shifted further toward the blue with rising temperature, though the extent of the intermixing of the constituent blocks increases as indicated by the SAXS data. This tendency contrasts with the results obtained from fluorescence spectra of AN solubilized into the hydrophobic core of the micelle. Intermolecular association may induce a change in the state of the PHEMA chains within the intermixing phase since the number of chains participating in the formation of the polymolecular micelle increases with rising temperature.

References and Notes

(1) Part 1 of this series is ref 3.
(2) (a) Department of Polymer Chemistry. (b) Department of Applied Physics.
(3) Ikemi, M.; Odagiri, N.; Tanaka, S.; Shinohara, I.; Chiba, A. *Macromolecules* **1981**, *14*, 34.
(4) Ikemi, M.; Odagiri, N.; Shinobu, T.; Shinohara, I. *Polym. J.* **1980**, *12*, 777.
(5) Utiyama, H.; Takenaka, K.; Mizumori, M.; Fukuda, M.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1974**, *7*, 515.
(6) Pleštil, J.; Baldrian, J. *Makromol. Chem.* **1973**, *174*, 183.
(7) Pleštil, J.; Baldrian, J. *Makromol. Chem.* **1975**, *176*, 1009.
(8) Price, C.; McAdam, J. D. G.; Lally, T. P.; Woods, D. *Polymer* **1974**, *15*, 228.
(9) Kotaka, T.; Tanaka, T.; Hattori, M.; Inagaki, H. *Macromolecules* **1978**, *11*, 138.
(10) Stacy, C. J.; Kraus, G. *Polym. Eng. Sci.* **1977**, *17*, 627.
(11) Tuzar, Z.; Petrus, V.; Kratochvîl, P. *Makromol. Chem.* **1974**, *175*, 3181.
(12) Tuzar, Z.; Kratochvîl, P. *Makromol. Chem.* **1972**, *160*, 301.
(13) Prasad, K. N.; Luong, T. T.; Florence, A. T.; Paris, J.; Vaution, C.; Seiller, M.; Puisieux, F. *J. Colloid Interface Sci.* **1979**, *69*, 225.
(14) Stryer, L. *J. Mol. Biol.* **1965**, *13*, 482.
(15) Anufrieva, E. V.; Birshtein, T. M.; Nekrasova, T. N.; Ptitsyn, O. B.; Sheveleva, T. V. *J. Polym. Sci., Part C* **1968**, *16*, 3519.
(16) Fenyo, J. C.; Braud, C.; Beaumais, J.; Muller, G. *J. Polym. Sci., Polym. Lett. Ed.*, **1975**, *13*, 669.
(17) Ghosh, S.; Basu, M. K.; Schweppe, J. S. *Biochim. Biophys. Acta* **1974**, *337*, 395.
(18) Wang, J. L.; Edelman, G. M. *J. Biol. Chem.* **1971**, *246*, 1185.
(19) McLaughlin, A. C. *J. Biol. Chem.* **1974**, *249*, 1445.
(20) Chiba, A.; Uzawa, S.; Usa, M.; Doi, S. *Rep. Prog. Polym. Phys. Jpn.* **1974**, *17*, 139.
(21) Radda, G. K. *Biochem. J.* **1971**, *122*, 385.
(22) Seliskar, C. J.; Brand, L. *J. Am. Chem. Soc.* **1971**, *93*, 5414.
(23) Azzi, A.; Chance, B.; Radda, G. K.; Lee, C. P. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *62*, 612.
(24) Stryer, L. *J. Am. Chem. Soc.* **1966**, *88*, 5708.
(25) Stryer, L. *Science* **1968**, *162*, 526.
(26) Seliskar, C. J.; Brand, L. *J. Am. Chem. Soc.* **1971**, *93*, 5405.
(27) Nêmethy, G.; Scheraga, H. A. *J. Chem. Phys.* **1962**, *36*, 3382.
(28) Hendricks, W.; Schmidt, P. W. *Acta Phys. Austriaca* **1967**, *26*, 97.
(29) The pure core radius, defined as $\gamma R - \alpha\gamma R$, reaches ca. 200 Å. The values seem to be too large for the PHEMA blocks to reach from the center of the inner core to its outer limit. This may arise from difficulty in determining the correct values of the boundary width since a partial mixing of the blocks continuously diminishes at the fringes of the boundary region. The values of the pure core radius are probably smaller than the values estimated from SAXS data.

