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FTIR Investigations of Crystallinity and Surface Reaction for *trans*-1,4-Polyisoprene Lamellar Structures Crystallized from Solution

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ABSTRACT: Infrared studies of *trans*-1,4-polyisoprene (TPI) and of block copolymer derivatives were carried out. TPI lamellar structures were reacted in suspension so that their surfaces were modified while their crystalline cores remained unchanged. The reactions used were epoxidation and hydrochlorination of the double bond. The infrared spectra of the modified surface were obtained, and tentative band assignments were made. A procedure was developed to obtain the percent crystallinity of TPI lamellar structures from the infrared spectrum by using measurements of the relative intensity of the 1664–1670-cm^{-1} band in the crystalline and semicrystalline spectra. Effects of pressure on as-prepared and surface-modified TPI lamellar structures were observed.

Introduction

Lamellar structures of the polydienes *trans*-1,4-polybutadiene, TPBD, and *trans*-1,4-polyisoprene, TPI, have been obtained by crystallization from solution under a variety of conditions; these structures have been characterized morphologically by using optical and scanning electron microscopy.[1-4] The crystalline/amorphous character of some of these preparations have been studied by physical methods, such as density and solid-state carbon-13 NMR.[1,3,5,6] In addition to depending on the assumption of a two-phase model, the calculation of crystallinity from density requires accurate crystalline and amorphous densities. Since there is some disagreement in the value of the crystalline density for β-TPI,[7-9] the development of alternative methods for crystallinity determination is desirable. One method employed for crystallinity measurement is infrared spectroscopy. A convenient and unambiguous procedure is to use a single band for which the band shape, position, and intensity are independent, or nearly so, of overall crystalline and amorphous chain conformations. A band due principally to a vibration of a group of atoms held in a relatively rigid conformation is a logical choice. A method for the quantitative determination of the crystalline fraction in semicrystalline TPI was developed in the present study by using the infrared spectroscopic band assigned principally to the C=C stretching vibration. The values obtained from infrared spectroscopy are found to be in close agreement with those from density measurements.

For quantitative assessment of chain folding at lamellar surfaces, a direct method involving chemical reaction in suspension, followed by carbon-13 solution NMR, was developed.[10-12] The polydienes are well suited for this type of study, due to the susceptibility of the double bond present in each repeat unit to addition reactions. However, it is crucial that the reaction at the surface is complete and is confined to that region. Considerable effort has been expended to establish reaction conditions that lead to complete reaction of the lamellar surfaces without crystal core penetration or cross-linking taking place to an appreciable degree. Two reactions for the modification of TPI, epoxidation using *m*-chloroperbenzoic acid[11] and hydrochlorination,[12] have been investigated to date. It has been shown that both of these reactions can be carried out under conditions that give single products preserving the stereochemistry of the double bond, as characterized by carbon-13 NMR.[11,12] When one or the other of these reactions is taken to completion at the lamellar surfaces of solution-crystallized TPI structures in suspension, a product having chemically modified blocks alternating with unmodified blocks results.

In the present work it is found that dried mats of solution-crystallized samples subjected to reaction in suspension with either *m*-chloroperbenzoic acid or with HCl yield an infrared spectrum containing all the crystalline bands observed for the original lamellas combined with a new set of bands, obtainable by subtraction, characteristic of the reaction. The changes in the spectrum for the amorphous surface component caused by chemical modification are found to be consistent with the band assignment made by correlation with the crystalline assignments.[13]

The effect of pressure on the crystallinity of TPI structures and on the spectrum for surface-modified TPI was also investigated, with the same decrease in the crystalline component being observed at all pressures used.

