ELSEVIER

PII: S0032-3861(97)00204-8

Polymer Vol. 39 No. 5, pp. 1177–1185, 1998
© 1997 Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00+0.00

Structural characterization of five polyethylene films and the diffusion of N,N-dimethylaniline within them. Attempted correlations between probe dynamics and pertinent macroscopic and microscopic polymer properties

Oscar E. Zimerman[a], Changxing Cui[a], Xiaochun Wang[a], Teresa D. Z. Atvars[b] and Richard G. Weiss[a,*]
[a]*Department of Chemistry, Georgetown University, Washington, DC 20057, USA*
[b]*Instituto de Quimica, Universidade Estadual de Campinas, Caixa Postal 6154, CEP 13084-100, Campinas, SP, Brazil*
(Received 2 May 1996; revised 16 September 1996)

The density, degree of crystallinity, melting temperature, thickness, frequency and type of unsaturated groups accessible and inaccessible to bromine in chloroform, and the frequency of methyl groups have been determined for five polyethylene (PE) films. Attempts to correlate the diffusion coefficients in the PE or the PE/methanol partition constants for N,N-dimethylaniline (DMA) and one of the microscopic or macroscopic properties of the polymers were unsuccessful. The only roughly physically meaningful relationships found are between the diffusion coefficients and the sum of the frequency of methyl groups and double bonds accessible to bromine in chloroform or the amorphous and interfacial contents of the films, For the PE film of highest crystallinity, two diffusion coefficients were required to obtain a good fit to the data. © 1997 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: crystallinity; density; diffusion)

INTRODUCTION

There are literally hundreds of types of polyethylene, each differing in its crystallinity, thermal history, mechanical history, number and type of chain branches, and degree and type of unsaturation[1]. Others[2,3] as well as ourselves[4,5] have developed methods for measuring the rates of diffusion and the diffusion coefficients of guest molecules using a variety of techniques that take into account the size, shape and polarity of the guest, temperature, the physical state of the polymer sample, and related factors, However, the factors that control the diffusion of guest molecules in polyethylene have not been fully characterized, and their influence remains to be quantified.

A great deal is known about polyethylenes[1]. Most are a combination of crystalline and amorphous parts in which crystallites are arranged in spherulitic arrays[6]. The thickness of an individual crystal is 120–150 Å and polymer chains are folded upon themselves in a lamellar fashion within it[7,8]. 'Interfacial' regions comprising extended, parallel polymethylene segments lacking lateral interchain order may lie along lateral faces of the crystallites[9]. Guest molecules reside primarily in the non-crystalline parts of the polymer in sites localized in the amorphous and interfacial regions[10]. The degree of crystallinity is dependent upon the number and type of chain branches, molecular weight and sample history[11].

The most commonly reported glass transition temperature (T_g) of polyethylene is about $-30°C$[12]. The melting point of polyethylene (T_m) ranges from 105 to 130°C, depending on the degree of crystallinity, number and type of chain branches, etc[1]. Generally, the higher the degree of crystallinity, the higher the melting point, and the smaller the amount of free volume per (potential) guest site[13].

Here, we analyse five samples of polyethylene by diverse methods, compare the results (and methods of analysis in some cases) to develop a comprehensive picture of each sample, and attempt to correlate the structures with the diffusion characteristics of a guest molecule, N,N-dimethylaniline (DMA).

EXPERIMENTAL

Reagents and polyethylenes

All solvents were ACS grade or better and were used without further purification unless indicated otherwise. Xylene (EM Science reagent) was distilled and the fraction of BP > 130°C was collected. N,N-Dimethylaniline (Aldrich, 99%) was vacuum distilled and stored under nitrogen.

The polyethylene samples were obtained in film form. They are: BLDPE (blown type NA-203, $M_w = 510\,000$ and $M_w/M_n = 10.4$ according to the manufacturer) and NBLDPE (type NA-677) are additive-free from Poliolefinas, Brazil; BHDPE, type ES-300 from Polialden Petroquimica, Brazil; and NDLDPE and ODLDPE, two batches of Sclair from Dupont of Canada (M_w of ODLDPE

---

* To whom correspondence should be addressed

is 112 600 according to the manufacturer). Before being used, films were immersed in three batches of chloroform for 1 day each (to remove any additives) and then dried.

Elemental analyses were performed by Desert Analytics of Tucson, Arizona.

Instrumentation

Ultraviolet/vis absorption spectra were recorded on a Perkin-Elmer Lambda-6 spectrophotometer with air as reference. A MIDAC *FT*i.r. spectrophotometer was used to record *FT*i.r. spectra with air as reference. Time-dependent fluorescence intensifies during DMA diffusion were measured on a Spex Fluorolog 111 spectrofluorimeter with a 150 W high pressure Xe lamp.

Heats and temperatures of phase transitions were measured on a Dupont 2910 differential scanning calorimeter (d.s.c.) that was controlled by a TA Module 2000 and data analysis system[14a]. The instrument was calibrated with indium for temperature (157.4°C) and heat flow[14b] and with n-butyl stearate for temperatures (14.8 and 26.1°C[14]. Samples (4–6 mg) were sealed in two-piece aluminum pan assemblies. Heating and cooling rates were 10°C min^{-1}.

Film preparation for infrared spectroscopy and film thickness

Thick polyethylene films were prepared by placing many layers of thin polyethylene films between two pieces of clean glass, which were heated on a hot plate to *ca.* 140°C while being pressed under hand pressure.

A very thin, *ca.* 5 μm film was cast from a warm solution of 0.05 g of BLDPE in 20 mL xylene onto a flat glass surface. Thin BHDPE and NDLDPE films were stretched by hand at room temperature to attain films of *ca.* 5 μm thickness.

The thicknesses of films, l, were determined from their i.r. interference fringes using equation (1).

$$l = \frac{N}{2n}\frac{1}{\nu_2 - \nu_1} \qquad (1)$$

Here, n is the refractive index of polyethylene (taken as 1.52 throughout), and N is the number of interference fringes between ν_2 and ν_1 (cm^{-1})[15]. A micrometer was used to measure thicknesses > 0.1 mm. The thicknesses of the as-received films are listed in *Table 1*.

Bromination of polyethylene films[16]

Pieces of cleaned, as-received polyethylene film were placed in a solution of bromine (40 g, Fisher reagent) in chloroform (200 g, Fisher SpectrAR). After 2 h in the dark, the pieces were removed under dim red light, washed with small amounts of chloroform, bathed consecutively in four 100 mL aliquots of chloroform for 2 h each, air dried, and stored in opaque bottles.

Table 1 Thicknesses, densities, and melting points of as-received polyethylene films at room temperature after removal of antioxidants and plasticizers

Polymer	Thickness, l (μm)	Melting point (°C)	Density[a], σ_{PE} (g cm^{-3})
NBLDPE	54	112 113°	0.916
BLDPE	140	109	0.917
ODLDPE	83 (76[b])	116, 121[c]	0.917 (0.92)[b]
NDLDPE	70	116	0.918
BHDPE	20	129	0.945

[a] Average values from three measurements at room temperature.
[b] From manufacturer.
[c] Second heating cycle.

The bromination procedure for thick films, prepared as described above, was the same as for as-received films, but the reaction time was 2 days. After being leached of unreacted bromine, the thick films were dried under vacuum overnight at room temperature.