Solvent-Dependent Conformations in Gels of Isotactic Polystyrene

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ABSTRACT: Using bulky hydrocarbon and substituted aromatic solvents, gels of isotactic polystyrene (iPS) were prepared by quenching the solution formed at high temperatures. It was found that the hydrocarbons induced the extended conformation, whereas either the threefold conformation or a mixture of threefold and extended conformations was obtained from aromatic solvents. Variations in the *d* spacings of the threefold helix structure were noted with the aromatic solvents. The observations are qualitatively explained on the basis of short-range interaction between adjacent phenyl groups.

Theoretical calculations on isotactic polystyrene (iPS) have shown that the nonstaggered conformations close to the tt state of the contiguous skeletal bonds are accessible without steric overlap.[1,2] This feature was shown to be common to most isotactic vinyl chains with planar substituents, including poly(*N*-vinylcarbazole).[3] The rotations $\Delta\phi_i$ and $\Delta\phi_{i+1}$ from perfect staggering (defined by (0°, 0°) for the tt state) required to relieve the overlaps were of the order of 15–20°, and the signs of the rotations fell into two classes: (+,+) or (−,−) for monosubstituted chains and (+,−) or (−,+) for disubstituted chains, as shown in Figure 1. Calculations on iPS showed that without the adjustments adopted to include the solvent effects,[1] the energy of the tt state was lower than that of the tg state. However, it is known that in the crystalline state iPS adopts a threefold helical conformation, with a repeat distance of 6.6 Å along the chain, and that this helical character is substantially maintained in good solvents.[4]

Keller et al.[5,6] reported a new X-ray diffraction pattern from gels of iPS prepared from *trans*-decalin. The characteristic features were a meridional reflection of 5.1-Å spacing and a layer line distance of 30.6 Å. Calculations of several authors[2,7-9] showed that this pattern could be accounted for by a helix containing 12 monomers within the repeat distance of 30.6 Å. The conformations of the skeletal bonds would then correspond to the nonstaggered tt state.

Wellinghoff et al.[10] studied the gelation of isotactic and atactic polystyrenes from various solvents as a route to preparing glassy polymer films. The interesting feature of these films is the fringe-micellar aggregation of the extended-chain domains, giving rise to a glassy film with microcrystalline regions. Using various types of solvents with differing solubility parameters, they concluded that dispersion forces control the solution behavior of these systems.

The gels of iPS are prepared by quenching the solution rapidly below the spinodal line. In the poor-solvent regime, segmental interaction of the polymer chain becomes operative. In the concentration range used for the gelation experiments, interchain forces also might play a role. In the threefold helical conformation of iPS, which is char-