Experimental Section

Surface Reactions. Unfractionated *trans*-1,4-polyisoprene, TPI, ($M_w = 1.7 \times 10^5$, $M_w/M_n = 4.8$)[14] was crystallized from 1% amyl acetate solution by precipitation at 0 °C and slow heating to 30 °C. Curved, overgrown, semicrystalline lamellas are obtained, with a crystalline core in the β form.[1]

TPI lamellas, suspended in 1-butanol, were reacted with an excess (3/1) of *m*-chloroperbenzoic acid at 0 °C for 5 days. TPI

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lamellas were also suspended in acetone and reacted at −7 °C with gaseous hydrogen chloride in large excess for 7 days. These chemically modified structures were washed, and mats were formed by filtration of the suspended material onto Teflon filters, followed by drying at room temperature. Fourier transform infrared spectra of the samples were obtained in the 450–4000-cm^{-1} region at 4-cm^{-1} resolution by using a Digilab FTS 40 spectrometer. A 100% crystalline spectrum, previously obtained,[13] was used for digital subtraction.

Crystallinity Measurements. The procedure given in the previous section but with the concentration reduced to 0.5% was used to prepare partially crystalline samples in the β form from unfractionated synthetic TPI, balata ($M_w = 2.2 \times 10^5$, $M_w/M_n = 2.2$), and gutta-percha ($M_w = 2.7 \times 10^5$, $M_w M_n = 4.3$).[15] The morphologies observed by interference contrast optical microscopy were (1) curved overgrown lamellas (synthetic TPI), (2) aggregates of cup-shaped lamellas (balata), and (3) spherulites (gutta-percha).[1]

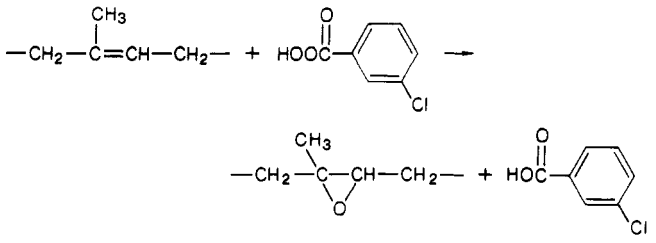
Semicrystalline samples in the α form were obtained from solution by using unfractionated synthetic TPI by two procedures. In one of these a 0.5% solution in amyl acetate was cooled directly to 30 °C giving a spherulitic morphology;[1] in the other a 0.05% solution in hexane was cooled to 0 °C, the resulting suspension heated slowly to 32 °C to effect dissolution, and then isothermal crystallization carried out at 20 °C. This procedure yields overgrown single lamellas.

Some samples were prepared by application of pressure in a Carver press to filtered mats for periods of time up to about 15 min. The minimum readable pressure on the press was 200 psi.

FTIR spectra were obtained on mats of these samples at ambient temperature. Relative infrared intensities were measured from the absorption peaks by cutting and weighing. Densities were measured by the gradient flotation method, and the weight fraction crystallinity was determined.[5] The sample crystallinity was calculated by using the density values for amorphous[16] and crystalline[8] TPI.

Results

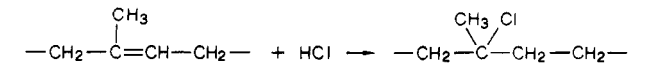
Surface Reactions. The reaction of suspended TPI lamellar structures with *m*-chloroperbenzoic acid in solution leads to the epoxidation of all exposed double bonds as follows:



The resulting block copolymer products have been characterized by proton NMR[17] and carbon-13 NMR.[11]

The Fourier transform infrared spectrum obtained for curved overgrown β-TPI lamellas epoxidized in suspension is given in Figure 1. This spectrum contains bands characteristic of both the β crystal core and the reacted surface. A 100% surface-reacted spectrum (Figure 2a) is obtained by subtraction of a 100% β-crystalline spectrum while simultaneously watching the disappearance of the crystalline bands at 1664, 877, and 800 cm^{-1}. No unreacted amorphous component is observed in the surface-reacted spectrum. The surface-epoxidized spectrum differs from the amorphous TPI spectrum (Figure 2b) mainly in the following respects: (1) the bands at 1668, 595, and 520/490 cm^{-1} disappear, (2) bands at 1122, 1069, and 685 cm^{-1} appear, (3) the band at 1250 cm^{-1} increases in intensity, and (4) the band at 842 cm^{-1} shifts to 880 cm^{-1}.

