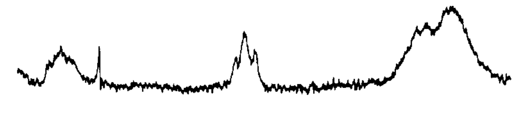

Figure 1. Nmr spectrum of 2% (w/v) Ala-160 in D_2O, at 29° at an apparent pD of 6.7 (measured at 24°) at a sufficiently high rf amplitude to ensure partial saturation. The chemical shifts were measured with respect to the coaxially inserted (external) standard tetramethylsilane. The peak at 4.25 ppm is a spinning side band of the HDO peak.

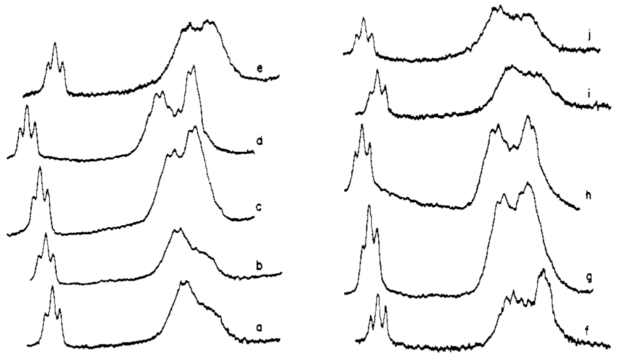

Figure 2. Nmr spectra (at partial saturation) in the ε-CH_2 and (β-, γ-, δ-CH_2 + β-CH_3) regions of Ala-160 and Ala-450 (all at 2% (w/v)) at various temperatures and salt concentrations, and at pD's given in Table I. Each spectrum is the result of the accumulation of at least 23 scans stored in a Varian Associates C-1054 Computer of Average Transients (CAT) to improve the signal-to-noise ratio. The chemical shifts vary slightly from curve to curve because they were each measured with respect to an external standard: (a) poly(D,L-lysine) in D_2O at 32°, (b) poly(D,L-lysine) in 0.2 *N* NaCl at 32°, (c) Ala-160 in D_2O at 29°, (d) Ala-160 in D_2O at 70°, (e) Ala-450 in D_2O at 32°, (f) Ala-450 in D_2O at 76°, (g) Ala-160 in 0.2 *N* NaCl at 32°, (h) Ala-160 in 0.2 *N* NaCl at 70°, (i) Ala-450 in 0.2 *N* NaCl at 32°, (j) Ala-450 in 0.2 *N* NaCl at 76°.

within the experiment error of ~15% (indicated in Table I), implying that T_1T_2 for poly(D,L-lysine) is essentially constant. Since *ratios* of areas are considered, any temperature dependence of χ_0 does not affect the result. These ratios, obtained from the spectra of Figure 2, at constant rf amplitude, are given in Table I.

The area ratios for Ala-160 and Ala-450 are larger than those for poly(D,L-lysine) because of the contribution from the β-CH_3 protons of alanine; the area ratio for Ala-450 is greater than that of Ala-160 because of the larger alanine content (Ala/Lys ratio) of the former polymer. Over the range of 2–0.2% (w/v) concentration, the area ratios are not dependent on the concentration within the experimental error; this, together with similar observations by Ingwall, *et al.*,[3] indicates that the polymers are not aggregated in this range of concentrations.

As the temperature increases, the relative area increases for both Ala-160 (by 31% in D_2O and 24% in 0.2 *N* NaCl) and Ala-450 (by 20% in D_2O and 42% in 0.2 *N* NaCl); this is a reflection of the increase in the random-coil content at higher temperatures.[8] When salt is added, the relative areas of Ala-160 are unaffected, but those of Ala-450 at low temperature decrease by 20% from 5.0 to 4.0 and by 31% from 5.2 to 3.6 in 2 and 0.2% solutions, respectively. The decrease in area is attributed[6] to an increase in T_1T_2 (because of an increase in T_1) arising from a stabilization of the hairpinlike conformations formed because of side-chain methyl–methyl hydrophobic bonds. Thus, these nmr data support the conclusion from ORD measurements[3] that hairpinlike bends of the α helix exist in the longer Ala-450 but not in the shorter Ala-160 polymer.

Further work is being carried out on similar block copolymers, which contain deuterated poly(D,L-lysine), to remove the lysine hydrogen resonances from overlap with those of the alanine protons, thereby permitting relaxation times to be determined from the peak widths.