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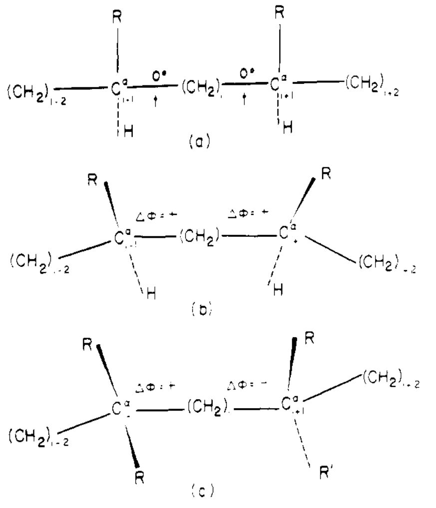
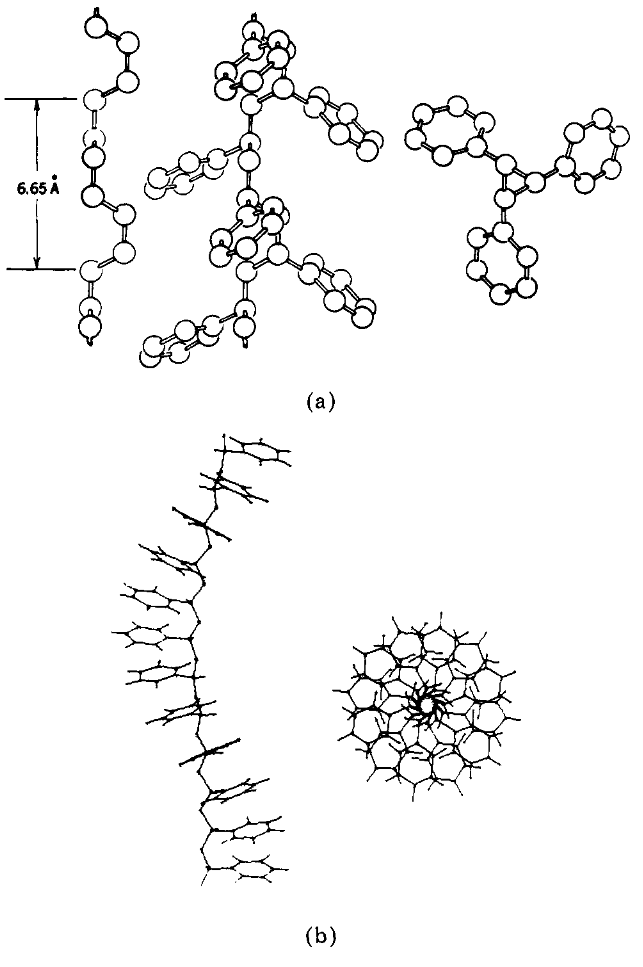


Figure 1. Schematic of the rotations required to minimize the energy in the tt state of meso dyads of vinyl chains: (a) projection in perfect staggering; (b) calculated shifts for monosubstituted chains; (c) calculated shifts for disubstituted chains. The signs of the rotations have been defined before.[15]



(a)

(b)

Figure 2. Projections of (a) the threefold and (b) the extended conformations of isotactic polystyrene.

acterized by the tg sequence of skeletal bonds, the phenyl groups on successive C^{α} atoms are far apart, as shown in Figure 2a, and there is very little interaction between them. They are in a suitable disposition to interact with the solvent molecules or neighboring chains. However, in the extended conformation, shown in Figure 2b, which is generated by the near-tt state of the skeletal bonds, the interaction between the phenyl groups appended to successive C^{α} atoms is significant. In poor solvents, in which the phenyl–solvent interaction is unfavorable, the adjacent skeletal bonds would tend to adopt the conformation that favors the phenyl–phenyl interaction. Thus, in solution, the polymer chain can be visualized to be surrounded by layers of solvent molecules, reminiscent of the hydrophobic interaction.

Table I
List of Solvents and Relevant Temperatures Used in This Study[a]

solvent	T_S, °C	T_Q, °C	T_X, °C
trans-decalin	165	0	R[b]
cis,trans-decalin	165	0	R
hexahydroindan	160	0	R
cyclodecane	165	0	R
cyclooctane	145	0	R
nitrobenzene	150	10	10, R
benzaldehyde	145	0	−20, R
ethylbenzene	130	−90	−10, −40
n-butylbenzene	160	−80	R
tert-butylbenzene	160	−40	R

[a] T_S = solution temperature; T_Q = quenching temperature; T_X = temperature at which X-ray patterns were recorded. [b] R = room temperature.