Hydrochlorination of TPI lamellar structures in suspension proceeds by Markovnikov addition:[12]



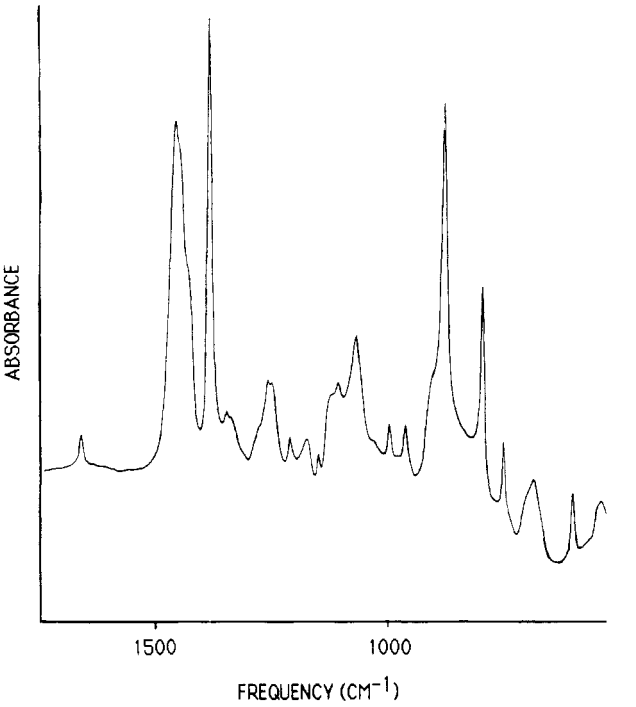


Figure 1. Infrared spectrum for surface-epoxidized TPI lamellar structures.

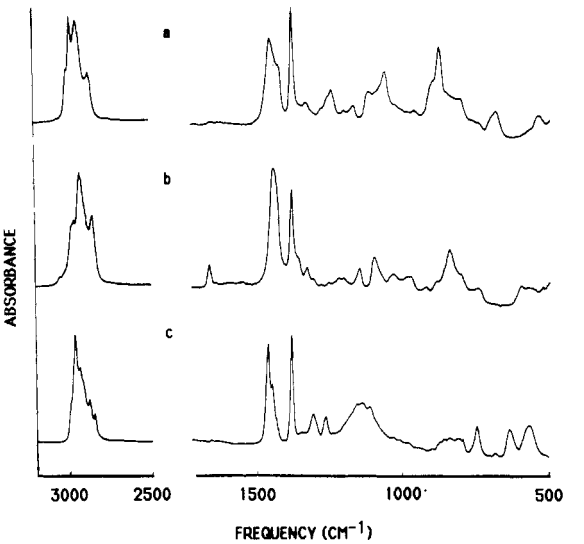


Figure 2. Infrared spectra for TPI and surface-reacted derivatives: (a) epoxidized; (b) amorphous; (c) hydrochlorinated.

The FTIR spectrum obtained for curved overgrown β-TPI lamellas hydrochlorinated in suspension shows bands characteristic of the unreacted crystal core and the reacted amorphous surface. Subtraction of the crystalline component yields the spectrum given in Figure 2c. Comparison of this spectrum with that for amorphous TPI shows (1) the absence of the bands at 1668, 595, and 520/490 cm^{-1}, (2) the absence of a strong band at 842 cm^{-1}, (3) the presence of bands at 1140 and 635 cm^{-1}, and (4) the increase in band intensity at 1305, 1261, 1155, 746, and 565 cm^{-1}.

The frequencies along with an estimate of the relative intensity for each band observed in the 450–1700-cm^{-1} range and the band assignments are given in Table I for amorphous TPI, epoxidized TPI, and hydrochlorinated TPI.

