so degraded that the dried film is brittle with no pliability for stretching. At the end of the 17-h period the gelatin is not degraded to that extent (polyproline does not produce pliable films on its own) but its molecular weight spectrum may be sufficiently changed for it to be regarded as a different gelatin for the purposes of the experiment. Second, the stand at elevated temperature may have promoted growth of polyproline crystals due to a decrease in solubility at high temperatures. This pattern indicates that gelatins could be a useful matrix material for obtaining oriented fiber patterns from polypeptides in general. Note that the gelatin could be added as a cool solution to prepared crystals in solution and that acidic conditions are not necessary for matrix formation.

Figure 1f comes from a 60% polyproline mix subjected to the same treatment (including stretching) as that which gave Figure 1e but the solution was allowed to stand at room temperature for 4 days before casting. The pattern shows four diffuse rings, matching with slightly modified spacings to the polyproline II rings in Figure 1b. In addition there are some other weak rings and the whole system, see Table II, does not correspond to any of the paste patterns observed by Sasisekharan.[16] The pattern also shows a pronounced equatorial streak ending in diffuse equatorial reflections at about 1.1 nm which may come from the gelatin. It seems likely that this pattern is of a previously unreported polyproline crystal form.

The suppression of the gelatin pattern in the mixes is an interesting phenomenon. Despite disappearance of the pattern, the gelatin matrix still lends mechanical integrity to the films, enabling them to be stretched with the plasticizing water vapor.

To analyze Figure 1a–f for the effect of polyproline on collagen renature (whether this occurs mostly in solution followed by aggregation of the renatured molecules[17-21] or during mechanical stretching of the films[11,12]) it is necessary to relate the strength of reflections, for instance the 1.05-nm equatorial,[11] to collagen content.

Aside from the 0.286-nm meridional, collagen/gelatin reflections have strengths which could be influenced by the nature of the molecular packing as well as the extent of renature. Quantitative data to show if relative reflection strengths do vary with sample treatments are not currently available.

The 0.286-nm reflection from a periodicity along renatured collagen molecules is too weak in the given patterns to be useful, but the 1.05-nm equatorial is clear in most of them. Thus the packing effects can be investigated through the 1.05-nm reflection.

The quantity of gelatin pattern predicted from a thin stretched sample on the basis of gelatin scattering mass in the beam is easily estimated assuming pattern attenuation by the polyproline phase is both slight (since the majority of X-ray photons pass through the sample unaffected by either phase) and about equal to that by gelatin itself. Pattern strength should then be proportional to gelatin concentration multiplied by net X-ray flux divided by sample extension. Allowing as well for the different print times of the photographs in the plate, these should respectively show 1, 1, 0.8, 1.5, 0.5, 0.25 units of gelatin pattern. The unit of gelatin pattern is standardized in terms of Figure 1a on the basis of the number of exposed film grains. The number of exposed film grains in the print is taken as being linearly proportional (where saturation has not occurred) to the number of X-ray photons photographically captured. Against this scale Figure 1c, for instance, should contain in features of its gelatin pattern 0.5 of the grains at equivalent features of Figure 1a. Compare, for example, the prominent equatorial signal at a spacing of 1.05 nm.

By inspection it is possible to appreciate the 1.05-nm equatorial reflection falls off quicker with increasing polyproline content than predicted above. This indicates that the two polymers do not totally segregate and the polyproline poisons gelatin packing to a degree. Analogously, low molecular weight fractions in a pure gelatin might also interfere with packing and modify equatorial and other nonmeridional signals. The latter reflections are thus potentially unreliable indicators of renaturation content.

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Registry No. Polyproline (homopolymer), 25191-13-3; polyproline (SRU), 25213-33-6.