[8] As the helix is converted to coil, the area increases because T_1T_2 decreases; *i.e.*, the increase[6,7] in T_2 (which would be reflected in a decrease in line width, if the isolated peak could be observed) is more than offset by a decrease in T_1. Figure 9-2 of ref 7 would imply that the correlation time in our experiments is $>10^{-8}$ sec, since T_1T_2 decreases (because of the decrease in T_1) with an increase in mobility (when helix is converted to coil).

Thermodynamic Interactions in Polymer Systems by Gas-Liquid Chromatography. II. Rubber-Hydrocarbons

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The application of gas-liquid chromatography (glc) to the study of thermodynamic interactions in polymeric systems is attractive in its ability to generate data rapidly and to extend these into high polymer concentration ranges which are difficult to study by conventional methods. Several recent publications[2-4] have shown that glc data can produce thermodynamically meaningful results, our most recent work[4] showing very good agreement in a comparison of thermodynamic interaction parameters calculated from glc and equilibrium sorption data for poly(dimethyl siloxane) (PDMS) interacting with selected hydrocarbons. The demand for accuracy in thermodynamic data is considerable, if, for example, these are to be of use in the resolution of varying predictions drawn from theories of solution thermodynamics. It is therefore prudent to extend the test of the rapid method's usefulness by comparing thermodynamic data calculated from conventional equilibrium sorption results and from glc data for additional polymers. The system natural rubber–hydrocarbons lends itself for such a comparison and is the subject matter of this report.

Experimental Section

The gas chromatograph and experimental procedure for the determination of retention volumes have been described in detail in an earlier publication.[4] In the present case, natural rubber was used as the polymer stationary phase. The sample, kindly supplied and characterized[5] by Professor B. M. van der Hoff, University of Waterloo, was used without further purification. The polymer was dissolved in benzene and coated onto Chromosorb W support (60/80 mesh, acid washed, DMCS treated). The exact polymer weight supported was determined by combustion and ashing methods.[6]

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TABLE I

V_g^0 (CM^3/G) FOR HYDROCARBONS ON NATURAL RUBBER

Solute	25.0°	40.0°	55.0°
(1) *n*-Pentane	65.10	40.83	25.96
(2) *n*-Hexane	204.7	112.6	65.83
(3) *n*-Heptane	618.7	309.0	164.9
(4) *n*-Octane	1852	844.8	415.9
(5) 2-Methylpentane	142.7	81.67	48.94
(6) 2-Methylhexane	419.3	217.8	119.6
(7) 2-Methylheptane	1236	583.7	297.8
(8) 2,2,4-Trimethylpentane	517.0	268.8	146.9
(9) Benzene	511.2	270.7	153.4
(10) Toluene	1587	776.8	404.6
(11) Ethylbenzene	4164	1880	923.1
(12) *p*-Xylene	4792	2131	1021

TABLE II

THERMODYNAMIC PARAMETERS FOR NATURAL RUBBER–HYDROCARBONS

		χ^*			$\bar{\chi}$		
Solute		25°	40°	55°	This work	Ref 8	X_{12}, cal/cm^3
1		0.758	0.714	0.717	0.580	0.565	2.57
2		0.658	0.651	0.651	0.534	0.474	2.07
3		0.607	0.602	0.609	0.504	0.433	1.72
4		0.575	0.564	0.567	0.478	0.475	1.62
5		0.686	0.671	0.674	0.558		2.05
6		0.626	0.616	0.625	0.524		1.97
7		0.586	0.577	0.577	0.498		1.74
8		0.589	0.571	0.580	0.483	0.513	1.56
9	0.55[a]	0.560	0.550	0.543	0.456	0.437	2.88
10		0.433	0.418	0.422	0.350	0.391	2.00
11		0.409	0.391	0.382	0.346		1.67
12		0.345	0.338	0.348	0.270		1.33

[a] Benzene–rubber value from ref 7.

Solute specific retention volumes, V_g^0, were measured at 25, 40, and 55° for 12 hydrocarbon solutes. The results are summarized in Table I. The uncertainty in V_g^0 values reported is estimated to be about 1%.