Fractionation of NDLDPE

A 0.1 g piece of NDLDPE film was placed on ashless filter paper that was suspended in a 100 mL round-bottomed flask, well above the level of the extracting liquid, *ca.* 25 mL of xylene. After 2 h of reflux (a 4 h extraction dissolved all of the film), the remaining *ca.* 30 mg of undissolved solid were dried under vacuum. The xylene was maintained at 60–70°C while a stream of nitrogen was passed over it until only a residue remained. Further treatment under vacuum at *ca.* 45°C produced *ca.* 60 mg of polyethylene.

Density measurements (Table 1)[17]

A piece of film was placed in a mixture of methanol and water (two non-swelling liquids) at room temperature. Less-dense methanol or more-dense water were added dropwise, as required, until the solid remained suspended. An aliquot of the final liquid mixture was transferred to a tared 10 mL volumetric flask and weighed. The density of the liquid is the density of the film. The measurements are very precise: addition of one drop of methanol or water to *ca.* 1 mL of their mixture was sufficient to cause a film to sink or rise.

Equilibrium constants for partitioning DMA between methanol and polyethylene films

A piece of weighed film was placed in 3.5 mL of a solution of DMA in nitrogen-saturated methanol for 24 h at room temperature in the dark; five different DMA concentrations, from 0.01 to 0.50 M, were employed. The film was removed and washed rapidly with methanol. DMA was extracted from the film by placing it in 3.5 mL of methanol for 24 h. The concentration of DMA in the methanol was determined from u.v. absorption spectroscopy.

For example, the DMA concentration (strictly speaking, the term 'concentration', implying a microscopically even distribution of solute in a medium, is not correct here. We use it to indicate the spatially averaged number of moles of guest molecules in a volume of film) present in BHDPE, $[\mathrm{DMA}]_{\mathrm{BHDPE}}$, for a 0.3 M initial concentration of DMA was determined as follows. The optical density of the extracted DMA in the methanol at 251 nm was 0.090. Applying Beer's law and using $\varepsilon_{251} = 11\,600\ \mathrm{cm^{-1}\,M^{-1}}$ for DMA[4], the concentration is 7.75×10^{-5} M. The volume of the film piece, $V_{\mathrm{BHDPE}} = 4.66 \times 10^{-3}\ \mathrm{cm^{-3}}$, was determined from its density and weight, and $[\mathrm{DMA}]_{\mathrm{BHDPE}}$ was finally obtained from the ratio of the number of moles of DMA in the methanol extract divided by V_{BHDPE}. The slope of a graph of the DMA concentration in the film after equilibration, $[\mathrm{DMA_p}]$, *versus* the initial concentration of DMA in the methanol doping solution $[\mathrm{DMA_m}]$, is K (*Table 2*); the extrapolated intercepts were zero within experimental error.

Diffusion of DMA from films by fluorescence intensities[5]

A *ca.* 2 × 0.5 cm strip of film was mounted on a glass yoke[4] and immersed overnight in a methanolic solution of 10^{-2} M DMA (allowing $\sim 10^{-3}$ M DMA to be imbibed).

Table 2 Diffusion constants (*D*) and partition coefficients (*K*) for DMA in polyethylene films at 25°C and the percentages of crystalline, amorphous, and interfacial regions of the films

PE	$10^9 D^a$ ($cm^2 s^{-1}$)	K (± 0.01)	K_A^b	Percentage crystalinity by d.s.c. X-ray	Θ	Amorphous[g] (%)	Interfacial[h] (%)
NBLDPE	5.51 ± 0.05	0.29	0.41	29	4	57	14
	6.02 ± 0.09				3		
BLDPE	8.68 ± 0.03	0.26	0.38	31, 59[f]	4	56	13
	9.23 ± 0.02				4		
ODLDPE	8.24 ± 0.02[c]	0.2[d]	0.31	35	4	56	9
				37[e]	4		
NDLDPE	7.21 ± 0.02	0.27	0.47	42	4	55	3
	6.81 ± 0.01				5		
BHDPE	1.68 ± 0.02 (81%)	0.21	0.72	71, 91[f]	6	37	(− 8)[i]
	0.092 ± 0.007 (19%)				3		
	1.98 ± 0.03 (86%)						
	0.083 ± 0.0012 (14%)						

[a] χ^2 values were $< 2.0 \times 10^{-4}$ in each run using equation (4) and $< 2.5 \times 10^{-4}$ using equation (5).

[b] $k/(V_{total} - V_{cryst})$, see text.

[c] Data reinterpreted from Ref. [18].

[d] Reference [4].

[e] Second heating cycle.

[f] From powder diffraction measurements[41].

[g] $100 - \Theta$.

[h] Θ − % crystalline; see text.

[i] See text.

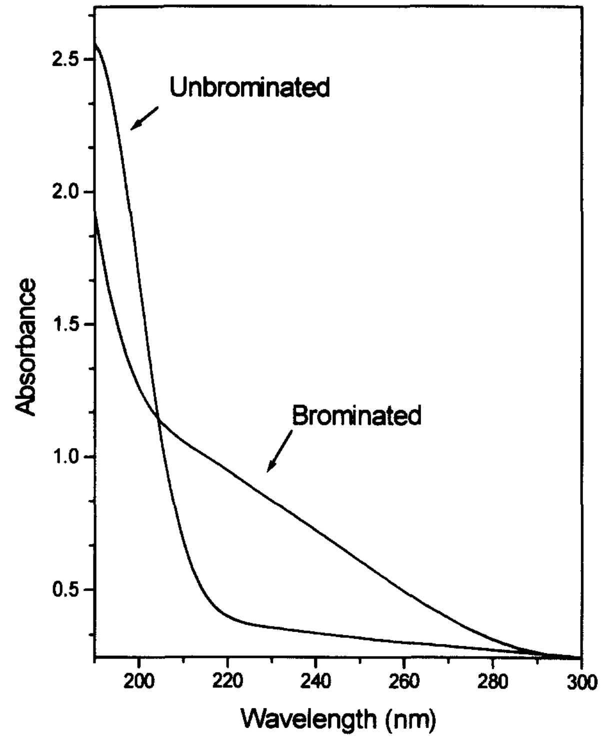

Figure 1 Ultraviolet absorption spectra of brominated and unbrominated BLDPE

Upon being removed from the bath, the film was washed quickly with a small quantity of methanol to remove any DMA on the surfaces and dried in the air for 1–2 min. The film, together with the yoke, were placed promptly in a quartz cuvette containing 3 mL of N_2-saturated 2 N hydrochloric acid which had been temperature equilibrated (25 ± 0.5°C) in the cell compartment of the spectrofluorimeter. The angle between the film surface and the incident radiation was *ca.* 45°. Fluorescence intensifies at 330 nm measured at 90° with respect to the incident radiation (λ_{ex} 300 nm) as a function of time. Duplicate runs were made in each case and the results are presented in *Table 2*.

The data sets were recovered as ASCII files and compared to theoretical curves using the origin software package (MicroCal Software, Inc.) and a non-linear least-squares regression to assess the goodness of the fits. When expressions with one diffusion coefficient (the only fitting variable) were unsatisfactory, a more complex expression with two diffusion coefficients and a weighting factor was employed (*vide infra*). The calculated fits were deemed acceptable when the deviation in χ^2 between successive iterations was 0.01.

