by Kitaigorodskii.[12] The value of K for the 4M-MPTA (0.71) falls into the average value (0.681) of 70 polymer compounds investigated in ref 12. However, the coefficients of other aromatic polyamides (PBA, 0.82; PPTA, 0.80; MPIA, 0.77) deviate significantly from the mean value, which shows that these polymers have highly ordered forms and pack very compactly. The looseness of packing in the solid state of 4M-MPTA is closely related to the good dyeing ability of this polymer compared with other aromatic polyamides.

Registry No. 4M-MPTA (SRU), 59113-46-1; 4M-MPTA (copolymer), 84892-96-6.

References and Notes

(1) Morishita, N. *Nikko Materiaru* **1986**, *4*, 14–17.
(2) Cochran, W. *J. Sci. Instrum.* **1948**, *25*, 253–255.
(3) Smith, P. J. C.; Arnott, S. *Acta Crystallogr.* **1978**, *A34*, 3–11.
(4) Okuyama, K.; Arikawa, H.; Chen, M.; Takayanagi, M.; Chatani, Y.; Hasegawa, R.; Tadokoro, H. *Sen'i Gakkaishi* **1989**, *45*, 141–146.
(5) Northolt, M. G. *Eur. Polym. J.* **1974**, *10*, 799–804.
(6) Kakida, H.; Chatani, Y.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 427–435.
(7) Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 91–101.
(8) Pineault, C.; Brisse, F. *Acta Crystallogr.* **1983**, *C39*, 1434–1437.
(9) Orii, S.; Nakamura, T.; Takai, Y.; Sasada, Y.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 788–793.
(10) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 71–147.
(11) Tashiro, K.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1977**, *10*, 413–420.
(12) Slonimskii, G. L.; Askadskii, A. A.; Kitaigorodskii, A. I. *Vysokomol. Soedin.* **1970**, *A12*, 494–512.
(13) Johnson, C. K. Report ORNL-5138, 1976; Oak Ridge National Laboratory: Oak Ridge, TN.

Use of Moment Analysis in Inverse Gas Chromatography

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ABSTRACT: The use of the statistical moments of the outlet concentration profile in inverse gas chromatography is critically examined. With the help of a data acquisition procedure that limits the incidence of noise on the chromatogram and a chromatographic assembly where most extra column contributions to dead volume are suppressed, a viable moment analysis of the elution profiles can be performed. The first moment provides the proper measure of retention, reproducible and independent of flow rate. Measurements carried out on polystyrene deposited in a packed column show that the drop in the retention diagram, usually observed at the glass transition temperature, T_g, when retention volumes are calculated from the position of the peak maximum, is not an indication of the onset of a different retention mechanism but rather an artifact of the use of an inappropriate retention parameter. Calculations of the activity coefficient of chloroform at infinite dilution in polystyrene further demonstrate the importance of using the first moment of the elution profile instead of its maximum, even at temperatures much higher than T_g.

Introduction

During the last 20 years, inverse gas chromatography (IGC) has become a widely used method for the physicochemical characterization of polymeric materials.[1-12] materials.[1-12] It is an invaluable tool for the study of the polymer structure: melting or glass transitions are largely reflected in the retention of a volatile solute because of the changes they induce, respectively, in the solubility and the rate of diffusion of the low molecular weight probe in the polymer. The sensitivity of the retention behavior on the structure of the stationary phase has prompted a large variety of investigations by IGC, for instance, studies of the kinetics of polycondensation[13] or the morphology of inorganic material–polymer composites.[14] Thermodynamic studies of polymer–solvent interactions also constitute a large part of IGC measurements. The weight fraction activity coefficient, the Flory–Huggins interaction parameter, and the partial molar enthalpy of mixing of the volatile probe at infinite dilution in the polymer can be derived from retention data, provided equilibrium conditions are achieved between the mobile and the stationary phases. The method has been extended to mixed stationary phases, allowing for measurement of the interaction between the two components of a polymer blend and the study of their miscibility. In addition to equilibrium parameters, dynamic properties can be studied by IGC. The diffusion coefficients of volatile liquids in the bulk polymer, again at infinite dilution of probe, can be estimated from the effect of the polymer resistance to mass transfer on the shape of the chromatographic peak.[15-18] The knowledge of diffusion coefficients has a large industrial importance, e.g., in the production of thermoplastic foams or the removal of residual monomer and solvent after polymerization.[19]

The experimental procedure of IGC recently underwent a critical evaluation by Munk et al.[9-11,17] Such aspects as the role of inert support[10] or the effect of the amount of probe injected[11] have been investigated, improving the reliability of the IGC method. However, one facet still needs clarification in the case of thermodynamic studies, namely the effect of ignoring the asymmetry of the elution curve. The primary datum gathered by IGC is V_N, the net retention volume, which represents the volume of carrier gas required to elute the probe. It is calculated from the average flow rate in the column and the net retention time of the solute, i.e., the difference between the first statistical moments of the elution curves of the solute and a marker gas.[8] With a few exceptions,[16,20] the difference between the peak maxima is quite generally used in the literature, thereby assuming peak symmetry. This assumption is notoriously invalid for polymers at temperatures close to their glass transition.[6] In this range, the difference between V_N and V_N^{max}, the net retention volume calculated from the peak maxima, is of no consequence for qualitative

