Conformational Studies of Polymers and Copolymers of Poly(L-aspartate esters). IV. Infrared Studies of the Side-Chain Orientations in Solid Films

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Received July 12, 1971

ABSTRACT: Theoretical studies of Scheraga and his coworkers of isolated molecules of poly(L-aspartate esters) have predicted the existence of two side-chain conformations, transverse for the long side chains and longitudinal for short side chains. In the transverse orientation, the side chain is wrapped tangentially around the helix, while for the longitudinal orientation it is more parallel to the helix axis. An investigation using polarized infrared spectroscopy has been made of the side-chain orientations of a series of poly(L-aspartate esters). It is shown that poly(β-benzyl L-aspartate), which can be prepared in either the right-handed or left-handed helical form, has different side-chain conformations depending on the helix sense, although both can be classified as transverse rather than longitudinal. All right-handed poly(L-aspartate esters) have the same side-chain conformation as right-handed poly(β-benzyl L-aspartate). The effect of the length of the side chain is shown from a comparison of left-handed methyl L-aspartate with the left-handed form of benzyl L-aspartate; the side-chain conformations are different although the helix sense is the same. However, both orientations are closer to the transverse than to the longitudinal. These studies confirm the general effects predicted by Scheraga, although there are substantial differences in detail. The latter may result from packing considerations of the solid film, which are not included in Scheraga's calculations.

Polymers of L-aspartate esters have been the subject of extensive investigation, both experimental and theoretical. The reason for this interest lies in the versatility of conformational behavior exhibited by these polypeptides. Thus, in the series of polymers of aliphatic L-aspartate esters, poly(β-methyl L-aspartate) was found to be in the left-handed form of the α helix,[1,2] while the polymers of ethyl, n-butyl, n-propyl, and isopropyl L-aspartates were all found to assume the right-handed α-helical conformation.[2] Whereas poly(β-benzyl L-aspartate) was shown to be in the left-handed α-helical form,[3,4] it has been shown for aspartate polymers with aromatic rings in the side chain that para substitution of the benzene rings with a nitro,[5-7] chloro, methyl, or cyano[8-10] group results in a reversal of helix sense to the right-handed form. More recently, Erenrich, Andreatta, and Scheraga[11] have also shown that poly(β-p-chlorobenzyl L-aspartate) is in the right-handed α-helical conformation but that polymers of the ortho and meta isomers were found to form left-handed helices.

Other factors are also found to affect the helix senses of aspartate polymers, in particular the conformations of copolymers in which the two homopolymer components take up opposite helix senses. Thus, random copolymers of β-ethyl L-aspartate with β-benzyl L-aspartate have been shown to undergo transitions from the right-handed to the left-handed helix sense as the temperature is increased, the inversion temperature increasing with increasing proportion of the ethyl L-aspartate component.[2] Similar helix inversions with temperature were found for copolymers of β-benzyl L-aspartate with β-p-nitrobenzyl L-aspartate.[7] Helix inversions have also been found to take place for copolymers of benzyl L-aspartate with the para-substituted L derivative on varying the components of a mixed-solvent system.[9]

Further conformational transitions have been observed for poly(β-benzyl L-aspartate). Malcolm has found that when this polymer is cast from 10% dichloroacetic acid–90% chloroform solutions as monolayers on water, it is in the right-handed helical conformation.[12,13] Exposure of dried films from collapsed monolayers to the vapor of 10% DCA–90% $CHCl_3$ results in a swelling of the film, and the polymer undergoes a reverse transition from the right-handed helix back to the left-handed form. Heating solid films of left-handed poly(β-benzyl L-aspartate) results in a different conformational transition, from the α helix to a 4.0_{13} helix, called the ω helix.[14] It has been shown that this transition depends on the presence of a benzene ring in the side chain and has led to the suggestion that the energy required for the distortion of the α helix to the ω helix comes from the packing of benzene rings in four stacks around the fourfold helix.[14,15]

The conformational versatility of aspartate polymers has made them extremely useful models for theoretical studies, and Scheraga and his coworkers have calculated the helix senses of most of the polymers mentioned above. An outcome of the work of Scheraga and his coworkers is the prediction of four possible side-chain orientations for L-aspartate polymers, two conformations for the right-handed helix and two conformations for the left-handed helix. These were designated Rt(−), Rl(−), Lt(−), and Ll(+), where R and L stand for right-handed and left-handed, respectively; t stands for transverse orientation, in which the side chains are