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Marker Retention in Inverse Gas Chromatography Experiments on Polymers

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Introduction

In gas–liquid chromatography, an ideal marker is a substance which has no retention on the stationary phase of the column. While any real marker must have a nonzero retention, in standard GC application a marker is con-

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sidered satisfactory when its retention is negligibly small in comparison to the retentions being measured. In the case of inverse gas chromatography experiments (IGC) on polymers, a flame ionization detector is typically employed, necessitating the use of methane as the marker. The retention of methane on the polymer, if not properly accounted for, can introduce a significant systematic error into the retention data. The correction for methane retention becomes particularly important when IGC is used for characterizing polymer–polymer interactions in blends, since such studies are exceedingly sensitive to experimental error sources and artifacts.

In this paper, a procedure is described for the evaluation of IGC retention data while taking into account a nonzero net retention for methane. The procedure is outlined by applying it to several sets of data. The data used have been taken from IGC studies involving poly(vinyl acetate) (PVA), polycaprolactone (PCL), and polyepichlorohydrin (PECH). Methane retention on GLC columns has been known and investigated before;[1-5] the method offered here, however, is simpler and more directly relevant to IGC work on polymers.

Background

Consider the elution volume of a probe in an IGC system $V_r^{(P)}$. The net retention volume $V_n^{(P)}$ is normally obtained as

$$V_n^{(P)} = V_r^{(P)} - V_r^{(M)} \quad (1)$$

where $V_r^{(M)}$ is the marker elution volume. Equation 1 is inexact because it assumes that $V_r^{(M)}$ represents $V_r^{(M)}$ void volume of the column, V_0. Since the marker is slightly retained on the column, the apparent value $V_r^{(M)}$ must be corrected to V_0 (which is the elution volume of an ideal marker). The net retention of the marker is characterized by the difference

$$V_n^{(M)} = V_r^{(M)} - V_0 \quad (2)$$

and $V_n^{(P)}$ must therefore be calculated as

$$V_n^{(P)} = V_r^{(P)} - V_r^{(M)} + V_n^{(M)} \quad (3)$$

The net retention of a probe $V_n^{(P)}$ depends on the mass of the polymer coating, w; the specific retention volume $V_g^{(P)}$ is computed as

$$V_g^{(P)} = V_n^{(P)}/w \quad (4)$$

and a similar expression can be written for the marker

$$V_g^{(M)} = V_n^{(M)}/w \quad (5)$$

The strategy for estimating the retention of the marker can be briefly described as follows: Assuming zero retention for methane, $V_g^{(P)}$ data for a homologous series of normal alkanes are correlated against the number of carbons in the alkane, n. The data are then extrapolated to the marker in order to obtain a first estimate for $V_g^{(M)}$, $V_n^{(M)}$, and V_0. Next, a second iteration is performed by computing corrected $V_g^{(P)}$ values to obtain a second estimate of $V_g^{(M)}$ and the process can be repeated if necessary. An accurate value for $V_g^{(M)}$ is thus obtained and the retention data are corrected as is shown for the data presented below.

Experimental Section

All IGC experiments were performed on 5-ft columns of $^1/_4$-in.-o.d. copper tubing, using acid-washed DMCS-treated Chromosorb W (60/80 mesh) as the inert support. The polymers were coated onto the support by using a partial soaking method which was developed to eliminate errors associated with the weight measurement of the polymer on the column.[6] High-purity nitrogen was used as the carrier gas with a nominal flow rate of 16 mL/min. A modified Varian 2100 Aerograph GC unit equipped with a flame-ionization detector was employed as described earlier.[6] The flow rate was measured by a soap bubble flow meter thermostated at 25 °C. IGC data acquisition was performed digitally by using a Hewlett-Packard 3478A voltmeter and a Tandy 3000 personal computer. The elution signal was registered on the digital voltmeter and was simultaneously read by the computer during the course of a run. The computer was interfaced to the volt meter via a GPIB interfacing board manufactured by National Instruments. This data handling configuration afforded a remarkable resolution and reproducibility of about 0.1 s in the retention time measurement. (The shortest elution time intervals measured were on the order of 100 s.)