RESULTS

Type and degree of unsaturation

Ultraviolet/vis absorption spectroscopy. The absorption maximum of an isolated C=C bond is near 185 nm[18], which is slightly below the lower detection limit of our spectrophotometer (190 nm). However, there is adequate absorbance at 190 nm to approximate the degree of unsaturation in regions accessible to bromine in chloroform.

On the basis of the lack of significant spectral differences between the UV/vis absorption spectra of brominated and unbrominated BHDPE films, we conclude that either the polymer has few C=C bonds or bromine did not access the regions where unsaturation exists. If C=C bonds are in the interior of crystalline regions of BHDPE, they will contribute to the absorbance near 190 nm. However, the absorption spectrum of unbrominated BHDPE shows a smooth increase in absorbance from 0.85 at 300 nm to 1.3 at 190 nm, indicative of few double bonds.

Ultraviolet absorption spectra of brominated and unbrominated BLDPE (*Figure 1*) and NDLDPE films are very different. For instance, there is essentially no absorption above 215 nm, when light scattering is considered, by the unbrominated film. The nearly uniform increase by 0.3 absorbance units starting from 300 nm can be attributed to light scattering by microcrystalites, The

Table 3 Elemental analyses of brominated films and estimated degrees of non-saturation from the brominated films

Polymer	Percentage C	Percentage H	Percentage Br	Total percentage	C=C/1000 CH_2^a
NBLDPE	85.12	14.45	0.37	99.94	0.33
BLDPE	84.03	14.84	0.43	99.30	0.38
NDLDPE	84.83	14.56	0.56	99.95	0.50
BHDPE					*ca.* 0[b]

[a] Approximate frequency of unsaturated bonds accessible to bromine in $CHCl_3$ assuming two bromine atoms per double bond and based upon the amount of carbon present (using elemental analyses).

[b] The u.v./vis absorption spectra before and after treatment with bromine were virtually the same.

Table 4 Concentrations (C_M) of C=C bonds AND CH_3 groups per 1000 CH_2 units in polyethylene estimated from infrared spectroscopy

Film	Vinyl-idene	Vinyl	*Trans*-vinylene	C_M^a	AC^b	CH_3
NBLDPE	0.65	0.03	0.0	0.68	0.35	21
BLDPE	0.29	0.12	0.02	0.43	0.05	41
ODLDPE	0.47	0.15	0.06	0.68	—[c]	5.7
NDLDPE	0.08	0.37	0.04	0.49	*ca.* 0	38
BHDPE	0.07	0.14	0.0	0.21	0.21	12

[a] The concentration of *cis*-vinylene is assumed to be negligible.

[b] C_M inaccessible to Br_2 in $CHCl_3$; see *Table 3*.

[c] Not determined.

increase is much larger (0.9) for BHDPE as a result of its greater crystallinity[16]. The absorbance increase in the spectrum of BLDPE is nearly linear (from 0.3 at 285 nm to 1.2 at 205 nm), due primarily to the presence of C–Br bonds[19]. Since some absorbance at 190 nm remains after bromination, a portion of the isolated C=C bonds is intact, Assuming that the residual absorbance at 190 nm is due exclusively to C=C bonds (i.e. there is no absorption by C–Br bonds at 190 nm), a *lower limit* to the concentration of brominated double bonds can be calculated from Beer's law: taking the C=C extinction coefficient at 190 nm to be the same as that *trans*-4-methylpent-2-ene (9900 cm^{-1} M^{-1} at 190 nm)[18], and since the thickness of the film is known to be about 140 μm, the concentration of the *accessible* C = C bonds in BLDPE is $\geq 0.7/(9900 \times 0.014) = 0.005$ M, or $\geq$ 8 C=C bonds per 100 000 CH_2 units (using the density measured). A similar analysis leads to $\geq$ 15 C=C bonds per 100 000 CH_2 units of NDLDPE.

Due to the imprecision of these numbers, we have greater confidence in elemental analyses as a measure of the frequency of double bonds accessible to bromine in chloroform (*Table 3*). In these calculations, the frequency of accessible double bonds is assumed to be the ratio between one-half the number of bromine atoms and the number of carbon atoms. Even here, we suspect the errors are rather large; the data are most useful in establishing trends.

Double bond and methyl group concentrations by FTi.r. spectroscopy[20]. *FTi.r.* spectra in the region of 850–1000 cm^{-1} of the polyethylene films of differing thicknesses are shown in *Figure 2*. Peaks at 888, 909 and 965 cm^{-1} are related to C–H bending vibrations of vinylidene (>C=CH_2), vinyl (–CH=CH_2), and vinylene (–CH=CH–) groups, respectively[16]. The BHDPE film contains small concentrations of vinylidene and vinyl groups; the BLDPE, NBLDPE and ODLDPE films have mainly vinylidene groups; and the NDLDPE film contains mostly vinyl groups.

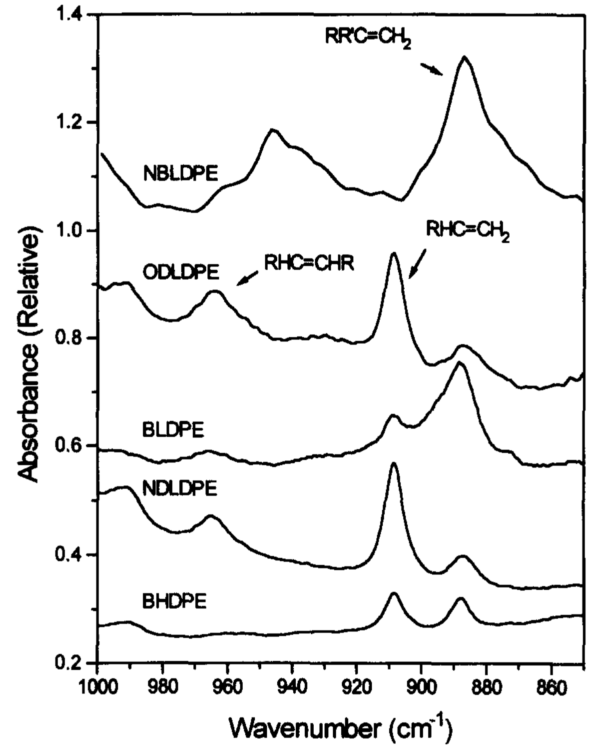

Figure 2 *FTi.r.* spectra of polyethylene films in the region of 850–1000 cm^{-1}. Film thicknesses were 0.83 (ODLDPE), 0.64 (NDLDPE), 0.79 (BLDPE), 0.43 (NBLDPE) AND 0.71 mm (BHDPE)

Concentrations of these double bonds (*Table 4*) have been estimated from *Figure 2* and knowledge of the film thickness, density and the group absorptivities of the various forms of unsaturation (see Appendix A[20])[21]. They represent double bonds in all regions of a film (i.e. those accessible and inaccessible to bromine in chloroform). The *total* and *accessible* concentrations follow the same trend: BHDPE, BLDPE, NDLDPE, ODLDPE and NBLDPE are calculated to have a *total* of about 20, 40, 50, 70 and 70 C=C bonds per 10 000 CH_2 units, respectively.