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wrapped tangentially around the helix roughly perpendicular to the helix axis; and l stands for longitudinal, in which the side chains lie more nearly parallel to the helix axis. In the transverse side-chain conformation, the (−) indicates that the side chain wraps itself around the helix in an anticlockwise manner looking from the N-terminal end of the helix, while (+) indicates a clockwise rotation. For the longitudinal side-chain conformation, the (+) indicates that the side chains point toward the C-terminal end, and the (−) indicates that they point toward the N-terminal end. For poly(aspartate esters) with short side chains, *e.g.*, ethyl and methyl L-aspartates, the longitudinal conformations were calculated to have the lower energies, while for the aspartate polymers with longer side chains, the transverse conformations were found to be preferred irrespective of helix senses.[16] To obtain information on the orientations of the side chains of aspartates with different helix senses we have made a detailed polarized infrared spectroscopic study of oriented films. Although Scheraga's calculations pertain to isolated molecules in a vacuum, certain patterns of behavior are predicted which may persist in the solid state although the precise side-chain conformation may be expected to be different as a result of the energy of packing; *e.g.*, the conformations of short side chains are predicted to be significantly different from those of long side chains. It is also of considerable interest to see, when packing energies are taken into consideration in the theoretical calculation of side-chain conformation, whether they agree with the experimental results.

The polymers and preparation techniques available allow a study of the side-chain conformations (a) of a short side chain (methyl L-aspartate) with a long side chain (benzyl L-aspartate), both polymers having the same helix sense; (b) of benzyl L-aspartate in both the right-handed and left-handed helical conformations; and (c) of a series of right-handed helical polymers including one with a short side chain, ethyl L-aspartate. Thus, it should be possible to evaluate the factors involved in determining the gross features of side-chain conformations in poly(L-aspartate esters) in the solid state. In a previous study, a comparison was made of the side-chain conformations of left-handed poly(β-benzyl L-aspartate) and right-handed poly(ethyl L-aspartate), and it was shown that considerable differences existed in the conformations of these side chains.

Experimental Section

Materials. The homopolypeptides were prepared by polymerization of the *N*-carboxy anhydride of the appropriate L-aspartate ester, while the random copolymers were obtained by the alcoholysis procedures described in a previous communication.[2]

Infrared Spectroscopy. The infrared spectra were recorded on a double-beam in-time microspectrometer designed and built in this laboratory and based on a Grubb-Parsons S3A monochromator with sodium chloride optics. The microspectrometer was designed for the examination of small areas (0.1 × 1 mm) of oriented films of macromolecules.[17] The orientation was produced by unidirectional shearing of viscous solutions until dry on barium fluoride plates by using a ground-horn spatula. Dichroic effects in the films were observed with a Perkin-Elmer gold wire polarizer placed behind the exit slit in the monochromator. All spectra were calibrated internally by the use of a thin film of polystyrene which could be inserted into the beam during a clear spectral region of the sample to give a calibration polystyrene peak. The accuracy and position of the bands was to within 3 cm^{-1} for the 1500–1200-cm^{-1} region and to 2 cm^{-1} for wavelengths longer than 1500 cm^{-1}; for the amide A region the accuracy was to within 10 cm^{-1}.

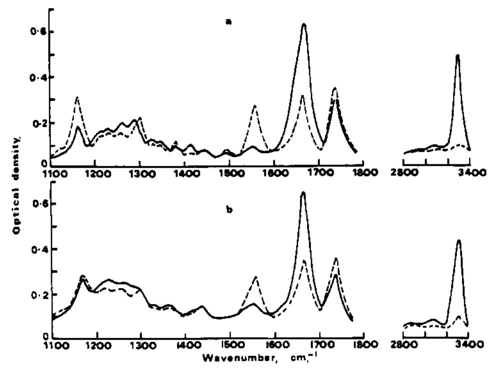

Figure 1. Polarized infrared spectra of (a) poly(11.5% methyl L-aspartate-*co*-88.5% benzyl L-aspartate) and (b) poly(87.5% methyl L-aspartate-*co*-12.5% benzyl L-aspartate): (———) *E* vector parallel and (- - - - -) *E* vector perpendicular to stroking direction.

Oriented films of poly(β-benzyl L-aspartate) in the right-handed α-helical conformations were obtained by casting a monolayer film from chloroform solution on water in a Langmuir trough, as described by Malcolm,[12,13] and collected on a BaF$_2$ plate. The collapsed monolayer was found to have a high degree of orientation.