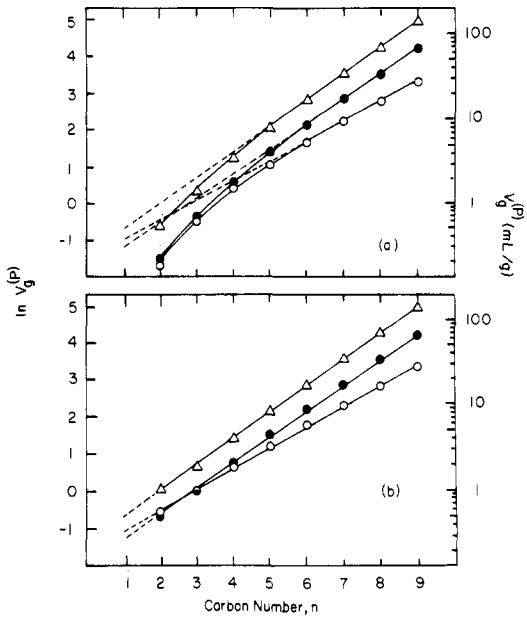

Figure 1. Specific retention volumes, $V_g^{(P)}$ for n-alkanes plotted logarithmically against number of alkane carbons, n: (a) data prior to marker correction; (b) data after implementing first marker correction. Dotted lines show extrapolation to $n = 1$ for estimating marker-specific retention volume, $V_g^{(M)}$. (○) Poly(vinyl acetate) at 100 °C; (●) polyepichlorohydrin at 80 °C; (△) polycaprolactone at 80 °C.

Results and Discussion

The correction procedure for marker retention is based on the linearity of ln $V_g^{(P)}$ versus carbon number plots. This linear correlation is now well established for normal alkane retentions on liquid phases. Retention data are first plotted against carbon number in this fashion as shown in Figure 1. The data points in Figure 1a depict direct experimental values obtained before any correction for methane retention. From this data a preliminary estimate of $V_g^{(M)}$ is made by extrapolating the ln $V_g^{(P)}$ data for the higher alkane probes (C_6–C_9) to $n = 1$. The $V_g^{(P)}$ values for the lower alkanes contain greater uncertainity, due to the methane retention being unaccounted for at this stage. The first estimate of $V_g^{(M)}$ obtained is next used to compute corrected values for $V_g^{(P)}$ and $V_n^{(P)}$ according to eq 3 and 4. The updated values of $V_g^{(P)}$ are then replotted as ln $V_g^{(P)}$ against n to obtain a second more accurate estimate of $V_g^{(M)}$ by extrapolating to $n = 1$. These plots are shown in Figure 1b. The linearity of the graphs becomes apparent after implementing the first correction. The corrected retention data are hence computed. From our experience, the second and first estimates of $V_g^{(M)}$ obtained by this procedure were nearly identical, indicating that additional iterations are not necessary.

The magnitude of the errors introduced into the retention data by failing to correct for the retention of the

Table I
$V_g^{(P)cor}/V_g^{(P)unc}$ for *n*-Alkane Retentions[a] on Three Polymers

probe	PVA	PECH	PCL
ethane	2.944	2.080	2.048
propane	1.660	1.391	1.357
butane	1.280	1.164	1.128
pentane	1.148	1.077	1.060
hexane	1.077	1.036	1.028
heptane	1.044	1.018	1.014
octane	1.025	1.009	1.007
nonane	1.015	1.004	1.003

[a] PVA data at 110 °C; PECH and PCL data at 80 °C.

Table II
Flory-Huggins Interaction Parameters[a] χ_{12} for *n*-Alkanes with Three Polymers, Both with and without the Marker Correction

	uncorrected data			corrected data		
probe	PVA	PECH	PCL	PVA	PECH	PCL
propane	1.682	1.651	1.267	1.167	1.325	.963
butane	1.589	1.660	1.123	1.339	1.511	1.003
pentane	1.665	1.722	1.202	1.526	1.649	1.143
hexane	1.684	1.754	1.218	1.610	1.719	1.190
heptane	1.802	1.846	1.277	1.759	1.828	1.264
octane	1.916	1.945	1.351	1.891	1.936	1.344
nonane	2.056	2.051	1.424	2.041	2.047	1.421