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structural investigations[21] but prevents reliable studies of polymer–solute interactions. A lower temperature limit located about 40–50 deg above the glass transition temperature, T_g, has been suggested[20] for thermodynamic measurements. Even at higher temperatures, $V_N^{\max}$ often depends on the flow rate of carrier gas, and values extrapolated at zero flow rate are then computed.[22-24] Since (i) the flow-rate dependence is not necessarily linear and (ii) there is no theoretical basis for an extrapolation to zero flow rate,[8] the question arises whether thermodynamic parameters actually free from all kinetic factors can be obtained by this procedure. In a similar fashion, the use of the peak width at half-height,[12,19] instead of the second central moment of the profile, as an estimate of peak spreading for measurements of diffusion coefficients, relies on the assumption that the outlet concentration distribution is nearly Gaussian. In the course of IGC measurements primarily intended to measure the enthalpy of dilution of cholesteric liquid-crystalline polymers, the elution profiles of various probes, including noninteracting gases, were recorded.[25] Even at temperatures well into the polymer liquid range, a significant amount of peak asymmetry, hardly noticeable on full-scale plots, but quite apparent on enlargements or upon comparison between the first moment and the position of maximum of the concentration distribution, was consistently observed. Recent computer simulations of IGC by Munk et al.[18] showed that a chromatographic model, which considers the diffusion of solute both in the carrier gas and in the liquid polymer but no adsorption at the polymer–gas interface, is able to explain the main features of experimental elution profiles, including in the vicinity of T_g. In agreement with our observations, the model predicts that a significant asymmetry is always to be expected even when the equilibrium is reached instantaneously or in the absence of net retention. Despite the fact that the statistical moments of the chromatogram are the only accurate measures of retention and peak broadening, they experience very little popularity among IGC researchers, because (i) the parameters currently used, peak maximum and half-width, are much easier to determine than the moments, which require recording the whole chromatogram over a long period of time, and (ii) the measurements of statistical moments are allegedly subject to unacceptably large experimental errors.[18,26] Munk et al.[18] rather propose to apply numerical corrections to $V_N^{\max}$ and the back and front half-height bandwidths to take asymmetry into account. Laurence and co-workers[16] used statistical moments in the course of a study of diffusion processes by capillary column IGC but reported difficulties related to signal noise and baseline drift. A high variability and significant flow rate dependence of the first moment was observed for heavily tailed chromatograms. The authors therefore limited the measurements at temperatures higher than T_g.

The purpose of this work is to investigate the conditions in which moment analysis can reliably be applied to IGC using packed columns. The study has been carried out on a well-known stationary phase, polystyrene (PS), and the results are discussed in terms of the dependence of retention volume on carrier gas velocity and the change brought about in the retention diagram by using the first moment instead of the peak maximum. Activity coefficients of chloroform at infinite dilution in polystyrene have been calculated using both peak maxima and first moments and compared with literature data.

Experimental Section

Materials. A commercial sample of polystyrene having a narrow molar mass distribution (nominal molecular weight 50 kg·mol^{-1}, polydispersity index 1.06) was obtained from Pressure Chemicals Co. Ethylcellulose (degree of substitution 2.4, viscosity of a 5% solution = 100 cP) was purchased from Aldrich Co. Chloroform, acetone, and 1,1,1-trichloroethane (Aldrich Co.) were at least 99% pure and were used without further purification. Several physicochemical parameters of the pure compounds are needed to calculate thermodynamic parameters from retention data. The volume of chloroform in the 50–200 °C temperature range was taken from ref 27. Its vapor pressure was calculated using the Antoine equation, with constants taken from ref 28. Second virial coefficients were estimated using the equation of Pitzer and Curl,[29] which was observed to fit experimental data[30] better than the Berthelot equation. The specific volume of PS was interpolated from published dilatometric data at zero pressure.[31]

Calorimetry. The heat capacity of polystyrene was measured between 40 and 180 °C using a Setaram C-80 Calvet microcalorimeter. The data of Figure 7 was obtained on 0.537 g of polymer heated at 0.2 deg·min^{-1}. The base line, recorded on the empty cell in the same conditions, was subtracted from the thermogram.

Column Preparation. Chromosorb W (acid-washed and treated with dimethylchlorosilane) was obtained from Chromatographic Specialty Inc. It was chosen because a preliminary experiment, conducted with a 1-m column packed with the pure dried support, had shown a negligibly small retention of chloroform, acetone, and 1,1,1-trichloroethane at temperatures above 60 °C. Such was not the case for probes like normal alkanes, which are commonly used with Chromosorb W. In that case, correction for retention of the probe on the support should be applied.[10] Two coating methods have been described in the literature. The conventional technique involves deposition from a solution of the polymer by first stirring the support–solution mixture and then slowly removing the casting solvent in a rotary evaporator. Because part of the polymer is deposited onto the glassware, the amount on the chromatographic support has to be determined afterward by calcination or Soxhlet extraction of the coated material. Neither are very accurate nor reproducible methods. Munk[9] proposed an alternate route involving the addition of part of the polymer solution to the support, followed by drying and mixing of the powder. Care is taken to avoid any contact between wet support and the walls of the vessel. The procedure is repeated until all the solution, including rinsings of the solution flask, has been added. Deposition of the polymer could be achieved in 10–20 additions. Although the resulting powder contains a precisely known amount of polymer, the thickness of the polymer film is likely to be nonuniform: a casting procedure, which uses a limited number of steps in which most but not all of the support is wetted, will generate a distribution of thicknesses. The magnitude of this effect and the consequences on the results are difficult to ascertain. In any case, we suggest the following procedure, which combines the advantages of the two above methods. After coating and drying using the first technique, the powder is transferred to another vessel. Pure solvent is added to the flask where stirring and slow drying were performed. After soaking for a few hours with intermittent gentle stirring, the resulting very dilute solution is added to the powder using the method of Munk et al. After drying, the operation is repeated until the flask has been thoroughly rinsed (at least 5 times). Two columns have been used in this work. The supports for columns I and II were, respectively, coated with polystyrene and ethylcellulose from solutions in dichloromethane (1–2% polymer by weight). The supports were packed in copper columns (i.d. 0.635 cm). The respective length, loadings, and total weight of polymer are 1.0 m, 5.0%, and 0.375 g for column I and 1.8 m, 5.0%, and 0.496 g for column II.

Chromatograph. Measurements were performed in a Hewlett-Packard 7620A chromatograph, equipped with a thermal conductivity detector (TCD) (thermal conductivity bridge Model 7655A) and a flame ionization detector (FID) (electrometer Model 7650A). Dried helium was the carrier gas. Methane was used as the marker. The temperatures of the detector and the injector were maintained at 200 and 180 °C, respectively, throughout the experiments. The instrument was operated in the dual mode, using an identical column packed with pure chromosorb in the reference channel. The chromatographic system was similar to the standard arrangement suggested for physicochemical studies,[32] except for an extra mercury manometer, connected between the column and the detector in order to determine the outlet pressure, P_0. A three-way valve, also placed at the column outlet, allowed for the selection of the detector. The flow rate of carrier gas was measured at the outlet of the TCD detector, using a soap bubble flowmeter. The latter was composed of a thermostated buret and an inverted U-tube, which prevented errors due to permeation of helium through the soap film. When it was required to vary P_0 to a large extent, a needle valve replaced the detector between the column and the flowmeter. The atmospheric pressure was monitored near the chromatograph with a Fortin mercurial barometer (Princo Instruments, Southhampton, PA).