FTi.r. spectra of four 'thick' brominated polyethylene films are shown in *Figure 3*. Most of the double bonds have

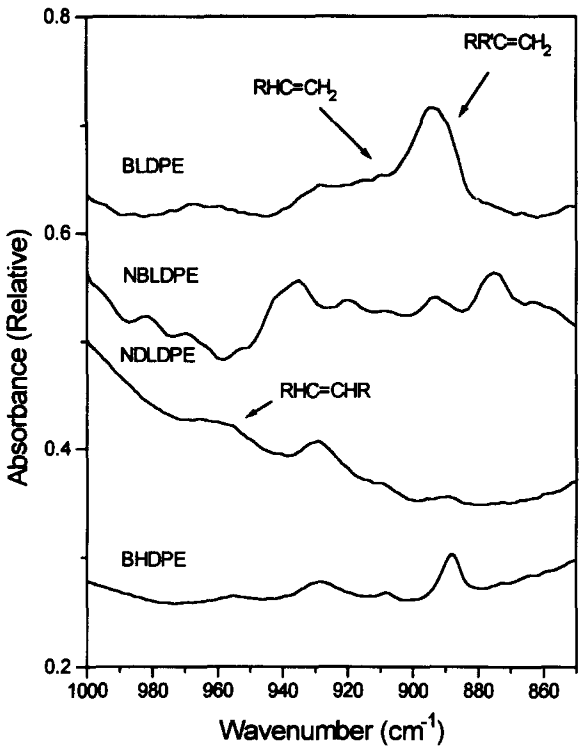

Figure 3 *FT*i.r. spectra of brominated polyethylene films in the region of 850–1000 cm^{-1}. See *Figure 2* for comparisons

been brominated. However, the vinylidene groups of BHDPE and BLDPE appear most intact; no double bonds can be detected in the spectrum of the brominated NDLDPE and NBLDPE films. Since chloroform can swell only the non-crystalline regions of polyethylene[22], the vinylidene groups may be located primarily in the crystalline regions of BHDPE and BLDPE. However, the vast majority of vinylidene groups of NDLDPE must be in the non-crystalline part. Not coincidentally, NDLDPE is mostly amorphous.

Peaks at 1352 and 1368 cm^{-1} and at 1378 cm^{-1} are related to asymmetrical deformations and wagging vibrations of –CH_2– and CH_3–groups in somewhat disordered environments[23], respectively. The concentration of methyl groups can be estimated quantitatively from the spectral intensities if correction is made for the partial overlap by the peak at 1378 cm^{-1} of those at 1368 and 1352 cm^{-1}.

We have employed an approach that is an adaptation of a method stretched the methyl for analysing guest molecular orientations in stretched polyethylene films[22]. The deformational vibration of the methyl groups at 1378 cm^{-1} is not correlated with the vibration of the methylene groups. For that reason, i.r. spectra from two polyethylene samples containing different amounts of methyl groups (*Figure 4*a) provide the information needed to extract the 'pure' vibrational spectra of the methyl and methylene groups. Thus, multiplying the spectral intensity of BLDPE by a series of constants and subtracting the resultant spectra from that of BHDPE until the spectral feature at 1378 cm^{-1} is at zero yields the spectrum of the methylene portion (*Figure 4*c). Similarly, the methyl portion of the spectrum can be separated (*Figure 4*b). The absorbance of the methyl group for any polyethylene can then be estimated by multiplying the 'methylene spectrum' by a series of constants and subtracting the resultant spectra from the measured spectrum until the features at 1368 and 1352 cm^{-1} disappear. The net absorbances and calculated numbers of methyl groups per 1000 methylene groups for the four polyethylenes analysed in this way are listed in *Table 4*. According to Woodbrey and Ehrlich[21], the methyl absorptivity, 1.27 cm^2 g^{-1} (as 1000 CH_2 groups per CH_3 group), overestimates the methyl content by 15%; no correction has been made.

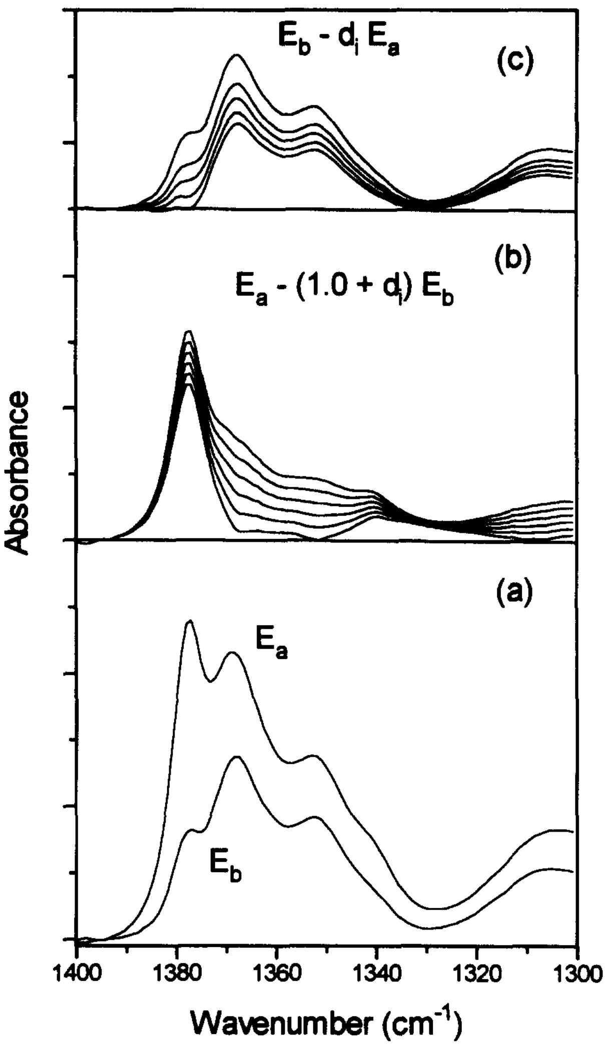

Figure 4 (a) *FT*i.r. spectra of NDLDPE (E_A) and BHDPE (E_B) films. (b) Subtraction of the spectrum of the symmetric methyl deformation. Note that peaks at 1368 and 1352 cm^{-1} can be made to nearly disappear. d_i = 0.0, 0.1, 0.2, 0.25, 0.34 from top to bottom. (c) Subtraction of the spectrum of the methylene wagging. Note that the peak at 1378 cm^{-1} can be made to nearly vanish. d_i = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 (from top to bottom); the last d_i values are the optimal ones

Degrees of crystallinity

Heats of melting and melting points were determined from d.s.c. thermograms, and the percentages of crystallinities (*Table 3*) were calculated using equation (2) (in which ΔH is the heat of melting of 1 mg of polyethylene and ΔH^*, 286 J, is the heat of melting of 1 mg of a single crystal of polyethylene)[14a]. The glass transitions in ODLDPE and NDLDPE occur, as expected[12], near −30°C. The appearance of the thermograms from first and second heating cycles of ODLDPE (*Figure 5*) and NDLDPE change dramatically. The broad endotherm centred at 116°C (first heating) separates into a broader one at ~110°C and a narrower one at 121°C (second heating). This is a clear indication that these polyethylenes are mixtures whose components separate somewhat upon melting[24]. D.s.c.