Crystallinity Measurements. A procedure using the 1664–1670-cm^{-1} infrared bands, due primarily to a C=C stretching vibration, was developed to obtain the crys-

Table I
Infrared Frequencies and Band Assignments for Amorphous, Epoxidized, and Hydrochlorinated TPI[a]

EP TPI	TPI	Cl TPI	assignment[b]
	3025 (w)		ν(=C–H)
3022 (w)			ν(–C–H)
2991 (s)	2976 (s)	2983 (s)	
			$\nu_{as}(CH_3)$
2964 (vs)	2961 (vs)	2957 (vs)	
2932 (vs)	2934 (vs)	2933 (vs)	
			$\nu_{as}(CH_2)$
2926 (vs)	2920 (vs)	2928 (vs)	
2914 (s)	2912 (s)	2912 (s)	$\nu_s(CH_3)$
2875 (s)	2875 (s)	2873 (s)	
			$\nu_s(CH_2)$
2858 (s)	2848 (s)	2842 (s)	
	1668 (m)		ν(C=C)
	1574 (vw)		
	1541 (vw)		
1462 (s)	1450 (s)	1460 (s)	$\delta(CH_2)$; $\delta_{as}(CH_3)$
1433 (sh)	1430 (sh)	1446 (sh)	$\delta(CH_2)$
1387 (s)	1380 (s)	1383 (s)	$\delta_s(CH_3)$
	1360 (sh)		
1336 (w)	1329 (m)	1344 (w)	$\delta_s(CH_3)$ + ν(C–C)
			$\delta_s(CH_3)$ + $\gamma(CH_2)$
1312 (sh)	1307 (sh)	1305 (m)	$\gamma(CH_2)$
1280 (sh)	1281 (w)		$\gamma(CH_2)$
1260 (sh)	1253 (w)	1261 (m)	$\gamma(CH_2)$
1250 (ms)			ν_s(EP)
		1234 (vw)	
	1220 (w)		
			$\delta(=CH)_{ip}$
	1205 (w)		
1208 (w)			
1174 (m)	1150 (m)	1155 (ms)	
			$\gamma(CH_2)$
		1140 (ms)	
1122 (ms)			ν_{as}(EP)
1099 (sh)	1099 (m–s)	1110 (m–s)	ν(C–C)
1069 (s)			ν_{as}(EP)
1032 (sh)	1033 (m)	1031 (sh)	$\gamma_r(CH_3)$ + ν(C–C)
1010 (sh)	987 (m)	1010 (sh)	$\gamma_r(CH_3)$ + ν(C–C)
990 (sh)	976 (m)	976 (sh)	$\gamma_r(CH_3)$
965 (w)	924 (w)	950 (w)	$\gamma_r(CH_3)$
900 (sh)			
880 (s)			δ(–C–H)$_{op}$
853 (sh)			
	884 (sh)		
	862 (sh)		$\delta(=CH)_{op}$
	842 (s)		
		876 (w)	
		855 (w)	
		837 (w)	
800 (m)	800 (m)	804 (w)	ν(C–CH_3)
765 (sh)	764 (sh)		
		746 (ms)	$\gamma_r(CH_2)$
746 (m)	746 (m)		
700 (sh)			
685 (ms)			δ(EP)
		684 (w)	
		635 (m)	ν(C–Cl)
	595 (m)		
			δ(C=C–C)
	570 (m)		
		565 (m–s)	ν(C–Cl)
540 (m)			δ(–C–CH_3)$_{op}$
	520 (m)		
			$\delta(=CCH_3)_{op}$
	<505 (m)		

[a] EP = epoxidized, Cl = hydrochlorinated, s = strong, m = medium, w = weak, sh = shoulder. [b] ν= stretch; δ = bend; γ = twist, wag; γ_r = rock; EP = epoxy ring.