Collection of the Outlet Concentration Profile and Moment Analysis

The retention time of a gaseous probe on a stationary phase is the mean residence time t_p, i.e., the first statistical moment or center of gravity of the distribution of residence times. The latter is measured from the concentration of probe in the carrier gas stream at the detector as a function of time, $c(t)$, and therefore:

$$t_p = \frac{\int tc(t)\,dt}{\int c(t)\,dt} \tag{1}$$

Moments of higher order, i, centered about the mean for convenience, fully characterize the distribution:[8]

$$M_i = \frac{\int (t - t_p)^i c(t)\,dt}{\int c(t)\,dt} \tag{2}$$

The second central moment ($i = 2$) is the square of the standard deviation of the elution profile, σ. The number of theoretical plates of the column, N, is given by:[26]

$$N = \frac{t_p^2}{M_2} \tag{3}$$

The third and fourth central moments are often used to derive the skewness, S, and the excess, E, of the peak[8]

$$S = \frac{M_3}{M_2^{3/2}} \tag{4}$$

and

$$E = \frac{M_4}{M_2^2} - 3 \tag{5}$$

In practice, the continuous output of the detector is converted into an array of discrete values of detector response or peak height $h(t)$. Equations 1 and 2 then become

$$t_p = \frac{\sum t\,h(t)}{\sum h(t)} \tag{6}$$

and

$$M_i = \frac{\sum (t - t_p)^i\,h(t)}{\sum h(t)} \tag{7}$$

Moment analysis has been seldom used in IGC because of the following difficulties:[18,26] (1) the noise superimposed to the true signal can adversely affect the results; (2) the use of a finite, necessarily small number of points may not suffice to represent concentration distributions having a complex shape; (3) the detector base line may drift; (4) the data collection could be prematurely terminated in the case of heavily tailed peaks; and (5) dead-volume accessories in the flow system contribute to tailing, which may alter the statistical moments and make them an invalid measure of retention. All the above problems have been addressed by a careful choice of experimental procedure and conditions.

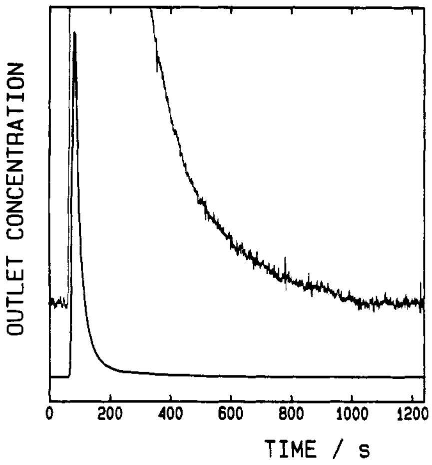

Figure 1. Chromatogram collected after injection of 5 μL of chloroform vapor in the polystyrene column at 89.5 °C and an average gas linear velocity of 1.47 cm·s^{-1}. The upper curve is the same elution profile, enlarged 100 times and shifted along the vertical axis for clarity.

Transformation of the detector signal was performed by means of a voltage-frequency converter (full-scale, 0–100 kHz; linearity, 0.01%). In order to avoid the loss of resolution at low values, the operational frequency range was limited to the middle third of the scale. The typical resoluiton of the interface is therefore better than 10^{-4} for a collection interval of 0.3 s. The main advantage of this type of interface over a conventional analog–digital converter resides in the capacity of accumulation over longer times, which considerably reduces the noise. The data conversion was controlled by an IBM Personal System 2, also used for the moment analysis. A typical chromatogram, comprising 4130 points collected at an interval of 0.3 s, is given in Figure 1 (bottom curve). It was recorded after injection of 5 μL of chloroform vapor in column I at 89.5 °C. The upper curve is the same elution profile, enlarged 100 times and arbitrarily shifted. Clearly, the data contain some random noise, but its magnitude is very small. A large number of calculations, performed on chromatograms under various flow and temperature conditions, showed that the standard deviation of the base line represented between 0.02 and 0.05% of the peak amplitude. This value could be reduced either by smoothing the data after acquisition (e.g., using Savitzky–Golay filters[33,34]) or by increasing the collection interval, but in either case the improvement induced no significant change in the first four moments. The incidence of noise on the moment analysis diminishes if the injected amount is increased. Preliminary tests showed that 3–30 μL of chloroform vapor (under its own vapor pressure at room temperature, thus corresponding to about 4–40 μg) is an optimal amount. It is small enough to approximate infinite dilution of the probe, while using a sensitivity scale of the FID low enough to keep a small noise level. Undoubtedly, the less sensitive TCD would not fulfill all the requirements. In this size range, the peak area is proportional to the quantity of probe injected while, as discussed later, the moments are independent from this amount. Most measurements reported here for chloroform on PS were therefore performed using injections of 5 μL of vapor (corresponding to about 6 μg or 0.004 μL of liquid). The optimal range of injection size depends on the probe and the particular column used and therefore should be determined in each case.

The second difficulty mentioned above is easily corrected upon increasing the collection rate. A compromise should then be achieved between requirements of factors

Table I
Moment Analysis of the Chromatogram of Figure 1[a]

param	mean value	standard deviation	95% confidence interval on the mean
t_p[b]	123.59	0.01_3	0.01 (0.008)
σ[b]	91.70	0.07	0.05 (0.06)
S	4.273	0.006	0.004 (0.1)
E	25.7	0.1	0.07 (0.3)

[a] Summations were performed on a single elution profile, using 10 different upper limits between 1025 and 1250 s. [b] In seconds.

Table II
Reproducibility of Moment Analysis for Several Injections at the Same Temperature and Flow Rate[a]

injection size, μL	t_p, s	σ, s	S	E
25	281.18	22.35	5.47	66.2
25	279.26	21.83	4.89	62.2
20	281.75	22.21	5.71	73.1
20	280.05	21.72	5.09	61.4
15	280.75	22.61	5.84	67.1
10	280.62	22.08	4.77	62.9
mean value	280.6_0	22.1_3	5.3_0	$65._5$
standard deviation	0.8_7	0.3_3	0.4_4	$4._3$
95% confidence interval	0.9_2 (0.3)	0.3_5 (1.6)	0.4_6 (8.7)	$4._6$ (7.0)

[a] Six chromatograms were collected at a 0.3-s interval after injection of the indicated quantity of chloroform vapor in column II at 92.6 °C and a helium linear velocity of 0.81 cm·s^{-1}. For each profile, the summation was performed from 0 to 700 s.