[a] PVA data at 110 °C; PECH and PCL data at 80 °C.

marker can be seen from the quantity $V_g^{(P)cor}/V_g^{(P)unc}$ for the alkane probes, which is listed in Table I for the three polymers. Here $V_g^{(P)cor}$ and $V_g^{(P)unc}$ designate respectively the corrected and uncorrected specific retention data. The table demonstrates that even for a well-retained probe like *n*-octane an error of over 2% in $V_g^{(P)}$ and $V_n^{(P)}$ can be introduced by failure to account for the marker. The magnitude of this error will obviously depend on the polymer, probe, and temperature, but, ideally, it should not depend on the extent of polymer loading since the marker and the probes are equally affected by a change in polymer mass. The corrected specific retention data for the three polymers are shown on the right-hand axis of Figure 1 to further illustrate this point. The retentions of the various probes on PVA are comparable to those on PECH but the lower slope of the PVA line suggests a higher value for the ratio $V_g^{(P)cor}/V_g^{(P)unc}$.

The errors incurred in the values of $V_g^{(P)}$ from ignoring the retention of methane are carried into the calculation of the probe-polymer interaction parameter. In IGC studies on polymers, the Flory-Huggins interaction parameter χ_{12} is the routine choice for reporting such interactions.[7-9] In Table II, χ_{12} for the three polymers is listed for the *n*-alkanes C_3-C_9. The values of χ_{12} are given both with and without the marker correction. As expected, the correction is most important for the least retained probe, propane, and remains significant even for the high alkanes. The error introduced by the conventional analysis is most pronounced for PVA and is smaller for PECH and PCL.

In conclusion, the marker correction procedure explained above significantly improves the quality of IGC data and allows a more meaningful analysis and comparison of data from different IGC experiments.

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Registry No. PVA, 9003-20-7; PECH (homopolymer), 24969-06-0; PECH (SRU), 61710-61-0; PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4; ethane, 74-84-0; propane, 74-98-6; butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; methane, 74-82-8.

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Reactions of n-Type (Reduced) Polyacetylene with Alkyl Halides[1]

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The reactions of charge carriers (typically carbenium ions or carbanions) in "doped"[4] conductive polymers with various reagents[5] can be a major limitation to technological applications as well as a useful approach for the synthesis of new materials,[7] although very little is known about reaction mechanisms. Of particular interest is whether the carriers may act as oxidants/reductants or acids (or electrophiles)/bases (or nucleophiles)[8] and under what conditions one mechanism may predominate. We have elected to study the reactions of n-type (reduced) polyacetylene,[9] $[(CHNa)_y]_x$ or n-PA, with alkyl halides due to the extensive literature on similar reactions with small molecule radical anions[10] and dianions.[11] Our experiments suggest that extensive alkylation of n-PA occurs and proceeds by initial electron transfer to R-X followed by radical coupling (Scheme I) and that the reactivity patterns of various alkyl halides (Table I) parallel those observed with disodium tetraphenylethylene (TPE).[11a,b] Furthermore, we find that this chemistry provides a versatile route to the preparation of modified polyacetylenes having interesting physical properties.

Treatment of n-PA films[12] with, for example, 1-bromopentane in dry THF leads to alkylkation of the PA[14] to a level of ca. one n-C_5/ten CH units (Table I). Interestingly, the film swells considerably as the reaction proceeds and the THF solution becomes yellow-orange (λ_{max} ca. 380 nm) and slightly viscous, indicating the presence of a soluble, conjugated polymer.[14] Several observations support the reaction mechanism[11a,b] outlined in Scheme I wherein an alkyl radical,[15] initially formed by electron transfer from n-PA, can either couple with a PA radical or undergo reduction to the corresponding carbanion.[17] That the first step is an electron transfer rather than a nucleophilic attack is suggested by the detection of reduction products and the observation that a tertiary alkyl chloride (entry 10) reacts even faster with n-PA than a corresponding primary substrate (entries 1,2) and affords nearly the same extent of alkylation. Reactions with primary alkyl chlorides consume only ca. 50% of substrate,

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