Results

It has been shown that there is a frequency–conformation correlation for poly(L-aspartate esters) in the different helical forms.[10,15] Figure 1 gives the dichroic spectra of two copolymers of benzyl L-aspartate with methyl L-aspartate; both of these residues as homopolypeptides favor the left-handed α-helical form, and the amide frequencies of 1666 cm^{-1} for the amide I and 1557 cm^{-1} for the amide II for both copolymers also show them to be in the left-handed form. The similar dichroism of the amide A, I, and II bands indicates that the degrees of orientation of the two copolymers are very similar, and this allows a comparison to be made of the side-chain conformations. The main side-chain absorption bands are from the largely ester C═O stretching vibration at 1735 cm^{-1}, the ester C—O—C stretching vibration at 1165 cm^{-1}, and the bending mode of C$_\beta$H$_2$ at 1414 cm^{-1}. It can be seen in Figure 1 that the dichroism of these bands is different for the two copolymers. For the largely methyl L-aspartate copolymer, the dichroism of the ester C═O stretching band is higher, while that from the C—O—C stretching vibration is lower than for the largely benzyl L-aspartate copolymer; furthermore, although slightly overlapped by a band from a δ-CH$_3$ mode, the dichroism of the δ-C$_\beta$H$_2$ is very much less than for the largely benzyl L-aspartate copolymer, in which it shows a very high parallel dichroism. As the ester bands are clear of the absorptions of other vibrations, their dichroic ratios can be used to obtain the approximate orientation with respect to the helix axis of the transition moments associated with these vibrations. The angles between the two transition moments of the ester group vibrations have been estimated from the polarized infrared study of poly(ethylene suberate).[18] The transition moment of the ester carboxyl vibration was shown to lie at about 19° to the C═O bond, inclined toward the bisector of this bond and the adjacent

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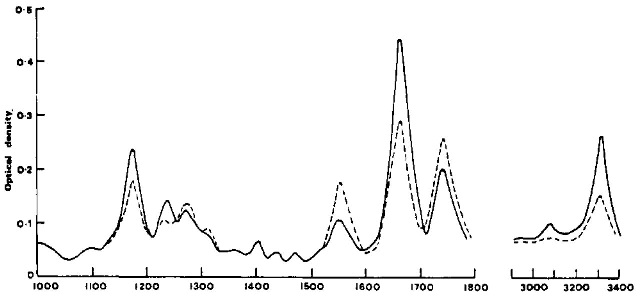

Figure 2. Polarized infrared spectrum of the right-handed α-helical form of poly(β-benzyl L-aspartate): (———) E vector parallel and (- - - - -) E vector perpendicular.

TABLE I

TRANSITION MOMENT DIRECTION WITH RESPECT TO HELIX AXIS FOR A SERIES OF COPOLYMERS OF BENZYL L-ASPARTATE WITH METHYL L-ASPARTATE

Methyl L-aspartate, %	Dichroic ratio: Main chain NH	Dichroic ratio: Side-chain ester C=O	Dichroic ratio: Side-chain ester C—O—C	f[a]	Angle,[b] deg C=O	Angle,[b] deg C—O—C
0					54	69
11.5	5.6	0.68	0.58	0.73	57	64
25.5	5.1	0.85	0.63	0.70	58	63
38.0	6.8	0.88	0.56	0.68	57	66
60.0	8.5	0.75	0.60	0.87	55	62
87.5	4.2	0.75	0.95	0.63	61	56

[a] f = fraction of polymer oriented. [b] Angle transition moment makes with main chain.

C_β—C_γ bond, while the transition moment of the C—O—C stretching vibration was along the line joining the C_γ—C_ϵ atoms. By using a model where a fraction (f) of the chains is considered fully ordered and $(1 - f)$ is considered disordered, it is possible to calculate the orientation of both of these transition moments with the helix axis for both the right-handed and left-handed α helices.[19] The direction of the transition moment of the N-H stretching vibration in the α helix has been estimated to be about 18° to the helix axis, and, for a perfectly ordered sample with fiber-type orientation, the dichroic ratio R_0 would be 15:1. From the observed dichroic ratio R of the NH stretching vibration, the fraction f of fully ordered chains can be found from[20]

$$f = (R - 1)(R_0 + 2)/(R_0 - 1)(R + 2)$$

By using this value of f, the angle θ which other transition moments make with the helix axis can be calculated from

$$R = \frac{f\cos^2\theta + (1/3)(1 - f)}{(1/2)f\sin^2\theta + (1/3)(1 - f)}$$

where R is the observed dichroic ratio for the band under consideration.