(1) and (2). For a constant noise level, the calculated moments hardly depended on the acquisition interval between 0.1 and 0.5 s. We therefore concluded that a chromatogram composed of more than 1000 data points contained all the relevant information for IGC purposes. Throughout this work, accumulation times between 0.1 and 0.3 s were used, depending on the elution duration. The number of data points then varied from 2000 (for the marker gas at the highest temperature) to 7000 (for the probe well below T_g).

The third difficulty depends on the detector. In our experience, the proper base-line stability can be obtained using a thoroughly cleaned FID, provided that sufficient time is allowed for column conditioning, i.e., the removal of all volatile substances from the column. The continuous collection of the base line and its real-time display on an enlarged scale was used to inspect its stability prior to any injection.

The use of a chromatogram where the collection was prematurely ended (fourth difficulty) can be avoided by verifying that the peak moments do not depend on the choice of the last point in the summations of eq 6 and 7. An example of such calculations, performed on the data represented in Figure 1, is given in Table I. The first four moments were calculated using points between $t = 0$ and 10 different upper limits selected at 25-s intervals between 1025 and 1250 s. Values of the mean and standard deviation of the sample, as well as the 95% confidence interval on the mean of the population (estimated using Student's t statistics) are listed for t_p, σ, S, and E. The confidence interval on the four parameters is remarkably low, although it appears to increase with the order of the moment, a trend that reflects the increased weight of the noise in the analysis. The example of Figure 1 is for data obtained 20 deg below T_g, i.e., well in a range where the highest peak asymmetry is generally encountered in the course of IGC studies.

The last source of error associated with the moments of the elution curve seems unescapable: it is not possible to inject and detect the probe in the gas stream, to measure the column inlet and outlet pressures, or to connect a three-way valve in order to select the detector, without introducing some dead volume in the system. It is however possible to drastically decrease extra-column contributions by using a flow system stripped of all unnecessary parts, namely an arrangement reduced to injector, column, and flame ionization detector. The data discussed above (Figure 1 and Table I), as well as the results of Table II and Figures 4–9 were obtained with such an assembly. Two findings concur to indicate that, for a standard 1-m-long column, the dead volume introduced by the injector and the FID is negligibly small compared to the total volume of gas in equilibrium with the liquid stationary phase. The number of theoretical plates N of the polystyrene column in the 160–180 °C range is calculated to be on average 240 from the chromatograms of the marker gas but only 40 from those of chloroform (the data, in the form of $1/N$ vs T, are represented in Figure 7). Since any extra-column dead volume would equally affect both gases, the shape of the probe peaks appears to be controlled essentially by column processes. Furthermore, the elution profiles of the marker are not only quite sharp but also nearly symmetric, especially at high temperature where the difference between the position of the maximum and the first moment is lower than 0.5%.

A severe test of the feasibility of moment analysis consists in comparing calculations performed on several injections in identical conditions. Results for chloroform on ethylcellulose at 92.6 °C and an average linear velocity of 0.81 cm·s^{-1} are given in Table II. Six chromatograms were obtained, using four injection sizes. The reproducibility of the method can be evaluated from the standard deviation and 95% confidence interval of t_p, σ, S, and E. Substantial intervals are calculated for S and E. However, the first moment appears to be remarkably constant. The confidence interval on σ represents less than 2% of the absolute value, showing that a quite meaningful value of this flow-rate-dependent parameter can also be obtained by moment analysis.

Data Reduction

A consequence of the use of a chromatograph solely composed of injector, column, and detector is that the parameters needed for the calculation of the flow rate cannot be measured any more, and a reevaluation of the conventional IGC data reduction is necessary. The partition coefficient of a volatile substance between the liquid stationary phase and the carrier gas phase K_c is related to the net retention volume $V_N{}^0$ according to[8]

$$K_c = \frac{m_2 v_2}{V_N{}^0} \qquad (8)$$

where m_2 is the mass of stationary phase and v_2 its specific volume. The net retention volume is calculated[35] from the flow rate F_o at the column outlet (i.e., at the column temperature, under P_o) and the retention times of the probe, t_p, and a marker gas, t_o

$$V_N{}^0 = jF_o(t_p - t_o) \qquad (9)$$

where j is a compressibility factor introduced to correct for the difference between P_o and the inlet pressure P_i:

$$j = \frac{3((P_i/P_o)^2 - 1)}{2((P_i/P_o)^3 - 1)} \qquad (10)$$

The volume of gas phase in equilibrium with the stationary liquid, V_o, is a constant, characteristic of the column and independent of flow rate or temperature. According to James and Martin[35] and in the absence of extra-column contributions

$$V_o = jF_o t_o \tag{11}$$

so that eq 9 becomes:

$$V_N{}^0 = V_o \frac{t_p - t_o}{t_o} \tag{12}$$

The parameter $(t_p - t_o)/t_o$ is K_m, the mass ratio of the solute distributed at equilibrium between the mobile and stationary phases[36]

$$K_m = \frac{m_2 v_2}{V_o K_c} \tag{13}$$

which can be evaluated without measuring F_o, P_i, and P_o. The specific retention volume arbitrarily converted from the column temperature T to 0 °C is $V_g{}^0$

$$V_g{}^0 = \frac{273 V_o K_m}{T m_2} \tag{14}$$

which is the parameter commonly used to represent retention data. The weight fraction activity coefficient, $(a_1/w_1)^\infty$, and the Flory-Huggins interaction parameter, χ, are related[2] to $V_N{}^0$ through eq 15 and 16 where $P_1{}^0$ and

$$\ln (a_1/w_1)^\infty = \ln \frac{RTm_2}{P_1{}^0 M_1 V_N{}^0} - \frac{P_1{}^0(B_{11} - V_1)}{RT} \tag{15}$$

$$\chi = \ln \frac{RTm_2 v_2}{P_1{}^0 V_1 V_N{}^0} - \left(1 - \frac{V_1}{M_2 v_2}\right) - \frac{P_1{}^0(B_{11} - V_1)}{RT} \tag{16}$$