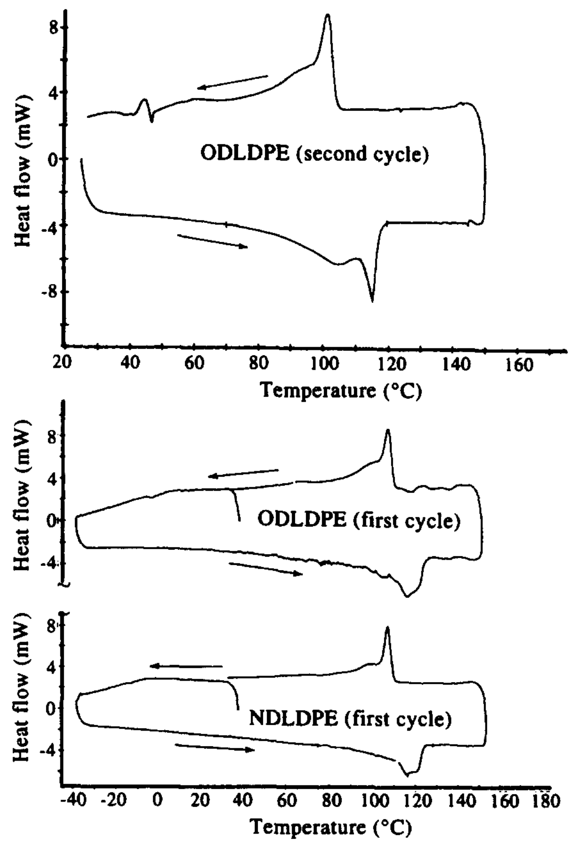

Figure 5 D.s.c. thermograms of ODLDPE (first and second heating/cooling cycles) and NDLDPE (first cycle) films. Heating and cooling rates are 10°C min^{-1}

thermograms of NDLDPE, and its fractions dissolved and undissolved in xylene are shown in *Figure 6*. The second heating thermograms of the other PE films display shifts of T_m to slightly higher temperatures, but do not split into two endotherms.

$$\% \text{ Crystallinity} = 100\Delta H/\Delta H^* \quad (2)$$

In principle, the per cent of interfacial volume can be calculated as the difference between Θ, the sum percentage of the crystalline and interfacial parts (measured from the density, σ_{PE}), and the degree of crystallinity (from d.s.c. methods) since the tightly packed chains of the interfacial region do not contribute to the heat of melting[25]. Taking the densities of completely amorphous and crystalline PE to be 0.852 and 1.00 g cm^{-3}, respectively[26], the Θ values can be calculated from equation (3) by assuming that the densities of the interfacial and crystalline regions are equal. They and the interfacial contents are listed in *Table 2*. Since the actual interfacial density must be somewhat less than 1 g cm^{-3}, but $\gg$ 0.852 g cm^{-3}, the values of Θ from equation (3) *underestimate* the interfacial component (obtained as the difference between Θ and the d.s.c.-derived crystalline component. This intrinsic error and the imprecision of the data treatment, especially in calculating the areas of melting endotherms that lead to ΔH values, is highlighted in the calculations involving BHDPE (where a negative interfacial volume is predicted).

$$\Theta = 100(\rho_{PE} - 0.852)/(1.00 - 0.852) \quad (3)$$

DMA diffusion coefficients in polyethvlene films[4,5]

Excitation of DMA molecules located in a polyethylene film leads to their characteristic fluorescence[4]. Intensities of the fluorescence at low absorbances are directly proportional to the concentration of DMA. In our experiment, DMA molecules diffuse with time from a film into a very large volume (with respect to the volume of the film) of 2 N hydrochloric acid. Once in the aqueous phase, the DMA molecules no longer absorb radiation used for excitation of DMA in the film due to protonation by the strong acid. As a result, their presence does not interfere with measurements of the remaining DMA in the films, and back-diffusion from the aqueous phase into a film is negligible.

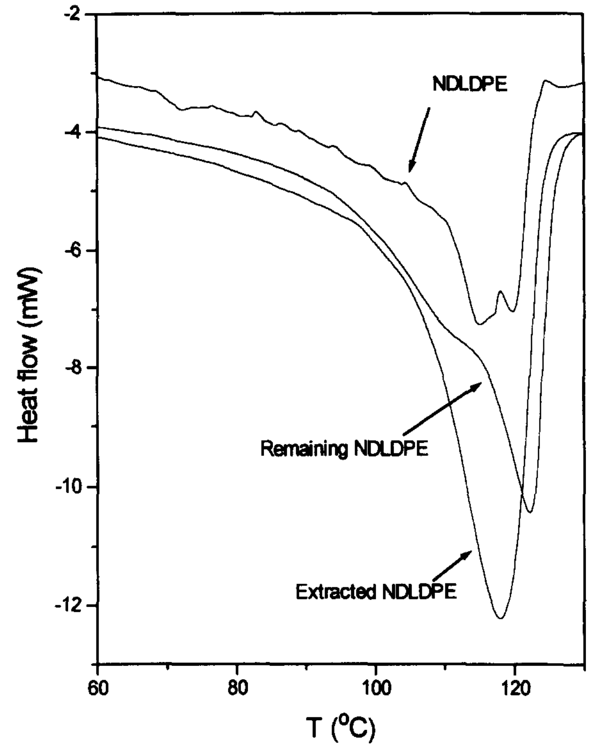

Figure 6 D.s.c. heating thermograms (10°C min^{-1}) of an NDLDPE film (4.5 mg), the xylene soluble portion (6.8 mg), and the insoluble portion (5.3 mg)

The fluorescence data for all the films except BHDPE are treated according to an integrated form of Fick's second law [equation (4)][27] in which the infinite series is truncated after the first 16 terms. Previously, we have shown that no more than four terms are necessary to obtain good fits to data sets[28], and inclusion of up to 50 terms does not improve the fits perceptibly. The ratio C_t/C_0 can be expressed in terms of fluorescence intensifies: $(I_t - I_\infty)/(I_0 - I_\infty) = C_t/C_0$, where I_0, I_t and I_∞ are the intensities at 0, t, and ∞ time. C_t is the concentration of DMA remaining in the film at time = t, C_0 is the concentration at zero time, l is the film thickness, and D is the diffusion coefficient[29].

$$\frac{I_t - I_\infty}{I_0 - I_\infty} = \frac{8}{\pi^2}\sum_{n=0}^{15}\frac{1}{(2n+1)^2}\,e^{\frac{-D(2n+1)^2\pi^2 t}{l^2}} \quad (4)$$

I_∞ is taken to be when the fluorescence intensity decreases by less than 1% of its intermediate values during a 30 min period. At early times (0–60 s), our system does not obey equation (4), probably due to inhomogeneities in the surface, dynamics of film 'wetting', data not being collected during the first few seconds after a film is placed in the aqueous acid, temperature equilibration, and other factors related to our intrumentation. Thus I_0 has been taken from the extrapolated intercept of the linear portion of a plot of fluorescence intensity *versus* $t^{1/2}$ [30]. At long times, slight