The dichroism of the side-chain bands and the angle their transition moments make with the helix axes for the copolymer series are given in Table I, and it can be seen that although the helix sense remains the same and the degree of orientation does not change markedly, there is a reorientation of the side-chain ester groups. Furthermore, the highly dichroic band for the $C_\beta H_2$ deformation mode at 1414 cm⁻¹ of the predominantly β-benzyl L-aspartate copolymer shows that its transition moment, which is the bisector of the HCH angle, is closely parallel to the helix axis. This high dichroism would indicate that only one side-chain orientation is present in the ordered film and that $C_\beta H_2$ occupies therefore only one rotamer. For the predominantly methyl L-aspartate copolymer, this band is largely nondichroic and the transition moment either lies close to 55° (or 125°) to the helix axis or several side-chain orientations are present which on the average result in a low dichroism for this band. If one side-chain orientation only is present, then $C_\beta H_2$ has reoriented itself through approximately 55° (or 125°) to occupy another rotamer of $C_\beta H_2$ around the C_α–C_β bond.

It is clear from these studies of copolymers of methyl L-aspartate and benzyl L-aspartate that although the left-handed helix sense persists throughout the series, the conformations of the side chains differ markedly for the two components. If the direction delineated by the two carbon atoms of the ester groups (C–O–C), *i.e.*, the oxygen-linked carbons, is taken as a rough indication of the side-chain orientation, then Table I shows that both side chains have a transverse orientation but that the longer benzyl L-aspartate side chain lies closer to the perpendicular to the helix axis than the shorter methyl side chain.

Considering next the effect of helix sense on the side-chain orientation, Figure 2 shows the dichroic spectrum of the right-handed helical form of poly(β-benzyl L-aspartate). This was obtained in the manner described by Malcolm of collapsing a monolayer cast on water in a Langmuir trough. The frequencies of the amide bands, 1658 cm⁻¹ for the amide I and 1553 cm⁻¹ for the amide II, are characteristic of the right-handed α-helical form of poly(L-aspartate esters). The dichroic spectrum for the left-handed form of poly(β-benzyl L-aspartate) is identical with the spectrum in Figure 1a of poly-(88.5% benzyl L-aspartate-*co*-11.5% methyl L-aspartate). It can be seen by a comparison of Figure 2 with Figure 1a that a considerable change in the side-chain conformation has taken place: the ester C=O stretching band has a higher perpendicular dichroism for the right-handed form, while the dichroism of the ester C—O—C stretching band has reversed, going from perpendicular in the left-handed form to parallel in the right-handed form, and the δ-CH_2 band goes from highly dichroic to nondichroic in the right-handed form. The directions of the transition moments for the ester vibrations of the left-handed form are given in Table I and are 54° for the C=O stretching vibration and 69° for the C—O—C vibration, while for the right-handed form these angles are found to be 62 and 42°, respectively. The change in dichroism of the band from the $C_\beta H_2$ deformation from strongly parallel for the left-handed form to nondichroic for the right-handed form indicates a change in direction of the HCH bisector from parallel to the helix axis to 55° (or 125°) to the axis. As in the case of the conformation of the methyl L-aspartate side chain, it appears that if a single conformation is present for the right-handed form of benzyl L-aspartate, then the $C_\beta H_2$ group occupies a different rotamer with respect to the polymer backbone than it does in the left-handed form.

Further questions which arise are whether the new side-chain conformation found above for the right-handed form of poly(β-benzyl L-aspartate) is also found for other right-handed helical forms of poly(L-aspartate esters) with long side chains, and whether right-handed poly(L-aspartate esters) with shorter side chains, *e.g.*, poly(β-ethyl L-aspartate), have a different side-chain orientation. The dichroic spectrum

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TABLE II

TRANSITION MOMENT DIRECTIONS WITH RESPECT TO HELIX AXIS FOR A SERIES OF COPOLYMERS OF BENZYL L-ASPARTATE WITH VARIOUS ESTERS