B_{11} are the vapor pressure and second virial coefficient of the gaseous solute and V_1 is the molar volume of the liquid solute. These expressions can also be written as

$$\ln \left(\frac{a_1}{w_1}\right)^\infty = \ln \frac{RTm_2}{P_1{}^0 M_1 V_o K_m} - \frac{P_1{}^0(B_{11} - V_1)}{RT} \tag{17}$$

and

$$\chi = \ln \frac{RTm_2 v_2}{P_1{}^0 V_1 V_o K_m} - \left(1 - \frac{V_1}{M_2 v_2}\right) - \frac{P_1{}^0(B_{11} - V_1)}{RT} \tag{18}$$

The partial molar enthalpy of mixing at infinite dilution of the probe in the polymer, $\Delta H_1{}^\infty$, is the partial derivative of $\ln (a_1/w_1)^\infty$ with respect to the reciprocal temperature. Since V_o is a constant, relative values of activity coefficients and χ parameters and an absolute value of $\Delta H_1{}^\infty$ can be obtained merely from measurements of t_p and t_o. The latter also provides a measure of the linear velocity of the carrier gas, u, averaged over the column length L:

$$u = L/t_o \tag{19}$$

In order to use K_m instead of $V_N{}^0$, the applicability of the model of James and Martin[35] to standard IGC packed columns must be carefully verified. If (i) the carrier gas is ideal, (ii) its linear velocity at any point of the column is proportional to the pressure gradient, and (iii) the area occupied by the gas phase at each section of the column is constant (assumption of a uniform packing), the flow rate at the column outlet obeys the relation

$$F_o = kP_o\left(\left(\frac{P_i}{P_o}\right)^2 - 1\right) \tag{20}$$

where k is a constant for a given column. The flow rate F_o can be calculated from the flow rate measured with a bubble flowmeter at the outlet of the chromatograph at room temperature T_r, under atomspheric pressure P_{atm}, using

$$F_o = \frac{T(P_{atm} - P_w)}{T_r P_o} F_r \tag{21}$$

where P_w is the saturated vapor pressure of the soap solution at T_r. It is worth pointing out that the ratio of pressures in the right-hand side of eq 21 *do not* simplify to $1 - (P_w/P_{atm})$, since any detector, including a FID,[16] introduces a pressure drop (typically as large as the pressure drop in the column itself). Figure 2 gives typical data computed for column I at 71, 130, and 171 °C. In the range of pressures experimentally significant for IGC studies, eq 20 appears to be remarkably well obeyed. The constant of column I, measured between 70 and 180 °C, is represented in Figure 3. A monotonous decrease with temperature is observed. This can be understood by considering[7] that k not only takes into account the packing and porosity of the support but also is inversely proportional to the viscosity of the carrier gas. In Figure 3, the temperature dependence of the column constant varies between $T^{-0.6}$ and $T^{-1.0}$, in fair agreement with the expected $T^{-1/2}$ for an ideal gas. As a consequence of the validity of eq 20, F_o can be calculated from P_i and P_o alone, provided

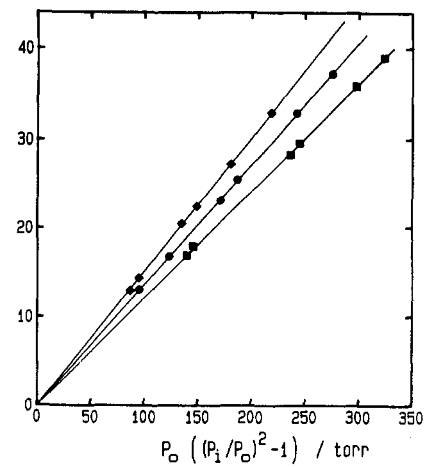

Figure 2. Flow rate at the column outlet, F_o, as a function of $P_o((P_i/P_o)^2 - 1)$, where P_o and P_i are the outlet and inlet pressures. A needle valve, replacing the detector between column and flowmeter, allowed a change of the pressures in a wide range. As predicted from the James–Martin model, a direct proportionality is observed at all temperatures between 70 and 180 °C. For clarity, only data at 177 (■), 130 (●), and 71 °C (◆) are represented.

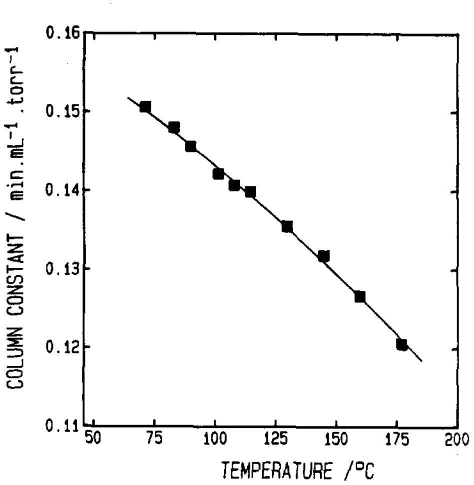

Figure 3. Column constant k as a function of temperature. The constant was calculated by a least-squares linear fit of F_o as a function of $P_o((P_i/P_o)^2 - 1)$, assuming zero flow rate at zero pressure drop.

that the column is calibrated in a separate experiment. This is of particular interest in the case of destructive detectors like a FID, for which the direct accurate measurement of flow rate is quite involved.[37] A simple method, consisting in the diversion of the gas stream by means of a three-way valve, is most generally mentioned in the IGC literature, although it is not clear if the proper correction in the calculation of F_0 is then applied. In effect, a close examination of eq 20 reveals that F_0 depends almost exclusively upon the pressure drop $(P_i - P_0)$ and to a negligible extent on the absolute values of P_i or P_0. In our experience, switching from the FID to the TCD (or directly to the flowmeter) promoted a change of a few percent in the pressure drop (typically 2–3 Torr when P_0 and P_i are about 850 and 900 Torr), thereby inducing a change of a similar magnitude in F_0. It is therefore essential to monitor P_i and P_0 in both instances when the flowmeter or the FID are connected to the column, each set of values being then used to determine k and F_0, respectively.