tallinity of semicrystalline TPI samples. A 100% crystalline spectrum for each sample is obtained from the semicrystalline spectrum taken at ambient temperatures by subtraction of the amorphous spectrum obtained at 65 °C. This subtraction is carried out by watching the disappearance of the 842-cm^{-1} band until negative amorphous components appear throughout the spectrum. The crystallinity is then calculated from the relative areas of the 1664–1670-cm^{-1} band before and after subtraction. This procedure is illustrated in Figure 3, which shows on the left-hand side a semicrystalline band envelope in the 1690–1645-cm^{-1} frequency region and the scaled amorphous component in the same region subtracted from it. The 100% crystalline band, shown on the right-hand side, is the difference between these two bands. The crystallinities of samples from five types of TPI preparations differing in morphology and/or crystal form, as obtained by the infrared method, are given in Table II. Crystallinities from density measurements for 7 of the 19 samples studied are also included in Table II. The area under the 1664–1670-cm^{-1} band was found to be the same within experimental error for a semicrystalline sample at ambient temperature and for the same sample in the melt at 75 °C, showing the above subtraction method to be a valid one.

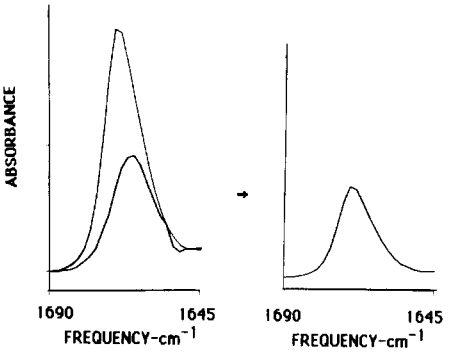


Figure 3. Spectral subtraction in the 1645–1690-cm^{-1} region to obtain 100% crystalline components for TPI lamellar structures.

Table II
Crystallinity of TPI Samples from Solution

sample	solvent	T_c, °C	crystal form	% crystallinity IR	% crystallinity density
synthetic 1	AA	0/30	β	63	62
synthetic 2				65	63
synthetic 3				65	64
synthetic 4				63	
synthetic (pressed 1)				57	
balata 1				61	
balata 2				61	61
balata 3				59	61
balata 4				60	
gutta-percha 1				60	60
gutta-percha 2				60	
gutta-percha 3				59	58
synthetic 5		30	α	54	
synthetic 6				56	
synthetic 7				55	
synthetic (pressed 2)				50	
synthetic 8	hexane	20		56	
synthetic 9				54	
synthetic 10				55	

Infrared crystallinities were measured on mats of TPI structures subjected to a pressure of 200–2000 psi. Application of 200 psi, the smallest pressure registered on the press used, causes a 5–7% decrease in crystallinity. Higher pressures up to 2000 psi did not bring about any further change in crystallinity. The results obtained are included in Table II. It was also found that pressure application to mats of chemically modified lamellar structures caused the appearance of an unmodified amorphous TPI component in the infrared spectrum taken after pressure re-

lease. This amorphous component was completely subtractable.

Discussion

The approximate band assignments given in Table I for amorphous TPI were obtained and discussed previously.[13] These were taken from the assignments made for crystalline α- and β-TPI by using single-chain calculations. The amorphous bands were assigned by a transfer of the potential energy distribution for both α and β crystalline bands with which an amorphous band completely overlaps. In one case (1329 cm^{-1}) two assignments are given since those for α- and β-TPI disagree. For the band at 1450 cm^{-1}, the calculations yielded two sets of bands with different assignments; these were the same for the α and β forms.

Epoxidation and hydrochlorination of TPI lamellas in suspension have been used previously to determine the average number of monomer units per fold in these structures.[11,12] For this method to be successful, reaction of all of the surface component must occur. The absence of an amorphous component after reaction would show that all of this component was present at the surface initially and that all of it has reacted. Since the reaction site is the double bond, one important criterion for complete reaction is that all of the infrared absorption bands due to vibrations involving this group in the amorphous region vanish. For amorphous TPI the bands that should disappear are those at 1665 (C=C stretching), 1220 and 1205 (=C–H in-plane bending), 884, 862, and 842 (=C–H out-of-plane bending), 595 and 570 (C=C–C bending), and 520 and <505 cm^{-1} (=C–CH_3 out-of-plane bending).[13] The epoxidation and hydrochlorination reaction conditions used in the present work clearly cause the loss of the more prominent of these bands from the amorphous spectrum. In some cases, however, an amorphous band is replaced by one or more new bands in the same frequency region. For example, the bands at 595 and 570 cm^{-1} are replaced by one at 565 cm^{-1} in surface-hydrochlorinated material and at 540 cm^{-1} in surface-epoxidized TPI.