Benzyl L-aspartate with	Copolymer, %	Dichroic ratios Main Chain NH	Dichroic ratios Side Chain C=O	Dichroic ratios Side Chain C—O—C	f^a	Angle,[b] deg C=O	Angle,[b] deg C—O—C
Ethyl L-aspartate	18	3.5	1.0	0.69	0.55	55	64
	21	2.5	0.84	0.77	0.40	60	64
	40	4.5	0.59	1.37	0.65	65	48
	86	3.0	0.71	1.28	0.49	64	47
	100	2.9	0.65	1.31	0.47	67	47
n-Butyl L-aspartate	56	4.2	0.89	0.71	0.63	57	62
	67	6.8	0.84	0.100	0.80	58	55
	82	3.9	1.00	1.20	0.59	64	48
n-Propyl L-aspartate	20	6.0	1.0	0.63	0.76	54	62
	53	5.5	0.91	0.61	0.73	56	63
	81.0	6.4	0.56	1.40	0.78	64	48
	90.5	3.4	0.65	1.22	0.58	64	50
Phenethyl L-aspartate	90	2.5	0.72	1.23	0.4	66	48

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I

TABLE III

Poly(L-aspartate ester)	Helix sense	Angle of transition moment to helix axis, deg C=O[a]	C—O—C[b]	$\delta = C_\beta H_2$[c]
Methyl	LH	61	56	~55 (or 125)
Benzyl	LH	54	69	~9
Benzyl	RH	62	42	~55 (or 125)
Ethyl	RH	65	48	~55 (or 125)
n-Propyl	RH	64	50	~55 (or 125)
n-Butyl	RH	64	48	~55 (or 125)
Phenethyl	RH	66	48	~55 (or 125)

[a] Transition moment lies at 19° to the C=O bond inclined to the bisectors of this bond and the adjacent C—C. [b] Transition moment lies along the line joining the two carbon atoms. [c] Transition moment lies along the bisector of the H—C—H angle and in the H—C—H plane.

of poly(β-ethyl L-aspartate) is shown in Figure 3, and it can be seen that the dichroism of the side-chain absorption bands is very similar to that of the water-induced right-handed form of β-benzyl L-aspartate, shown in Figure 2, indicating similarity of side-chain conformations. For a series of copolymers of benzyl L-aspartate with ethyl L-aspartate, the transition from the left-handed form of benzyl L-aspartate to the right-handed form of ethyl L-aspartate can be followed using the frequencies of the amide bands as a guide. The transition takes place between 20 and 40% β-ethyl L-aspartate content, and, as can be seen from the data in Table II on the orientation of the ester group transition moments, this is the range in which the side chains show a reorientation of their conformations. The fact that the conformation does not change on going from 40 to 100% ethyl L-aspartate content shows that the side chains from both components have the same conformation in the right-handed form. Identical behavior to ethyl L-aspartate was found for *n*-butyl L-aspartate, *n*-propyl L-aspartate, and phenethyl L-aspartate, as shown in Table II, and it can be concluded that the right-handed forms of these polymers and the right-handed form of poly(β-benzyl L-aspartate) all have similar side-chain conformations.

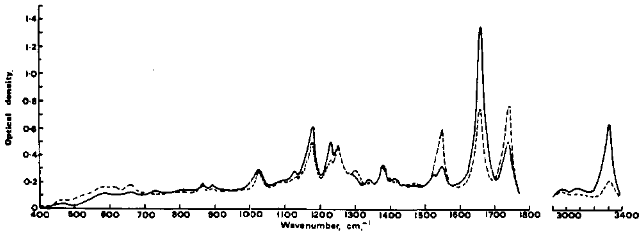

Figure 3. Polarized infrared spectrum of poly(β-ethyl L-aspartate): (———) *E* vector parallel and (- - - - -) *E* vector perpendicular.

Discussion

Table III summarizes the data obtained for the side-chain orientations of seven poly(L-aspartate esters) in the left- and right-handed helical conformations. Because the absorption bands are very weak, the angles given for the transition moment of the δ-$C_\beta H_2$ vibration are very approximate. As can be seen from Figure 1, however, this band has a high parallel dichroism for the left-handed form of poly(β-benzyl L-aspartate) which is compatible with only one of the three rotamers of the $C_\alpha H$-$C_\beta H_2$ bond being occupied. The nondichroic δ-$C_\beta H_2$ band observed for all other forms of the aspartate polymers shows that either of the rotamers or a mixture of both of the other two rotamers is possible.