In order to further test the James–Martin model and verify the overall validity of the reduction procedure, the volume of gas phase in the polystyrene column has been calculated at 11 temperatures between 70 and 180 °C, using eq 11 and the retention time of the marker gas. Two groups of values were obtained, according to the detector used. In the case of the TCD, F_0 was calculated from P_i, P_0, and the flow rate measured at the outlet of the detector (eq 21). When the FID was used, F_0 was calculated with eq 20 using P_i, P_0, and interpolated values of the column constant. At each temperature, duplicate injections of methane were performed under at least three different pressure conditions. The main features of the results are the following: (i) The calculated V_0 shows no dependence on flow rate. (ii) It is fairly constant with temperature, the standard deviation of either the FID (65 data points) or the TCD (131 data points) set for all temperatures combined being only 0.6%. (iii) The TCD data are consistently higher (about 3%) than those calculated from FID, probably because the former introduces a larger dead volume in the chromatographic assembly. Indeed, measurements using only the TCD without the three-way valve yielded a lower value of V_0. Also, the data scatter was substantially reduced (standard deviation on 50 data points 0.3%), indicating that it originates from extra-column contributions.

Moment analysis has been applied on the system PS + $CHCl_3$, for which thermodynamic data have already been published.[38-40] Also, the glass transition of polystyrene around 100 °C is well documented.[41]

Use of Moments in Structural Studies

Figure 4 gives the chromatograms recorded on column I at temperatures between 68 and 149 °C. The profiles have been plotted in the form of a reduced concentration $h(t)/\sum h(t)$ as a function of a dimensionless time parameter $(t - t_0)/t_0$, where t_0 is the first moment of the concentration profile of the marker gas, recorded in identical conditions. The position of the first moment is also indicated for each peak. The most striking feature is the difference between the temperature dependence of the peak maximum and that of the first moment. The time corresponding to the maximum outlet concentration features the usual drop as the temperature is decreased and crosses the glass transition. In contrast, the mean residence time increases monotonously, the difference between maximum and first moment increasing accordingly. The flow rate dependence of the mass distribution coefficient K_m is another indication of the inadequacy of the peak maximum as a measure of retention. The effect of the carrier gas velocity for different polymer–probe pairs is illustrated in Figure 5. Values of $(t_p - t_0)/t_0$ calculated from the maxima decrease when the flow rate increases, while the data determined from moment analysis show hardly any dependence. Of particular interest is the observation that, in some cases, the two sets do not extrapolate to the same value at zero flow rate. This feature is indicative of a strongly nonlinear dependence of V_N^{max} on flow rate, in agreement with results of capillary IGC.[16] The retention diagram of chloroform on PS, in the form of a plot of ln (V_g^0/V_0) as a function of the reciprocal temperature, is given in Figure 6. It gives yet another representation of the main results of Figures 4 and 5; namely, moment analysis yields a retention diagram, which exhibits neither a drop at T_g nor any significant flow-rate dependence. The plot is linear over a wide temperature interval, the glass transition affecting the diagram only by a slightly higher temperature dependence of ln V_g^0 and an increased data scatter below T_g. The lower reproducibility probably originates from the increased peak tailing at low temperature (Figure 4). The change in the shape of the concentration profile at T_g can

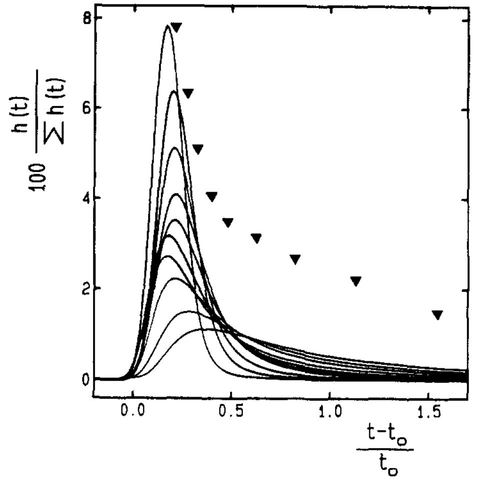

Figure 4. Elution profiles recorded for chloroform on PS at a flow velocity of 1.5 cm·s^{-1}. The chromatograms, plotted in the form of reduced concentration $h(t)/\sum h(t)$ as a function of reduced time $(t - t_0)/t_0$, have been measured, in increasing order of amplitude, at 68, 75, 82, 90, 100, 112, 129, 139, and 149 °C. The triangles, which have been drawn at the same ordinate as the corresponding peak maximum, indicate the position of the first moment.

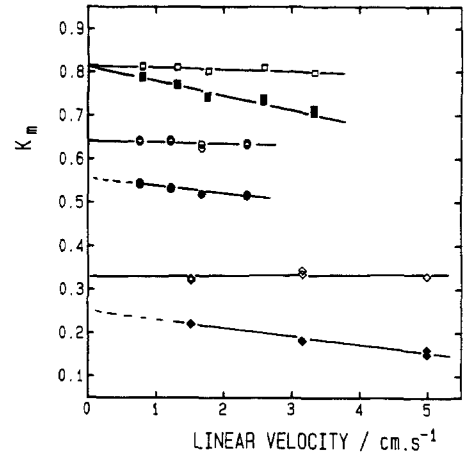

Figure 5. Effect of the average carrier gas velocity u on the mass distribution coefficient K_m for different polymer–solvent pairs: (■) 1,1,1-trichloroethane on EC at 93 °C; (●) acetone on EC at 81 °C; (◆) chloroform on PS at 129 °C. The times t_p and t_0 were taken either as the position of maximum (filled symbols) or the first moment (open symbols) of the concentration profile.

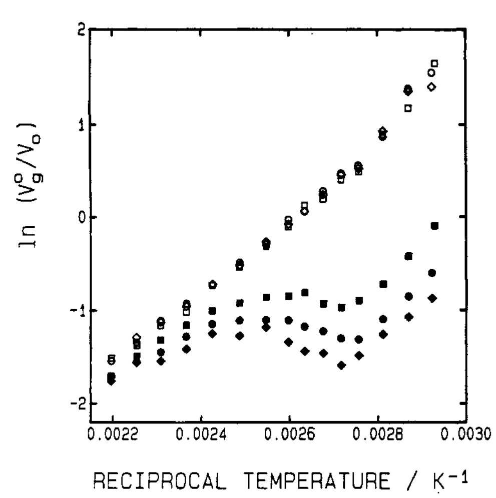

Figure 6. Retention diagram of chloroform on polystyrene at three flow velocities about 1.5 (■), 3.0 (●), and 5.0 (◆) cm·s^{-1}. Both the large drop and the tremendous effect of flow rate, observed on retention volumes calculated from the peak maximum (filled symbols), are absent on data gathered by moment analysis. Each point is the average result of at least two injections.