In the extended conformation, the stacking of the phenyl groups is similar to that in small-molecule aromatic systems. However, in this case, it is an *intra*molecular effect. Thus, apart from segmental interaction, short-range interaction of the type exhibited by the extended conformation is also important in poor solvent systems. The conformer population at any given temperature or solvent can be expected to be dictated to a large extent by the stereochemistry of the solvent molecule. Since the stereochemical calculations on isolated chains show that the tt state is as favorable as the tg state, either conformation can occur in varying proportions, depending on the solvent. Thus when the gel is prepared by quenching, the conformation of the iPS chain in the gel can be expected to be solvent dependent. Solvents of different molecular geometries have been used in this work to examine the occurrence of the extended conformation in iPS. It is shown that although gelation can be obtained from various solvents, the conformation of the chain is dictated by the stereochemistry of the solvent molecule.

Experimental Section

Three samples of isotactic polystyrene were used in this study: a commercial, pelletized iPS from Polysciences (sample A), a powder sample, also from Polysciences (sample B), and a powder sample, supplied through the courtesy of R. W. Lenz, University of Massachusetts (sample C). Sample A was amorphous as received, while samples B and C were crystalline and exhibited a threefold helical structure, as determined by X-ray diffraction. Proton NMR analysis,[11] using a Bruker WM250 spectrometer, showed the isotactic dyad content of samples A and B to be 60–65% and that of sample C to be 75–80%. Thus, sample A appears to be the pelletized form of sample B, the crystallinity of the latter having been lost during pelletization. All solvents (Table I) were of spectroscopic grade, with the exception of nitrobenzene, which was AR grade. A concentration of 10% by weight was used throughout. Gels were prepared by dissolving the polymer at temperatures given in Table I, followed by quenching after 30 min. Gels made from cyclic hydrocarbons were stretched and dried at room temperature, while those from benzene derivatives were dried at lower temperatures, due to their instability under ambient conditions.

The conformation of the chain in the gels was characterized mainly by X-ray diffraction and by DSC in a few cases. A box-type camera (William Warhus Co.) was used to record the diffraction patterns on films, and the camera was evacuated, whenever possible, to reduce scattering due to air. Copper Kα radiation

Table II
Spacing of Equatorial Reflections from Gels from Various Solvents

solvent	spacing, Å
trans-decalin	10.3, 20.5
cis,trans-decalin	11.3, 18.2
hexahydroindan	11.0, 18.2
cyclodecane	12.7, 18.4
cyclooctane	11.3, 18.4

(λ 1.5418 Å) was used. Some of the patterns, as mentioned in Table I, were recorded below room temperature, using the procedure described before.[12] The DSC traces were recorded with a DuPont Model 990 thermal analyzer.

Results and Discussion

A. Gels from Hydrocarbon Ring Solvents.

In addition to *trans*-decalin, other bicyclic and cyclic hydrocarbon ring systems induce gelation of iPS. In all these cases, the gels were, as with *trans*-decalin, initially transparent but developed turbidity over a period of time. They were rigid but stretching was possible.

The X-ray diffraction patterns of stretched gels showed a prominent meridional reflection at 5.1 Å. Equatorial reflections of spacings 20.5 and 10.3 Å were also present in the decalin gel. While the 5.1-Å reflection remains unchanged, the spacings of the equatorial reflections vary with the solvent, as shown in Table II. This seems to suggest that the intracrystalline regions are occupied by the solvent molecules and the interchain distance is influenced by the size and shape of the solvent molecule. Gels formed with *trans*- or *cis, trans*-decalin using sample A showed the diffraction pattern due to the extended conformation, but reflections corresponding to the threefold helix were also faintly present. However, with both samples B and C, these solvents promoted only the extended form. The influence of any atactic and amorphous material present in the pelletized commercial sample A in giving rise to mixtures of conformations is insufficiently understood at this time.