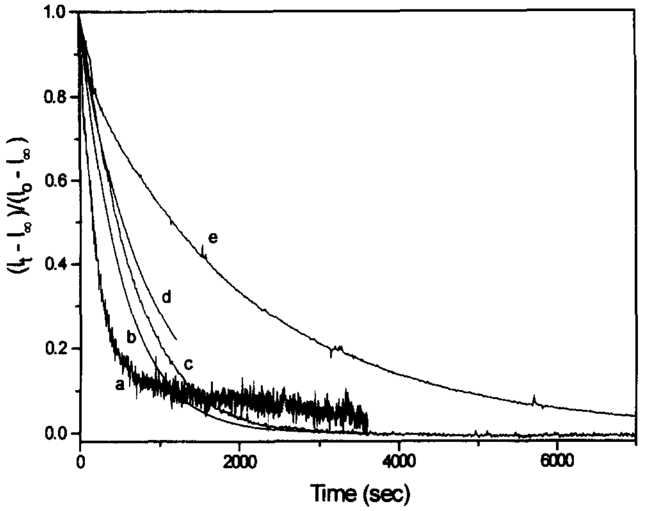

Figure 7 $(I_t - I_\infty)/(I_0 - I_\infty)$ *versus* time (*T*) for DMA fluorescence in (a) BHDPE, (b) NBLDPE, (c) NDLDPE, (d) ODLDPE[21] and (e) BLDPE at 25°C

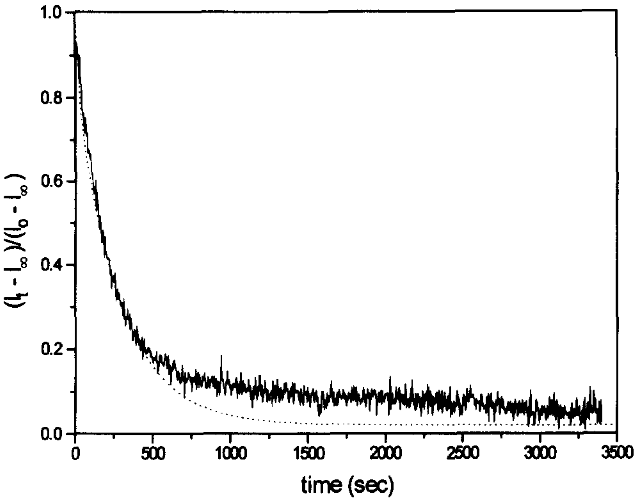

Figure 8 $(I_T - I_\infty)/(I_0 - I_\infty)$ *versus* time for DMA fluorescence in BHDPE (solid line) and the curve of best fit (dashed line) using the first 50 terms of equation (4). The *D*-value for the dashed line is 1.0×10^{-9} cm^2 s^{-1}

instabilities in the excitation lamp or photomultiplier tube of the fluorimeter can lead to large errors in $(I_t - I_\infty)/(I_0 - I_\infty)$, since the differences between the terms in the numerator become very small. An example of such an occurrence is shown in curve (e) of *Figure 7*. As a result, exact curve-fitting is least important at long times.

Figure 7 shows the changes in DMA fluoresdene intensity with time for diffusion in the polyethylene films. The data for ODLDPE have been taken from previous work[28]. The best values of *D*, found by a non-linear least-squares fit method based upon the minimization of the difference between a data set in *Figure 7* and synthesized curves using equation (4) or equation (5) are presented in *Table 2*.

For BHDPE, the experimental curves could not be fitted satisfactorily even when 50 terms were included in truncated equation (4) (i.e. when only one diffusion coefficient was considered operative; see *Figure 8*). The χ^2 values were extremely high. However, it was possible to obtain excellent fits to curve (a) of *Figure 7* using equation (5) in which D_1, D_2 and f_{D_1} were allowed to vary simultaneously. The physical model upon which equation (5) is based assumes that two *independent* (families of) sites are occupied by DMA molecules in BHDPE and that the rates of diffusion from them are measurably different.

$$\frac{I_t - I_\infty}{I_0 - I_\infty} = \frac{8}{\pi^2}\left\{ f_{D_1} \sum_{n=0}^{15} \frac{1}{(2n+1)^2} e^{\frac{-D(2n+1)^2\pi^2 t}{l^2}} \right.$$
$$\left. + (1 - f_{D_1}) \sum_{n=0}^{15} \frac{1}{(2n+1)^2} e^{\frac{-D(2n+1)^2\pi^2 t}{l^2}} \right\} \quad (5)$$

DISCUSSION

Detailed analyses of the factors influencing diffusion of molecules like DMA in polyethylene film have been presented elsewhere[4,5,28,31-33]. Essentially, the free volume of occupied sites and the ability of polymethylene chains to create temporal free volume along the routes to and from such sites determine the values of *K* and *D*[34]. Interestingly, we detect two distinct values of *D* for DMA diffusion in BHDPE. The other films require only one diffusion coefficient to obtain good fits to equation (4). In spite of this, we suspect that they, too, force DMA molecules to diffuse according to more than one process, but that we are unable to distinguish them kinetically. In previous work[35] we have obtained additional evidence for more than one dynamic process in NDLDPE when a much larger molecule, N,N-dioctadecylaniline, is employed. For the purposes of analyses here, we will focus on the faster diffusional component since a larger fraction of DMA molecules follows it.

Although considered inaccessible to guest molecules[22], some crystalline regions of polyethylene may have been accessed when bromine was introduced into films via the swelling solvent, chloroform. However, DMA should be restricted to non-crystalline regions of a film (that is, the interfacial and amorphous domains)[10]. In essence, this limits the fraction of the volume for possible diffusion to $V_{\text{total}} - V_{\text{cryst}}$ (where $V_{\text{cryst}}/V_{\text{total}}$, the crystalline volume fraction, is about the same as the fraction of crystallinity), and means that the dopant concentrations in the *non-crystalline regions* are really $V_{\text{total}}/(V_{\text{total}} - V_{\text{cryst}})$ multiplied by the macroscopically measured values. Using the percentages of crystallinity from d.s.c. experiments (*Table 2*), the available volume fraction for movement of DMA molecules within BHDPE is only about one-half that with the LDPE samples. Since the DMA molecules are not homogeneously distributed even within the non-crystalline regions[10], 'concentration' does not have the same meaning within the films as it does in normal solutions, even when the volume correction for crystallinity is made.

In spite of these limitations, it is interesting to note that virtually none of the double bonds in BHDPE were accessible to bromine in chloroform, but a large fraction was accessible in the low density samples. Our experiments indicate that the sterically disruptive unsaturated groups lie within the crystalline part of BHDPE.

The number of methyl groups per 1000 methylene groups can be calculated from the frequency of chain branches only if they are of equal length in each polyethylene type and that length is known; our analyses do not provide that information, but there is no reason to believe that they are of equal length, However, the fact that ODLDPE has fewer methyl groups than BHDPE (in spite of the former being of much higher density than the latter) suggests that, on average, the branches of BHDPE are much shorter than those of the LDPE. This hypothesis should be scrutinized by nuclear magnetic resonance analyses[36]. Regardless, it is reasonable to assume that the vast majority of chain branches reside in the amorphous regions[1].