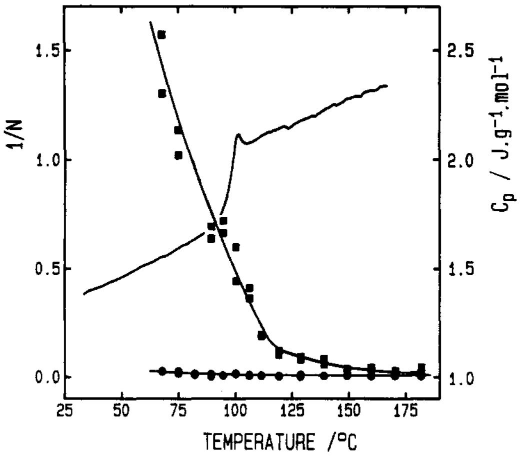

Figure 7. Reciprocal number of theoretical plates of column I as a function of temperature. Results obtained at a flow velocity of about 1.5 cm·s^{-1} for both the marker gas (●) and chloroform (■) are represented. The temperature variation of the heat capacity of polystyrene, plotted for comparison, shows that the transition from glass to liquid is completed at T_g = 108 ± 2 °C.

be monitored with the statistical moments. As shown in Figure 7, the standard deviation of the peak, in the form of the reciprocal number of theoretical plates of the column (eq 3), provides a very sensitive tool for the detection of the glass transition. A sharp increase of $1/N$ is observed between 110 and 120 °C, which compares favorably with a T_g value of 108 ± 2 °C, determined by microcalorimetry. At the same time, the value of $1/N$ calculated from the marker profiles remains consistently low, which confirms that the broadening of the peaks for chloroform originates solely from the resistance to mass transfer into the polymer.

Thermodynamic Parameters Calculated from the First Moment

Equation 17 has been used to calculate the weight fraction activity coefficients of chloroform at infinite dilution in PS. The results are represented in Figure 8, as well as some literature results from measurements of vapor pressure lowering,[38] piezoelectric sorption experiments,[39] and IGC.[40] Figure 8 exhibits essentially the same features as Figure 6. The activity coefficients obtained from the first moment give a plot that is linear until the glass transition and extrapolates to values in good agreement with the results of static measurements at low temperature.[38,39] In contrast, the coefficients obtained from the peak maximum, including literature data[40] collected at temperatures as high as 230 °C, appear to be of little use for thermodynamic purposes. They may even lead to erroneous conclusions. The partial molar heats of mixing, derived from the temperature dependence of activity coefficients in the linear portion of the curves, are reported in Figure 9. A small negative enthalpy, independent of flow rate, is derived from the first moment of the chromatograms. On the other hand, the peak maximum gives a ΔH_1^∞ value that increases rapidly, even changing sign, when the flow rate increases.

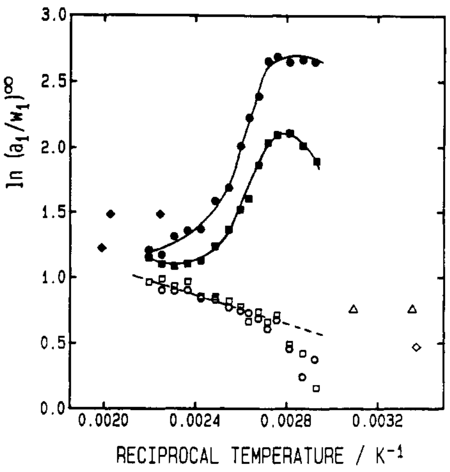

Figure 8. Weight fraction activity coefficients of chloroform at infinite dilution in PS. A value of V_0 = 26.35 mL, corresponding to the average of TCD measurements, has been used for the calculation. For clarity, the values calculated for only two carrier gas velocities have been drawn: (■) 1.5 and (●) 5.0 cm·s^{-1}. Open and filled symbols are for results determined using the first moment and the position of the maximum, respectively. Also represented are literature data obtained by (△) vapor pressure measurements,[38] (◇) piezoelectric sorption,[39] and (◆) IGC.[40]

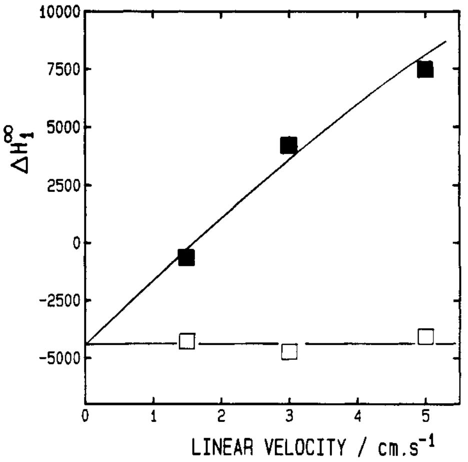

Figure 9. Partial molar enthalpy of mixing of chloroform at infinite dilution in PS, ΔH_1^∞, determined from the temperature dependence of the activity coefficients and plotted as a function of the carrier gas flow velocity. The results were calculated from the slope of the high-temperature part of the curves. Linear regression was applied to the data, considering the values above 115 °C (first moment, □) or 140 °C (peak maximum, ■).

Conclusion

A problem of linear nonideal chromatography, namely the determination of meaningful retention parameters from non-Gaussian chromatograms, has been addressed in this paper. The procedure to obtain reliable values of the first two statistical moments involves essentially (i) a data acquisition method that limits the incidence of noise on elution profiles and (ii) a chromatographic assembly where most extra-column contributions to dead volume have been eliminated. The mass ratio of the solute distributed at equilibrium between the mobile and stationary phases is obtained, from which relative retention volumes and absolute partial molar enthalpies, both independent of flow rate, can be calculated. Measurements of retention of chloroform on polystyrene confirm the inadequacy of the peak maximum as a measure of retention and the feasibility of moment analysis.

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Registry No. PS, 9003-53-6; chloroform, 67-66-3.

