -20°C and -40°C respectively, in order to preserve the characteristics of the gel. The DSC traces were obtained using a DuPont model 990 thermal analyzer.

Results and Discussion

In addition to decalin, the other cyclic hydrocarbons listed above promote gelation of iPS upon quenching. These gels were rigid but could be stretched. Although they were transparent when prepared, turbidity developed upon aging. The x-ray pattern for the gel prepared from cyclooctane is shown in Figure 2a. The reflections with spacings of 5.1A (meridional) and 10.3A (equatorial), which are characteristic (ATKINS et al, 1977) of the extended conformation, are seen here.



a b

Figure 2: X-ray diffraction patterns from the gels prepared from the solution of iPS in (a) cyclooctane and (b) nitrobenzene, by quenching.

Similar patterns were obtained for both samples A and B with the other cyclic hydrocarbon solvents. This shows that the extended conformation can be obtained by the proper choice of the solvent molecule.

DSC traces of the dried gels show the presence of two endotherms. The lower endotherm, which occurs between 45° and 120°C depending on the solvent, is associated with the melting of the extended conformation, as confirmed by x-ray diffraction patterns recorded after annealing the samples in this temperature range. The variation of the melting temperature could be due to the presence of the residual solvent, the differences in the degree of crystallinity promoted by the particular solvent and the crystallite size in the domains containing the extended conformation. The second endotherm occurred at 210-230°C, corresponding to the melting of the threefold helical domains (in the heating cycle, the increase in the temperature is itself sufficient to cause crystallization of the threefold helical structure). If the DSC traces are recorded after cooling the sample, the lower endotherm does not appear. The crystalline regions containing the extended conformation, once melted, do not reform, unless the gelation route is repeated. Thus, the description in the literature (GIROLAMO et al, 1976; WELLINGHOFF et al, 1979), of the iPS gels being reversible, does not imply that the extended and threefold helical crystalline structures can be interchangeably obtained upon cooling and heating.

The aromatic solvents also promote the gelation of iPS upon quenching the solution formed at high temperatures. The gels prepared from these solvents were highly elastic. The x-ray diffraction pattern from the gel prepared by quenching the iPS solution in nitrobenzene is shown in Figure 2b. The pattern is characteristic of the threefold helical structure. This shows that either the extended or the threefold helical conformation can be induced to crystallize in the gels of iPS by an appropriate choice of the solvent molecule. The aromatic solvent molecules, which can interact favorably with the phenyl groups, encourage the crystallization of the threefold helical conformation.

Conclusions

The occurrence of the extended conformation in the crystalline domains of the gels prepared from cyclic hydrocarbon solvents and the threefold helical conformation in the case of the aromatic solvents points to the effect of the intramolecular interaction between the adjacent phenyls in iPS. Either conformation can thus be induced to crystallize. The connectivity between the crystallites in one conformation is provided mainly by the portions of the chain in the other conformation. The gels containing the threefold form being more elastic compared to those with the extended conformation is interesting and offer a model to relate the effect of the short range conformational preference to the mechanical behavior of these systems.

References

ATKINS, E.D.T., ISAAC, D.H., KELLER, A., and MIYASAKA, K.: J. Polym. Sci., Polym. Phys. Ed. 15, 211 (1977)

ATKINS, E.D.T., ISAAC, D.H., and KELLER, A.: J. Polym. Sci., Polym. Phys. Ed. 18, 71 (1980)

CORRADINI, P., GUERRA, G., PETRACCOME, V., and PIROZZI, B.: Eur. Polym. J. 5, 1089 (1980)

GIROLAMO, M., KELLER, A., MIYASAKA, K., and OVERBERGH, N.: J. Polym. Sci., Polym. Phys. Ed. 14, 39 (1976)

LOVELL, R. and WINDLE, A.H.: J. Polym. Sci., Polym. Letters 18, 67 (1980)

SUNDARARAJAN, P.R. and FLORY, P.J.: J. Am. Chem. Soc. 96, 5025 (1974)

SUNDARARAJAN, P.R.: Macromolecules 12, 575 (1979)

SUNDARARAJAN, P.R.: Macromolecules 13, 512 (1980) and ref. therein

WELLINGHOFF, S., SHAW. J., and BAER, E.: Macromolecules 12, 932 (1979)

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