Thermodynamic Functions

The route from solute specific retention volumes to the thermodynamic parameter χ for polymer–solute interactions has been discussed in earlier reports.[2a,4] The pertinent relationship is

$$\chi = \ln\left(\frac{273.2Rv_{2,\mathrm{sp}}}{V_g^0 V_1 P_1^0}\right) - \left(1 - \frac{V_1}{\bar{M}_2 v_{2,\mathrm{sp}}}\right) - \frac{P_1^0}{RT}(B_{11} - V_1) \quad (1)$$

where V_1, P_1^0, and B_{11} are respectively the molar volume, the vapor pressure, and the gas-state second virial coefficient of pure solute at the temperature T°K; $v_{2,\mathrm{sp}}$ and $\bar{M}_2$ are the specific volume and average molecular weight of the polymer. In most practical cases involving polymers, the term $(V_1/\bar{M}_2 v_{2,\mathrm{sp}})$ can be neglected with a consequent simplification of eq 1. An important argument of our first publication in this context[2a] was to differentiate between χ values calculated on the basis of molar and hard-core volumes of solution components. Equation 1 expresses the interaction parameter in terms of the molar volume concept, while the analogous expression using the reduction parameters of recent theory[7] is

$$\chi^* = \ln\left(\frac{273.2Rv_{2,\mathrm{sp}}^*}{V_g^0 V_1^* p_1^0}\right) - 1 - \frac{P_1^0}{RT}(B_{11} - V_1) \quad (2)$$

where the quantities marked with asterisks are the hard-core volumes of the two components. The source of values for the various solute parameters have been reported earlier,[4] while the parameters for the natural rubber solvent were obtained from the published data of Eichinger and Flory.[7]

Results and Discussion

Table II presents a comprehensive summary of thermodynamic parameter calculations. Values of χ^* are tabulated for each of the three experimental temperatures, to indicate the magnitude of the temperature dependence of the parameter. The mean χ^* datum for benzene is compared with a value extrapolated from the published results of Flory and collaborators.[7] The principal objective of this work is the comparison of χ values calculated from our glc data and eq 1 with those of Bristow and Watson,[8] which were obtained from conventional swelling measurements at 25°. The comparison is made for pertinent solutes in Table II; in view of the very slight temperature dependence of χ, only average values, identified by the $\bar{\chi}$ notation, are entered. The same consideration made it impractical to attempt calculations of the heat of dilution of the solutes at infinite dilution, a thermodynamic computation which is inherent in the capabilities of the glc approach.[2a]

Taking into account experimental errors in V_g^0 evaluations and approximations inherent in eq 1 and 2,[2a,4] an apparent error of ±0.01 applies to the listed values of χ and χ^*. The general level of agreement between the values of this work and those of Bristow and Watson[8] is fairly good; that with the extrapolated χ^* value from Flory's recent work is excellent. The χ values for *n*-alkanes given in ref 8 indicate the existence of considerable error arising from the swelling experiments. Considering the superior agreement between the two sets of data for *n*-pentane and *n*-octane, the earlier values for *n*-hexane and *n*-heptane seem particularly suspect.

Recent publications of Flory and coworkers[7,9] show that χ^* at infinite dilution of solute and zero pressure can be written

$$\chi^* = \frac{P_1^* V_1^*}{RT}\left[\left(3\tilde{T}_1 \ln \frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_2^{1/3} - 1} + \tilde{V}_1^{-1} - \tilde{V}_2^{-1}\right) + \frac{X_{12}}{P_1^* \tilde{V}_2}\right] \quad (3)$$

and

$$\tilde{V}^{1/3} - 1 = \frac{\alpha T}{3(1 + \alpha T)}; \quad \tilde{T} = \frac{T}{T^*} = \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^{4/3}} \quad (4)$$

Here α is the thermal expansion coefficient; $\tilde{V}$ and $\tilde{T}$ are reduced quantities, and asterisked quantities are the reduction parameters. The first term of eq 3 is the equation of state contribution arising from differences in the thermal expansion coefficients of the components. The second term introduces X_{12}, the contact interaction stemming from differ-

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ences in the contact potentials of the components. Using reduction parameters for solutes already defined in our earlier work,[4] the X_{12} data for rubber–hydrocarbons were computed at 25° and entered as the final column of Table II.

An interesting difference is noted in comparing X_{12} in the present rubber–hydrocarbon systems with similar data reported earlier for PDMS–hydrocarbons.[4] In the present case, a systematic decrease in X_{12} (and χ^*) is noted as the number of C atoms in the solute increases. In contrast, both X_{12} and χ^* increased with increasing C atoms where PDMS was the interacting polymer. The difference is due to substantial contributions to χ from equation of state ($\tilde{v}_1$, $\tilde{v}_2$) terms in the case of natural rubber. This source of contribution was very much smaller in the PDMS case.