The behavior of sample A in giving rise to mixtures of conformations cannot be generalized either. The gels prepared from hexahydroindan, cyclodecane, and cyclooctane showed only the extended conformation, accompanied by diffuse scattering due to the solvent and amorphous material. The same results were obtained, but with less amorphous scattering, from samples B and C and the above three solvents. Thus, these bulky, nonpolar hydrocarbon molecules promote the extended conformation, irrespective of the initial crystallinity.

DSC traces of dried gels yield two principal endotherms. The position of the lower endotherm, which has previously[6,10] been identified to be associated with the melting of the gel conformation, varied from 45 to 120 °C, depending upon the solvent used for gelation. This could be due to the combined effect of the residual solvent and the "degree of crystallinity" and crystallite size in the extended-chain domains. The second endotherm occurred at 210–230 °C. If the gel was maintained at 230 °C for several minutes and the DSC traces were recorded after the sample was cooled to room temperature, the lower endotherm vanished. Thus, the extended conformation, which was induced by the solvent during gelation, melts at 45–120 °C but does not re-form unless the gelation route is repeated. These results were confirmed by recording X-ray data from gels annealed at temperatures above and below the lower endotherm. For the gel made from hexahydroindan, a broad endotherm was observed at 60–75 °C. The X-ray pattern of the gel annealed at 45 °C for 2 h showed reflections due to both the extended and threefold helices. Annealing at 80 °C removed the reflections due to the former.

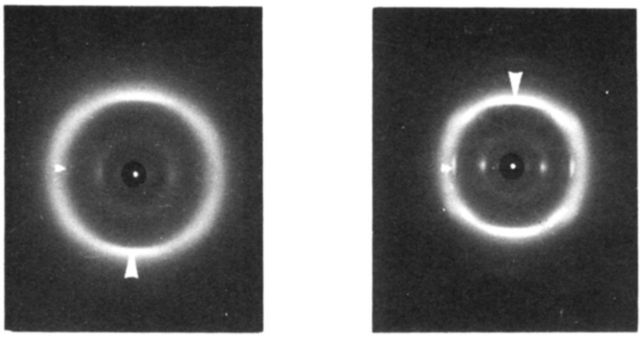


Figure 3. X-ray diffraction patterns from iPS–decalin gel, annealed at 40 and 60 °C. The meridional reflection due to the extended conformation and the equatorial reflection due to the threefold helix are marked by arrows.

The description in the literature[6,10] of the iPS gels as being "reversible" gels needs to be clarified. As seen from the DSC and X-ray diffraction results, once the extended conformation melts, it does not re-form upon cooling. Hence, the transformation from extended to threefold helix via melting of the former is an irreversible change. Only upon repeating the gelation procedure is the extended-chain conformation achieved. Further, upon annealing, the chains in the extended conformation do not continuously transform to the threefold helix. Figure 3 shows the X-ray diffraction patterns from the gels prepared from sample B, using decalin, and annealed at 40 and 60 °C. Although the reflections due to the threefold helix begin to appear at 40 °C, the intensities of the reflections due to the extended form remain unchanged. Thus, the chains participating in the extended conformation remain in that state up to its melting point.

Prolonged aging of the gels gave results similar to those for annealing. A gel made from sample A and decalin showed after nearly 3 months under ambient conditions the presence of only the threefold helical conformation. Similar gels from samples B and C, which originally contained only the extended form, displayed equal X-ray diffraction intensities due to both forms. This, again, could be interpreted as due to the combined effect of evaporation of occluded solvent and annealing at room temperature over an extended period of time.