D.s.c. analyses provide strong evidence that NDLDPE and ODLDPE are blends of two components. Partial dissolution of a sample in toluene yields two distinct fractions. If one is much more branched than the other (or is of very different average molecular weight), the fraction of each in the amorphous and crystalline regions may differ. The fact that the second heating thermogram of these LDPE includes two clear endotherms while the first heating thermogram has only one and a shoulder indicates that the as-received films have been processed to force microscopic mixing of the components.

The characteristics of the five films, taken in their totality, are difficult to correlate with the diffusional data. The partitioning constants indicate that the capacity of polyethylene to imbibe DMA is related roughly to the degree of branching (i.e. the number of methyl groups per 1000 methylene groups). Multiplying each K by $V_{\mathrm{total}}/(V_{\mathrm{total}} - V_{\mathrm{cryst}})$ gives K_a, the partitioning constants assuming that the accessible volume is limited to the amorphous and interfacial parts (*Table 2*). They suggest that the non-crystalline regions of BHDPE are actually more receptive to DMA molecules than any of the LDPE samples. The minor differences in crystallinity cannot explain why K_a of ODLDPE is so much smaller than that of NDLDPE. The numbers of neither the methyl nor double bond groups scale with K_a, either.

There is no correlation between D and K (or K_a) values. However, the D values correlate roughly with the sum of the frequency of the methyl groups and double bonds accessible to bromine in chloroform (i.e. the 'disturbing' groups in the non-crystalline part) or the *fraction of the amorphous and the interfacial parts.* The latter suggests, reasonably, that the vast majority of DMA reside and move within the least-ordered regions of the polymer. Structural details, except possibly those that pertain to the abundance of interfacial and amorphous guest sites, appear to have little influence on the movement of the DMA molecules.

A somewhat similar conclusion was reached many years ago by Eby who analysed the diffusion of ethane in one polyethylene that was quenched according to protocols that provided different crystallinities and lamellar sizes and anisotropies[37]. The results indicate that diffusion occurs near crystalline (lamellar) boundaries (i.e. interfacial regions). It is possible that the orientations and dimensions of microcrystallites in the five polyethylene films employed here also differ sufficiently to cause perceptible differences in D and K (or K_a). Our curious observation, that the smoothest (albeit non-linear) correlation is between D and the film thickness, may be related to the fact that microcrystallites near a film surface are most susceptible to orientation[37].

By contrast, investigations of the *reactions*[38] of guest molecules and the dynamics associated with them [39,40] in polyethylene films demonstrate unambiguously that local environment can be very important. It appears that the time scales of the processes under investigation determine whether microstructure, mesostructure or macrostructure is most important[41]. 'Slow' processes, like diffusion, are based upon an average environment of many stochastic events. Fast processes depend upon the nature of individual guest sites: a molecule responds to the one site in which it finds itself at the moment of transformation; each event is counted separately. Clearly, this work raises more questions than it answers.

For instance, is the origin of the dual diffusion coefficients in BHDPE related to DMA molecules being in amorphous and interfacial sites or interior and (near) surface sites? Do unsaturated groups 'create' guest sites, or do they discourage the approach of guest molecules like DMA? In spite of the limited information at hand, it is evident that the movement of guest molecules in polyethylene is a very complicated process that cannot be modelled by extrapolating from microscopic to macroscopic properties[40].

ACKNOWLEDGEMENTS

We are grateful to the National Science Foundation (grant CHE-9422560) and the Petroleum Research Fund administered by the American Chemical Society for their support of this work. We also thank Professor R. K. Eby and the referees for very useful comments.

APPENDIX A: CALCULATION OF THE FREQUENCY OF DOUBLE BONDS IN PE FILMS FROM INFRARED SPECTRA

The molar concentration of group X, $C_X = C_M\rho/FW_{\mathrm{CH_2}}$, and Beer's law lead to equation (A1)[15]. Polyethylene consists overwhelmingly of chains of methylene groups, $-(\mathrm{CH_2})_X-$, and has a density of ρ (g cm^{-3}). Thus, the number of 'moles' of $\mathrm{CH_2}$ units per cm^3 is $\rho/FW_{\mathrm{CH_2}}$, where $FW_{\mathrm{CH_2}}$ is 14, the sum of the atomic weights of a methylene group, and the number of X groups per $\mathrm{CH_2}$ unit is $C_X FW_{\mathrm{CH_2}}/(1000\rho)$ or, alternatively, the number of X groups per 1000 $\mathrm{CH_2}$ units (C_M) is $C_M = C_X FW_{\mathrm{CH_2}}/\rho$. A is the absorbance so that l is the film thickness in cm and K′ is in cm^2 g^{-1} (1000 $\mathrm{CH_2}$ for each group X). Calculated C=C bond concentrations of the films are listed in *Table 4*.

$$A = l\epsilon C_X = l\epsilon\rho C_M/FW_{\mathrm{CH_2}} = K'l\rho C_M \qquad \text{(A1)}$$

REFERENCES

1. (a) Brydson, J. A., *Plastic Materials.* Van Nostrand, London, 1966; (b) Crompton, T. R., *The Analysis of Plastics.* Pergamon, Oxford, 1984; (c) Quirk, R. P. and Alsamarraie, M. A. A., in *Polymer Handbook*, ed. Brandrup, J. and Immergut, E.H. Wiley, New York, 1989, p. V/15; (d) Axelson, D.E., Levy, G.C. and Mandelkern, L., *Macromolecules*, 1979, **12**, 41; (e) Glenz, W. and Peterlin, A. J., *Macromol. Sci. Phys.*, 1970, **B4**, 473; (f) Renfrew, A. and Morgan, P., *Polyethylene: The Technology and Uses of Polyethylene Polymers.* Wiley-Interscience, New York, 1957; (g) Hadley, D. W. in *Structure and Properties of Oriented Polymers*, ed. I. M. Ward. Wiley, Great Yarmouth, 1975, Chapter 9.
2. (a) Howell, B. F. McCrackin, F. L. and Wang F. W., *Polymer*, 1985, **26**, 433; (b) Wang, F. W. and Howell, B. F., *Polymer*, 1984, **25**, 1626.
3. (a) Goosey, M. T., in *Polymer Permeability*, ed. J. Comyn. Elsevier, London, 1965, p 309; (b) Saleem, M., Asfour, A. and Dekee, D. J., *Appl. Polym. Sci.*, 1989, **37**, 617; (c) Malik, J., Hrivik, A. and Tomova, E., *Polym. Degrad. Stab.*, 1992, **35, 61**; (d) Stilbs, P., *Prog. NMR Spectrosc.*, 1987, **19**, 1; (e) Jackson, R. A., Oldland, S. R. D. and Pajaczkowski, A. J., *Appl. Polym. Sci.*, 1986, **125**, 1297; (f) Johnson, M. and Westlake, J. F. J., *Appl. Polym. Sci.*, 1975, **19**, 1745; (g) Chang, S. S., Pummer, W. J. and Maurey, J. R., *Polymer*, 1983, **24**, 1267; (h) Braun, J. M., Poos, S. and Guillet, J. E. J., *Polym. Sci., Polym. Lett.*, 1976, **14**, 257.
4. (a) Naciri, J. and Weiss, R. G., *Macromolecules*, 1989, **22**, 3938; (b) Naciri, J., He, Z., Costantino, R. M., Lu, L., Hammond, G. S. and Weiss, R. G., in *Multidimensional Spectroscopy of Polymers*, ed.