New bands appear in the spectra for surface-reacted TPI due to the introduction of either the epoxy group or the chlorine atom. Bands at 1250, 1122, 1069 and 700, 685 cm^{-1} are tentatively assigned to symmetric epoxy ring stretching, assymetric epoxy stretching, and epoxy ring deformation, respectively. Bands at 635 and 565 cm^{-1} are both attributed to C–Cl stretching.[18,19] For surface-epoxidized TPI the strong band appearing at 880 cm^{-1} is assigned to –C–H out-of-plane bending. A number of the bands observed for surface epoxidized or surface hydrochlorinated lamellas correlate closely with those for amorphous TPI and are given the same assignments (see Table I). These bands are mainly due to CH_2, CH_3, and C–C vibrations or combinations thereof. There are some differences in relative intensities for the CH_2 bands, with larger ones being observed for the hydrochlorinated surfaces, apparently due to the larger number of CH_2 groups per repeat unit in this product. The weak bands at 1234, 876, 855, 837, and 684 cm^{-1} for surface-hydrochlorinated TPI and at 1208 cm^{-1} for surface-epoxidized TPI are unassigned.

The comparison of crystallinities from the infrared method developed in this work with those from density measurements for seven preparations of unfractionated TPI with different morphologies show agreement within 2 percentage units (Table II). Following the development of the infrared method to measure crystallinity, a concurrent but independent study was carried out on 15 β-TPI samples prepared from three molecular weight fractions by using different crystallization conditions.[20] In that study the techniques used to evaluate the crystallinity were the FTIR method described above, density measurement, and lamellar surface reaction combined with carbon-13 NMR; the crystallinities ranged from 0.51 to 0.67, and agreement between the three methods was within 0.03 units.

The successful use of infrared spectroscopy, as developed in this work, to determine crystallinity is believed to be a consequence of the choice of the C=C stretching band for these measurements. The C=C stretching band with maxima at 1664–1670 cm^{-1} for the different samples is separated from other bands, and therefore its area can be measured directly without deconvolution. In this way any assumptions and approximations resulting from peak separation are eliminated. This band also has a clear base line, which can be determined unambiguously. For this particular normal mode, it is found that the α and β crystalline and amorphous band envelopes are almost constant in position and in bandwidth. For this reason, in semicrystalline TPI a single band is observed. The total absorbance area for this IR band is independent of crystallinity from at least 50 to 0%; this area depends only on the total amount of material present and, therefore, on the sample thickness.

The constant position of the band envelope and its independence of crystallinity changes at constant sample thickness are believed to be due mainly to the constant geometry of the C=C bond, which is held in the trans configuration. Of all the different carbon–carbon bonds that are included in the TPI chain backbone, only the C=C bond has the same local conformation in both the two crystalline arrangements and in the amorphous state. A small shift in the vibrational frequency of this band in the two crystalline forms does occur because of the different C=C bond lengths in the two crystal forms.

It was found in this study that the application of pressures as small as 200 psi to a semicrystalline mat of solution-crystallized TPI causes a change in the infrared spectrum. These results are in quantitative agreement with density measurements that proceeded this work and that showed a 5–7% decrease in crystallinity for TPI lamellar mats upon pressure application.[21] In the current work it was seen that pressing of mats of surface-reacted lamellas also causes the appearance of an unmodified amorphous TPI component. Since before the application of pressure only a crystalline and a chemically modified surface component are present, the appearance of amorphous TPI must be accompanied by changes in some part of the crystalline core.