Of the three samples used here, sample A was initially amorphous, whereas samples B and C were crystalline. Earlier studies show that the helical character or molecular association in the crystalline state is preserved to a large extent in solution.[4] In order to verify if the initial crystallinity of the material has any influence at all, sample B was melt-quenched from 250 °C to room temperature. The X-ray patterns of the material showed only amorphous scattering. Gels prepared from this material from hexahydroindan, cyclodecane, and decalin were transparent, but they lacked rigidity and crumbled upon touching. The X-ray patterns showed reflections corresponding to both threefold and extended structures. This is in contrast to the result obtained from the gels prepared from the original material. The lack of rigidity could be attributed to partial degradation of the sample upon heating to 250 °C. However, the degradation of polystyrene at 250 °C is not extensive.[13] Thus, while the melt-quenched iPS behaved similarly to the amorphous sample A in containing both helical forms in the gel, this lack of rigidity is in contrast to the properties of the gel prepared from sample A.

Table III
Conformations in iPS Gels Prepared from Aromatic Solvents[a]

solvent	sample A	sample B	sample C
nitrobenzene	3_1	3_1	3_1
ethylbenzene	3_1	$3_1 + 12_1$	$3_1 + 12_1$
tert-butylbenzene	3_1		$3_1 + 12_1$
n-butylbenzene	$3_1 + 12_1$		$3_1 + 12_1$
benzaldehyde	$3_1 + 12_1$	$3_1 + 12_1$	$3_1 + 12_1$

[a] 3_1, threefold helix; 12_1, helix with 12 monomers per turn.

Table IV
Variations in *d* Spacings Observed with Aromatic Solvents

solvent	*d* spacings, Å	indices	conformation
n-butylbenzene	4.67	211	3-fold
	5.09	006	extended
	9.99	110	3-fold
tert-butylbenzene	4.69	211	3-fold
	5.11	006	extended
	9.99	110	3-fold
benzaldehyde	4.62	211	3-fold
	5.11	006	extended
	10.97	110	3-fold
ethylbenzene	5.10	006	extended
	5.47	220	3-fold
	10.56	110	3-fold

B. Gels from Bulky Aromatic Solvents. Gels of iPS could be prepared by using aromatic solvents, but these gels exhibit physical features different from those of iPS gels prepared with hydrocarbon solvents. These gels were extremely elastic and sticky to the touch but turned hard and brittle upon standing at room temperature. Hence, immediately after preparation, these were stored at below room temperature, and the X-ray patterns were recorded, in most cases, at below ambient temperature, as shown in Table I.

A summary of the conformations present in the gels from aromatic solvents is given in Table III. All of them contained the threefold helical form. The extended conformation was observed as an additional component in only a few cases. It is believed that the high elasticity upon formation is due to the presence of the threefold form.

Gels made from all three samples, using nitrobenzene, contained only the threefold helix, as seen from Table III. In the case of ethylbenzene and *tert*-butylbenzene, the conformation depends on the starting material. While sample A contained only the threefold helix, samples B and C exhibited the presence of both forms. The similarity of the results for ethyl- and *tert*-butylbenzene might be attributed to the geometric similarity of the solvents—both have substituents that can be approximated to a spherical domain. In contrast, gels made from benzaldehyde and *n*-butylbenzene contained both conformations, regardless of the starting material.

The X-ray patterns from gels prepared with these aromatic solvents exhibit variations in the *d* spacings attributable to the threefold helix. The relevant spacings are given in Table IV. It is seen that the 5.1-Å reflection remains unaffected and intense. However, the 4.85-Å reflection (corresponding to the 211 plane in the threefold helix structure) reduces to 4.6 Å, and the 10.97-Å equatorial reflection reduces to 9.9 or 10.56 Å. An increase of interchain distances in the lattice to include guest molecules is commonly observed. The decrease noted here seems to be due to the cohesion promoted by the aromatic guest molecules and perhaps the distortions in the relative rotations of the phenyl groups with respect to the skeletal bonds. The decrease of the spacing of only the 211 reflection, without a corresponding decrease in the 110 spacing, in the case of benzaldehyde is puzzling. The insufficient X-ray data to derive the unit cell dimensions for the extended structure prevent assignment of the reflections to one or the other structure. The variation of the threefold helical crystal structure of iPS with occluded solvent molecules of this type is as yet an unexplored phenomenon.