M. W. Urban, and T. Provder. American Chemical Society, Washington, DC, 1995, Chapter 25.

5. He, Z., Hammond, G. S. and Weiss, R. G., *Macromolecules*, 1992, **25**, 501.
6. Geil, P. H. *Polymer Single Crystals*. Wiley, New York, 1963.
7. Hosemann, R., *Polymer*, 1962, **3**, 349.
8. Hosemann, R., *Colloid Polym. Sci.*, 1982, **260**, 864.
9. Strobl, G. R. and Haaerdon, W. J., *Polym. Sci. Polym. Phys. Ed.*, 1978, **163**, 1181.
10. (a) Phillips, P. J., *Chem. Rev.*, 1990, **90**, 425; (b) Jang, Y. T., Phillips, P. J. and Thulstrup, E. W., *Chem. Phys. Lett.*, 1982, **93**, 66; (c) Meirovitch, E. J., *Phys. Chem.*, 1984, **88**, 2629; (d) Radziszewski, J. G. and Michl, J. J., *Phys. Chem.*, 1981, **85**, 2934.
11. Wignall, G. D., Londomo, J. D., Lin, J. S., Alamo, R. G. and Mandelkem, L., *Macromolecules*, 1995, **28**, 3156.
12. Davis, G. T. and Eby, R. K. J., *Appl. Phys.*, 1973, **44**, 4274.
13. Sema, C., Abbe, J. Ch. and Dupatre, G., *Phys. Stat. Solids A*, 1989, **115**, 389.
14. (a) Gray, A. P., *Thermochim. Acta*, 1970, **1**, 563; (b) *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast, 59th ed. CRC, Boca Raton, FL, 1979, p. B272; (c) Krishnamurti, D., Krishnamurthy, K. S. and Shashidar, R., *Mol. Cryst. Liq. Cryst.*, 1969, **83**, 339.
15. Harris, D. C., *Quantitative Chemical Analysis*. W. H. Freeman, New York, 1991, p. 354.
16. Rueda, D. R., Balta Calleja, F. J. and Hidalgo, A., *Spectrochim. Acta*, 1974, **30A**, 1545.
17. Stout, G. H. and Jensen, L. H., *Structure Determination*. Macmillan, New York, 1968, p. 12.
18. *DMS UV Atlas Vol. 1*, 1/A11. Plenum, New York, 1968.
19. Porret, D. and Goodeve, C. F., *Proc. Roy. Soc. (London)*, 1938, **A165**, 31.
20. de Kock, R. J. and Hol, P. A. H. M., *Polym. Lett.*, 1964, **233**, 339.
21. Woodbrey, J. C. and Ehrlich, P. J., *Am. Chem. Soc.*, 1963, **85**, 1580.
22. (a) Michl, J. and Thulstrup, E. W., *Spectroscopy of Polarized Light*. VCH, New York, 1986; (b) Nishijima, Y., Onocri, Y. and Asai, T., *J. Polym. Sci., Part C*, 1966, **15**, 237.
23. (a) Zerbi, G., Magni, R., Gussoni, M., Holland Moritz K., Bigotto, A. B. and Dirlikov, S. J., *Chem. Phys.*, 1981, **75**, 3175; (b) Del Zoppo, M. and Zerbi, G., *Polymer*, 1990, **31**, 657; (c) Agosti, E., Zerbi, G., Ward, I. M., *Polymer*, 1992, **33**, 4219.
24. (a) Keller, D. R. and Keller, A. J., *Mater. Sci.*, 1984, **19**, 447; (b) Hill, M. J., Barham, P. J. and Keller, A., *Polymer*, 1992, **33**, 2530.
25. Mandelkem, L., *Acc. Chem. Res.*, 1990, **23**, 380.
26. Elias, H. G. *Macromolecules*, Vol. 1, Plenum, New York, 1977, pp.163–164.
27. Crank, J., *The Mathematics of Diffusion*. Oxford University Press, London, 1956, p. 45.
28. Lu, L. and Weiss, R. G., *Macromolecules*, 1994, **27**, 219.
29. Guillet, J. E., in *Photophysical and Photochemical Tools in Polymer Science*, ed. M. A. Winnik and D. Reidel. Dordrecht, The Netherlands, 1985, p. 467.
30. Comyn, J., in *Polymer Permeability*, ed. J. Comyn. Elsevier, London, 1985, Chapter 1.
31. Jenkins, R. M., Hammond, G. S. and Weiss, R. G. J., *Phys. Chem.*, 1992, **96**, 496.
32. He, Z., Hammond, G. S. and Weiss, R. G., *Macromolecules*, 1992, **25**, 1568.
33. Cui, C., Naciri, J., He, Z., Jenkins, R. M., Lu, L., Ramesh, V., Hammond, G. S. and Weiss, R. G., *Quim. Nova*, 1993, **16**, 578.
34. Vrentas, J. S. and Duda, J. L. J., *Polym. Sci. Polym. Phys. Ed.*, 1977, **15**, 403.
35. Taraszka, J. and Weiss, R. G., *Macromolecules*, 1997, **30**, 2467.
36. (a) Vander Hart D. L., *Macromolecules*, 1979, **12**, 1232; (b) Hentschel, D., Sillescu, H. and Spiess, H. W., *Macromolecules*, 1981, **14**, 1605.
37. Eby, R. K. J., *Appl. Phys.*, 1964, **35**, 2720.
38. (a) Cui, C. and Weiss, R. G. J., *Am. Chem. Soc.*, 1993, **115**, 9820; (b) Ramesh, V. and Weiss, R. G., *Macromolecules*, 1986, **19**, 1486; (c) Yogev, A., Riboid, J., Marero, J. and Mazur, Y., *Am. Chem. Soc.*, 1969, **915**, 4559; (d) De Paoli, M. -A., *J. Macromol. Sci.-Chem*, 1981, **A163**, 251; (e) Hooker, R. H. and Rest, A. J., *Appl. Organometall. Chem*, 1990, **4**, 141; (f) Mordzinske, A., *Chem. Phys. Lett.*, 1988, **150**, 254; (g) Szadkowska-Nicze, M., Mayer, J. and Kroh, J., *J. Photochem. Photobiol. A.: Chem.*, 1990, **54**, 389; (h) Li, S. K. L. and Guillet, J. E. *Polym. Photochem.*, 1984, **4**, 21; (i) Uznanski, P. and Kryszewski, M. *Polym. Bull.*, 1991, **26**, 437.
39. (a) Klein, J., *Nature (London)*, 1978, **271**, 143; (b) Matsuoka, S., *Relaxation Phenoniena in Polymers*. Hanser, Munich, 1992; (c) Ohta, Y. and Yasuda, H. J., *Polym. Sci., Part B, Polym. Phys.*, 1994, **32**, 2241.
40. (a) Atvars, T. D. Z., Sabadini, E. and Martins-Franchetti, S. M., *Eur. Polym. J.*, 1993, **29**, 1259; (b) Talhavini, M., Atvars, T. D. Z., Cui, C. and Weiss, R. G., *Polymer*, 1996, **37**, 4365.
41. Weiss, R. G., Ramamurthy, V. and Hammond, G. S., *Acc. Chem. Res.*, 1993, **265**, 53026.