Synthesis of Diethynylbenzenes

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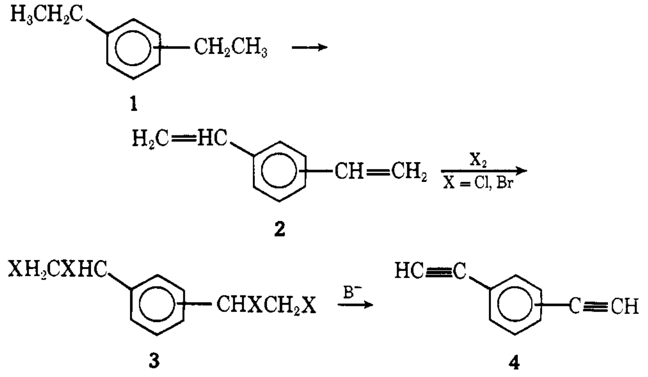
Substantial interest has recently been shown the use of diethynylbenzenes **4** in the preparation of thermally stable polymers.[1–4] The presently accepted route to these compounds is that first reported by Hay[5] (Scheme I). Although this route is in many respects acceptable, its usefulness is limited by several severe deficiencies. Among these are the difficulty of obtaining pure single isomers of diethylbenzene **1**, the tendency of the intermediate divinylbenzenes **2** to autopolymerize, low overall yields, and contamination of the product diethynylbenzenes **4** with vinylethynylbenzenes, which arise when dehalogenation rather than dehydrohalogenation of **3** occurs.

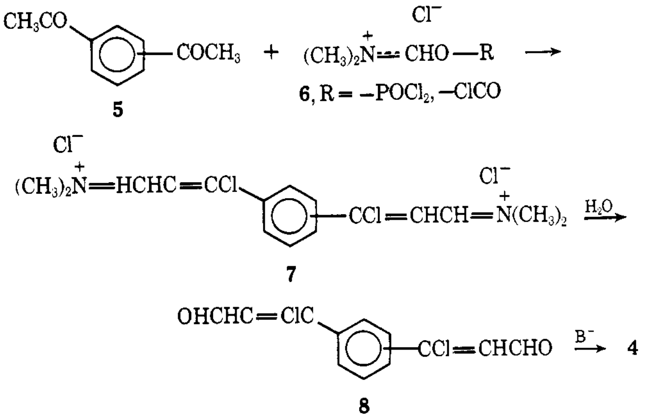
SCHEME I



Results and Discussion

We now wish to report that *m*- and *p*-diethynylbenzene (**4**) can be synthesized by dechlorocarbonylation of intermediate bis(1-chloropropen-3-al)benzenes **8**,[6] which are prepared by the reaction of the appropriate diacetylbenzene **5**[7] with a Vilsmeier complex **6**[8–14] which is prepared by the admixture of DMF with either $POCl_3$ or $COCl_2$ (Scheme II).

SCHEME II



The superiority of the present process relative to that of Hay (Scheme I) is most obvious in the case of *m*-diethynylbenzene, which can consistently be obtained in overall yields of 52–54% based on diacetylbenzene. The inherent tendency of *p*-diethynylbenzene to autopolymerize causes the yields thereof to be lower even though the yields of the intermediate β-chloroacrylaldehyde therefrom are actually superior to those obtained with the meta isomer. In addition, the remaining deficiencies of the Hay procedure are avoided herein as the product is free of vinylethynylbenzenes, and the intermediate bis(1-chloropropen-3-al)benzenes **8** are stable solids.

While either $POCl_3$ or $COCl_2$ is a suitable complexing agent for DMF, the latter is preferred in that it provides enhanced yields. Also, when $POCl_3$ is employed, the acidic reaction mixture containing the immonium salt **7** of the β-chloroacrylaldehyde **8** must be neutralized upon hydrolysis in order to liberate the free aldehyde, as the by-products of the chlorocarbonylation reaction (PO_2Cl and H_2O) combine with additional H_2O to generate H_3PO_4 and HCl, and the immonium salt **7** is stable therein. Such neutralization is not required when $COCl_2$ is employed, as the by-products therefrom are CO_2 and H_2O.

Experimental Section

1,3-Bis(1-chloropropen-3-al)benzene using $POCl_3$. Dimethylformamide (150 ml) was placed in a 1-l. stirred reactor which was cooled in an ice bath, and $POCl_3$ (115 g, 0.75 mol) was added thereto; the resulting deep red reaction mixture was stirred with continued cooling until the temperature decreased to 15°. A solution of *m*-diacetylbenzene (50 g, 0.31 mol) in DMF (75 ml) was added and the temperature of the resulting reaction mixture was maintained at 40° until the spontaneous reaction subsided (approximately 1 hr). Stirring at ambient temperature was continued for 18 hr; the reaction mixture was again cooled in an ice bath and was

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