Conclusions

Chemical modification of TPI lamellar surfaces gives infrared spectral changes consistent with complete reaction of the amorphous component.

An infrared method, using the intensity of the 1664–1670-cm^{-1} band, was developed that measures the crystallinity of semicrystalline TPI lamellas.

Infrared spectral measurements show that the application of pressure causes a decrease in the crystallinity for TPI lamellar structures.

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Registry No. TPI, 9003-31-0.

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Inverse Gas Chromatography. 5. Computer Simulation of Diffusion Processes on the Column

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ABSTRACT: The elution behavior of low molecular weight probes on IGC columns was simulated by using a computer. The IGC model was based on a polymer stationary phase of uniform thickness with a nonnegligible resistance to probe penetration. Three characteristic numbers were found to determine the whole process: Z_p characterizing the distribution of the probe between phases; Z_f describing the diffusion in the polymer phase, and Z_g related to diffusion in the gaseous phase. With Z_f vanishing or small, the elution curves differed slightly from the generally accepted ones: the appropriate correction factors were evaluated. For situations when $Z_p/Z_f < 2$, the standard evaluation procedures were virtually useless. The actual behavior of such systems was described.

Introduction

Inverse gas chromatography IGC (so-called because the material under investigation is packed on the column and a known material, probe, is injected onto the column) is a powerful investigative tool. The IGC technique has been used to study many properties of polymeric materials.[1-3]

The shape and position of the chromatographic elution curve depends on the many processes that occur on the column: diffusion of the probe in the gas phase, diffusion of the probe in the stationary phase, the partitioning of the probe between phases, adsorption of the probe on the polymer surface and on the support surface, void volume of the column, etc. Thus the elution curve contains a wealth of information, and so a method to carefully characterize it is of great importance.

We are primarily interested in the diffusion of the probe in the polymer and gas phases. In approaching this problem it would of course be desireable to describe the chromatographic process by a set of differential equations, the solution of which would yield all the required information. Unfortunately, analytical solution of such equations is very difficult-to-impossible even for the simpler chromatographic models.

Traditionally, the analysis of the peak position and shape has been performed by using either of two approaches. 1. It is tacitly assumed that chromatographic peaks, despite always being asymmetric, may be treated as symmetric Gaussian peaks, the relevant quantities being evaluated from the position of the peak maximum and from the width of the peak.[4-11] 2. The basic parameters of the system are evaluated from the moments of the elution curve.[12-14] The latter method is theoretically very elegant but suffers from an unacceptably large unreliability in the experimental measurement of the moments.

In the following, we will briefly review the traditional methods of analysis. We will then simulate the chromatographic process by using a computer and will modify the formulae utilized by traditional analysis. Mathematically, our simulation represents a numerical solution of the differential equations.

Van Deemter and co-workers[15] were among the first to analyze the shape and position of elution curves and attempt to relate these to the various column parameters and operating conditions. They used the plate theory to express the distribution of the probe on the column employing the concept of the height equivalent to one theoretical plate (HETP), H. H is essentially a measure of the separating power of the column and is related to the length of the column, L, and the total number of theoretical plates, n, as $H \equiv L/n$.

The HETP concept is applicable for elution curves which are symmetric and Gaussian in shape which allows the mathematics of statistical distributions to be utilized. In this approach, the peak parameters of interest are T_m, the elution time of the curve maximum, and $w_{1/2}$, the width of the elution curve at half its height. H_p is related to the variance of the peak, σ, by

$$H_p = L\sigma^2/T_m^2 \quad (1)$$

The subscript p denotes that the parameter is obtained from the dimensions of the elution peak. For Gaussian curves

$$w_{1/2}^2 = 8\sigma^2 \ln 2 \quad (2)$$

$$H_p = L(w_{1/2}/T_m)^2/8 \ln 2 \quad (3)$$

In broad terms the van Deemter relation for H_p may be expressed as[15]

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