C. Excursion into the Spinodal Region. It is known that rapid quenching of concentrated iPS solutions to below the upper critical solution temperature is essential to promote gelation. If the solution is cooled slowly to room temperature, precipitation occurs and the threefold conformation results. From rheological measurements, Tager et al.[14] found that concentrated solutions of polystyrene in decalin consist of two types of structures and that the molecular association is destroyed by variations in temperature over the temperature range 15–120 °C. It seemed of interest to examine the resulting conformation of iPS by varying the temperature *from which* the solution is quenched, since these systems exhibit a considerable range of metastability.

A solution of sample C in decalin, prepared as before at 165 °C, was slowly cooled to 80 °C and then quenched to 0 °C. The X-ray diffraction pattern from the resultant gel contained the 5.1-Å reflection, characteristic of the extended conformation, and there was no trace of the threefold helical form. Quenching from 40 °C also showed the same diffraction pattern. However, in this case, the absence of the threefold helix could not be confirmed due to extensive amorphous scattering. Upon cooling to room temperature, the solution turned turbid and upon quenching, only the threefold helix was detected. Thus, quenching the decalin solution anywhere from 165 to 40 °C results in gel formation and the extended conformation. The effect of temperature on crystallite size is not explored here.

Conclusions

The occurrence of the extended conformation in poor solvents reinforces the effect of interaction between adjacent side groups in iPS, which predominates over the polymer–solvent interaction. The occurrence of the extended and/or threefold helices in the gels indicates the differences in stereochemical compatibility between the substituted aromatic solvents and cyclic hydrocarbons. Although the theoretical calculations based on empirical methods have so far been unable to arrive at a minimum on the energy surface at the precise location of the extended conformation, the latter is close to the calculated minimum position. The actual minimum in the tt region of the meso dyad of polystyrene occurs at $(\phi_i, \phi_{i+1}) = (15°, 15°)$, which would promote flat and wide helices. In this case, the planes of the phenyl groups are not parallel and lattice stabilization of such wide helices with a large hole in the center is unfavorable. In the extended helix, the phenyl–phenyl overlap resembles that in low molecular weight aromatic molecules. Further, the conformations of this type with a (+,−) shift in $(\Delta\phi_i, \Delta\phi_{i+1})$ are the favored positions of minimum energy in the tt state of disubstituted chains[15,16] such as PMMA and poly(α-methylstyrene). It would seem that these conformations are prevalent to a larger extent than hitherto expected and predominate in poor solvent systems. Estimation of the relative proportions of the two structures is not attempted here.

The iPS system with the extended conformation has been visualized in terms of the fringe-micelle model.[6] The present study shows that either extended, threefold, or a mixture of the two conformations can occur in the gel, depending on the solvent. The connectivity between the crystallites containing one conformation is thus provided by the segments of the chain in the other conformations. The tacticity of the chain also seems to have an influence. The differences in the elasticity of the gels provide a good model for correlating the rheological behavior with conformer population and relative crystallinity and crystallite size of the two structures.

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References and Notes

(1) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.

(2) Sundararajan, P. R. *Macromolecules* **1979**, *12*, 575.

(3) Sundararajan, P. R. *Macromolecules* **1980**, *13*, 512.

(4) Kobayashi, M.; Tsumura, K.; Tadokoro, H. *J. Polym. Sci., Part A-2* **1968**, *6*, 1493.

(5) Atkins, E. D. T.; Isaac, D. H.; Keller, A.; Miyasaka, K. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 211.

(6) Girolamo, M.; Keller, A.; Miyasaka, K.; Overbergh, N. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 39.

(7) Lovell, R.; Windle, A. H. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 67.

(8) Atkins, E. D. T.; Isaac, D. H.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 71.