There are points of general agreement between the results of this experimental work and the predictions of Scheraga and his coworkers.[16] First, as predicted, several well-defined side-chain conformations exist for the different poly(aspartate esters). Second, it is predicted that all the long side chains have transverse orientations, Rt(−) for the right-handed helical forms and Lt(−) for the left-handed helical forms. If the line joining the carbon atoms of the ester C–O–C group is taken as an approximate indication of the side-chain orientation with respect to the helix axis, as shown in Figure 4, then the side-chain orientation of the left-handed poly(β-benzyl L-aspartate) and all of the right-handed helical forms could be regarded as lying closer to a transverse orientation than to the longitudinal orientations; this would include poly(β-ethyl L-aspartate), which Scheraga and coworkers pre-

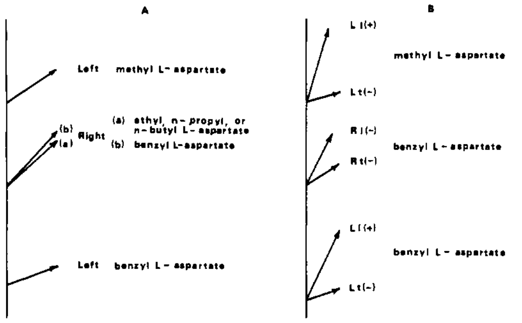

Figure 4. Direction of –C–O–C– line for poly(aspartate esters) (A) from solid films and (B) for isolated polymer chains (calculated).

dict as having a longitudinal orientation. This polymer, however, was also calculated to have a left-handed helix sense and not the observed right-handed sense. In the series of poly(alkyl aspartate esters), the helix sense is calculated to be left-handed for the methyl and ethyl aspartate polymers and right-handed for alkyl esters with longer side chains, while experimentally it is found that only the methyl L-aspartate polymer is in the left-handed form. Clearly, the parameters used in these calculations could be adjusted slightly to give agreement between observed and calculated helix senses. Such an adjustment may also produce a reorientation of the side chain to agree with the experimental results.

That the side-chain orientations can depend on the length of the side chain is shown by the comparison of poly(β-benzyl L-aspartate) with poly(β-methyl L-aspartate). Although both polymers favor left-handed helices, the side-chain conformations are markedly different. Using the criterion given above for describing the side-chain orientation, *i.e.*, the direction of the C–C line in the ester C–O–C group, it is clear, however, that the orientation of methyl L-aspartate must also be described as transverse rather than longitudinal as predicted. The orientation of left-handed benzyl L-aspartate side chain is also transverse.

Although there is some general agreement between the observed and calculated behavior of side-chain conformations, when a detailed comparison of the orientations is made, discrepancies are found which extend throughout the length of the side chain, including the $C_\beta H_2$ group. This is not completely unexpected, since the theoretical calculations apply to isolated molecules *in vacuo* and it would be surprising if the packing of such molecules into the solid state did not result in a modification to their side-chain conformations to allow a minimum of the packing energy. A full comparison of experimental and predicted side-chain conformations must therefore await calculations of conformation in the solid state.

Acknowledgments. This work is supported by the Science Research Council of Great Britain. We are grateful to Professor H. A. Scheraga for providing the atomic coordinates of the predicted Rt(−), Rl(−), Lt(−), and Ll(+) side-chain conformations for both poly(β-benzyl L-aspartate) and poly(β-methyl L-aspartate).

Thermodynamic Interaction in Polydimethylsiloxane–Hydrocarbon Systems from Gas–Liquid Chromatography

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ABSTRACT: Polydimethylsiloxane has been used as the stationary phase in gas–liquid chromatography. Retention volumes have been used to calculate the thermodynamic interaction parameters for a series of linear and branched alkanes and aromatic hydrocarbons interacting with the polymer. Values of the χ parameter have been compared with results for the same systems obtained from equilibrium (static) vapor-absorption experiments, and found to be in excellent agreement. The successful comparison indicates the potential value of the glc route as the source of rapidly obtained thermodynamic data at infinite dilution of the volatile phase. A number of the prerequisites are established for useful application of the glc method to polymer solution thermodynamics.

Numerous recent studies of gas–liquid chromatography (glc)[1-3] have established the method as a rapid and consistent means of determining thermodynamic functions for nonelectrolyte systems. The primary datum obtained by this flow method is the activity coefficient (γ_1^∞) of a volatile solute at Infinite dilution. This is related experimentally to the specific retention volume V_g^0 of the solute by a nonvolatile solvent (liquid or solid) in the stationary phase, through the equation

$$\gamma_1^\infty = RT/V_g^0 P_1^0 M_2 \qquad (1)$$

where M_2 is the solvent molecular weight and P_1^0 is the solute saturation vapor pressure.

Application of the method to polymeric solvents would represent a very convenient means of determining thermodynamic data at very high polymer concentrations, a region which is of inherent interest from both theoretical and applied points of view. Guillet and coworkers[4] have anticipated the

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