References and Notes

(1) Guillet, J. E. *Adv. Anal. Chem. Instrum.* **1973**, *11*, 187.
(2) Patterson, D.; Tewari, Y. B.; Schreiber, H. P.; Guillet, J. E. *Macromolecules* **1971**, *4*(3), 356.
(3) Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* **1974**, *7*, 530.
(4) DiPaola-Baranyi, G.; Guillet, J. E. *Macromolecules* **1978**, *11*, 228.
(5) Braun, J. M.; Guillet, J. E. *Adv. Polym. Sci.* **1976**, *21*, 107.
(6) Gray, D. G. *Prog. Polym. Sci.* **1977**, *5*, 1.
(7) Laub, R. J.; Pecsok, R. L. In *Physicochemical Applications of Gas Chromatography*; Wiley: New York, 1978.
(8) Conder, J. R.; Young, C. L. In *Physicochemical Measurement by Gas Chromatography*; Wiley: New York, 1979.
(9) Al-Saigh, Z.; Munk, P. *Macromolecules* **1984**, *17*, 803.
(10) Card, T. W.; Al-Saigh, Z.; Munk, P. *Macromolecules* **1985**, *18*, 1030.
(11) Munk, P.; Al-Saigh, Z.; Card, T. W. *Macromolecules* **1985**, *18*, 2196.
(12) Munk, P.; Card, T. W.; Hattam, P.; El-Hibri, M. J.; Al-Saigh, Z. *Macromolecules* **1987**, *20*, 1278.
(13) Grenier-Loustalot, M.-F.; Mouline, G.; Grenier, P. *Polymer* **1987**, *28*(13), 2275.
(14) Murakami, T.; Inui, T.; Takegami, Y. *Polymer* **1983**, *24*, 1596.
(15) Van Deemter, J. J.; Zuiderweg, F. J.; Klinkenberg, A. *Chem. Eng. Sci.* **1956**, *5*, 271.
(16) (a) Pawlisch, C. A.; Macris, A.; Laurence, R. L. *Macromolecules* **1987**, *20*, 1564. (b) Pawlisch, C. A. Ph.D. Thesis, University of Massachusetts, Amherst, 1985.
(17) El-Hibri, M. J.; Munk, P. *Macromolecules* **1988**, *21*, 264.
(18) Hattam, P.; Munk, P. *Macromolecules* **1988**, *21*, 2083.
(19) Hu, D. S.; Han, C. D.; Stiel, L. I. *J. Appl. Polym. Sci.* **1987**, *33*, 551.
(20) Schuster, R. H.; Grater, H.; Cantow, H. J. *Macromolecules* **1984**, *17*, 619.
(21) Sometimes, it may even be preferable, as results of the present work suggest that the glass transition is less heavily emphasized in retention diagrams built from V_N.
(22) Olabisi, O. *Macromolecules* **1975**, *8*, 316.
(23) Baralles-Rienda, J. M.; Vidal Gancedo, J. *Macromolecules* **1988**, *21*, 220.
(24) Deshpande, D. D.; Tyagi, O. S. *J. Appl. Polym. Sci.* **1987**, *33*, 715.
(25) Wang, J. Y.; Charlet, G., to be published.
(26) Anderson, D. J.; Walters, R. R. *J. Chromatogr. Sci.* **1984**, *22*, 353.
(27) Yaws, C. L. *Chem. Eng.* (*N.Y.*) **1976**, *83*(14), 81.
(28) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents—Physical Properties and Methods of Purification*; Wiley: New York, 1986.
(29) Pitzer, K. S.; Curl, R. F. *J. Am. Chem. Soc.* **1957**, *79*, 2369.
(30) Dymond, J. H.; Smith, E. B. In *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon Press: Oxford, 1980.
(31) Hellwege, K. H.; Knappe, W.; Lehmann, P. *Kolloid Z. Z. Polym.* **1962**, *183*, 110.
(32) See, for instance, Figure 3.1, p 98, in ref 8.
(33) Savitzky, A.; Golay, J. E. *Anal. Chem.* **1964**, *36*, 1627.
(34) Noggle, J. H. In *Physical Chemistry on a Microcomputer*; Little, Brown & Co.; Boston, 1985.
(35) James, A. T.; Martin, A. J. P. *Biochem. J.* **1952**, *50*, 679.
(36) This basic parameter of chromatography is also noted k[19], k',[7] and Z_p.[18]
(37) See, for instance, ref 7, p 69, or ref 8, p 102.
(38) (a) Bawn, C. E. H.; Wajid, M. A. *J. Polym. Sci.* **1954**, *12*, 109. (b) Bawn, C. E. H.; Wajid, M. A. *Trans. Faraday Soc.* **1956**, *52*, 1658.
(39) Saeki, S.; Holste, J. C.; Bonner, D. C. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 307.
(40) Gunduz, S.; Dincer, S. *Polymer* **1980**, *21*(9), 1041.
(41) Reding, F. P.; Faucher, J. A.; Whitman, R. D. *J. Polym. Sci.* **1962**, *57*, 483.

Infrared Dichroic Study of Orientation Using Ionomers

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ABSTRACT: A comparison was made of chain orientation in polystyrene (PS), poly[styrene-*co*-(methacrylic acid)s] (S-MAA) of different acid contents, and their sodium- and cesium-neutralized ionomers. Infrared dichroism measurements show that for a stretching temperature normalized to the glass transition temperature (T_g) chain orientation is much higher in ionomers than in either the copolymers or PS; moreover, the greater the ion content, the greater the observed orientation. This result can be attributed to the ionic aggregates in the ionomers, which act as effective cross-links, thereby modifying the density of the temporary network structure. On the other hand, it is found that the presence of randomly distributed hydrogen bonding interactions in the S-MAA copolymer does not lead to any increase of chain orientation compared to that of PS. These results indicate that the role of the rubberlike network is more important than that of specific intermolecular interactions to the chain orientation achieved in amorphous polymers stretched uniaxially above their T_g; an increase in network density results in a higher average chain orientation.

Introduction

The chain (or molecular) orientation attained in an amorphous polymer stretched uniaxially above its glass transition temperature is governed by two opposing processes. The first is the chain alignment, or orientation as such, in the stretching direction that is induced by the extensional forces. The second is the chain relaxation that inevitably occurs during stretching and that gives rise to a loss of orientation.

In the case of an amorphous rubber network, it has been shown both theoretically and experimentally[1-3] that molecular orientation is inversely proportional to the number

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