(9) Corradini, P.; Guerra, G.; Pirozzi, B. In "Preparation and Properties of Stereoregular Polymers"; Lenz, R. W., Ciardelli, F., Eds.; D. Reidel Publishing Co.: Boston, 1980; p 317.

(10) Wellinghoff, S.; Shaw, J.; Baer, E. *Macromolecules* **1979**, *12*, 932.

(11) Shepherd, L.; Chen, T. K.; Harwood, H. J. *Polym. Bull.* **1979**, *1*, 445.

(12) Sundararajan, P. R.; Hamer, G. K.; Croucher, M. D. *Macromolecules* **1980**, *13*, 971.

(13) Malhotra, S. L.; Hesse, J.; Blanchard, L.-P. *Polymer* **1975**, *16*, 81.

(14) Tager, A. A.; Dreval, V. E.; Lutsky, M. S.; Vinogradov, G. V. *J. Polym. Sci., Part C* **1968**, *23*, 181.

(15) Sundararajan, P. R.; Flory, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 5025.

(16) Sundararajan, P. R. *Macromolecules* **1977**, *10*, 623.

Conformational Characteristics of Poly(vinyl bromide) and Ethylene–Vinyl Bromide Copolymers

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ABSTRACT: Conformational energies are calculated for chain segments in poly(vinyl bromide) (PVB) homopolymer and the copolymers of vinyl bromide (VB) and ethylene (E) (PEVB). Semiempirical potential functions are used to account for the nonbonded van der Waals and electrostatic interactions. Rotational isomeric state (RIS) models are developed for PVB and PEVB from the calculated conformational energies. Dimensions and dipole moments are calculated for PVB and PEVB using their RIS models, where the effects of stereosequence and comonomer sequence are explicitly considered. It is concluded from the calculated dimensions and dipole moments that the dipole moments are most sensitive to the microstructures of PVB homopolymers and PEVB copolymers and may provide an experimental means for their structural characterization.

Introduction

We have recently utilized the chemical shifts observed in the ^{13}C and ^{19}F NMR spectra[1-3] and the molar Kerr constants[4-7] measured in electrical birefringence experiments to characterize the microstructures of vinyl homo- and copolymers. This characterization is achieved by our ability to predict both properties for a given microstructure.

A key ingredient in our recipes for predicting both properties is the conformational characteristics of the polymer chain. We must have knowledge of the allowed conformations and their relative probabilities. The purpose of this investigation is to gather such knowledge for poly(vinyl bromide) (PVB) and the copolymers (PEVB) of ethylene (E) and vinyl bromide (VB).

Recently, ^{13}C NMR studies have been reported[8,9] for PVB and its oligomeric model compounds 2,4-dibromopentane and 2,4,6-tribromoheptane. In addition, PEVB copolymers have been made via the facile reductive debromination of PVB and their ^{13}C NMR specta recorded.[10] We hope to be able to predict the observed ^{13}C NMR chemical shifts of these polymers and oligomers using the conformational characteristics developed here for PVB and PEVB.

Table I
Lennard-Jones 6-12 Parameters for PVB and PEVB

$$E(\text{van der Waals}) = -\frac{C_{ij}}{r_{ij}^{6}} + \frac{A_{ij}}{r_{ij}^{12}}$$

atom pair, ij	$C_{ij}{}^{a}$	$A_{ij}{}^{a}$
H,H	46.5	7 180
H,C	126	56 000
C,C	361	393 130
H,Br	420	250 000
C,Br	1200	1 700 000
Br,Br	4000	7 000 000

[a] The values given for C_{ij} and A_{ij} yield E(van der Waals) in kcal/mol when r_{ij} is expressed in Å.

First conformational energy calculations are performed on the various chain fragments occurring in PVB and PEVB. Next a rotational isomeric state (RIS) model[11] is developed for PVB and PEVB from the conformational

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