Heterogeneous reactions of polymers: 3. Conformational analysis of heterogeneously chlorinated polyethylenes

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Conformational features of chlorinated polyethylenes prepared by chlorination under heterogeneous conditions are deduced from their i.r. spectra in the 600–700 cm^{-1} region. The concentration of vicinal chlorides in materials obtained this way is estimated by ^{1}H–n.m.r. The effect of the reaction kinetics on the concentration of vicinal chlorides is discussed. It is shown that while conformational transitions do take place during heterogeneous chlorinations at room temperature of the low density polyethylenes, they do not occur during chlorinations of the highly crystalline high density polyethylene films. In such materials the distribution of conformers is determined by the initial conformation of the polymeric precursors and it deviates strongly from the thermodynamic equilibrium. Freezing of the thermodynamically unfavourable conformations in such materials is attributed to the low mobility of the chlorinated chains restricted by the adjacent crystalline regions. Thermal treatment of the products, above the melting temperature of the crystallites, leads to a thermodynamic distribution of the conformers. However, when such treatment is conducted under isometric conditions in a press, the conformational transitions remain severely restricted.

INTRODUCTION

I.r. spectroscopy provides a powerful tool for the study of the orientation and of the conformation of polymers[1–3]. The assignment of the CH_2 wagging and rocking modes corresponding to various conformational sequences of polyethylene is well established[4–6] and these conformationally sensitive bands were found to be very useful for its analysis[4]. For example, the effect of the local conformations of the methylenic chains on their chemical reactivity could be checked by following changes in the intensity of the conformation sensitive i.r. bands which occur during the heterogeneously conducted modifications of polyethylenes[7]. The stretching mode of the C–Cl bond was also found to be very sensitive to the conformation of the polymeric segments in its vicinity[8,9]. Thus, the frequencies of the i.r. absorption bands due to C–Cl stretching modes of poly(vinylchlorides), of the solution chlorinated poly(isobutylenes) and polyethylenes and of the chlorinated single crystals of polyethylene could be used for the determination of the conformational features of these polymeric systems[10–15].

The heterogeneous chlorination of the low and of the high density polyethylenes was investigated recently in this laboratory[16]. It was found that, under the prevailing experimental conditions, only the amorphous regions of the polymer were susceptible to chemical attack. The crystalline phase remained chemically unchanged, though the perfection of the crystallites was affected by the extensive chlorination of the adjacent amorphous regions.

Conformational features of the chlorinated products obtained under such heterogeneous conditions are discussed in this paper.

EXPERIMENTAL

High density polyethylene (HDPE) films used in the chlorination experiments were prepared from HiZex 7000F, $d = 0.955$ g cm^{-3}, MFI $= 0.04$, $\alpha^c = 60\%$, Mitsui (Japan). The 9 μm thick film A was prepared by compression moulding at 200°C and 2000 psi; the 9 μm thick film B was prepared by blow extrusion at a blow ratio of 10.1; the 24 μm thick film C was prepared by blow extrusion at a blow ratio of 4.2. The low density polyethylene (LDPE) film D (100 μm thick) was prepared by blow extrusion from Ipethene 100, $d = 0.923$ g cm^{-3}, MFI $= 0.3$, $\alpha^c = 27\%$, Petrochemical Industries (Israel).

The heterogeneous chlorinations of the polyethylene films were conducted as described elsewhere[16]. After completion of the reaction, films were rinsed with diethyl ether and soaked in it for 24 h (ether was changed every 8 h) in order to remove traces of the absorbed carbon tetrachloride. Films were dried at room temperature in vacuum (0.1 bar).

Infra-red measurements

The 457A Perkin-Elmer grating spectrophotometer equipped with silver bromide polarizers was used. Details of the experimental technique were discussed elsewhere[7].

N.m.r. measurements

N.m.r. proton resonance spectra of the chlorinated polyethylene samples in C_6D_9-Br were recorded at 90 MHz on a Bruker HFX-10 spectrometer. Measurements were performed at 110°C.
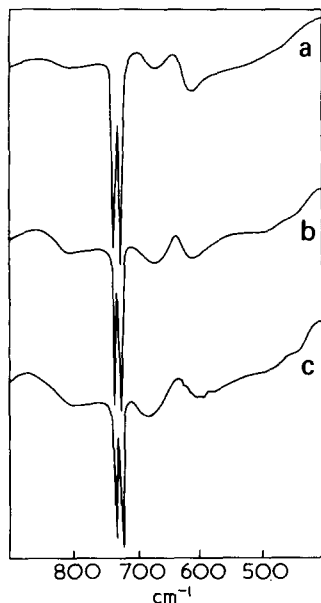
Figure 1 I.r. spectra of the heterogeneously chlorinated compression moulded high density polyethylene film A. (a) chlorine content 15.6%; (b) chlorine content 29.3%; (c) chlorine content 33.8%
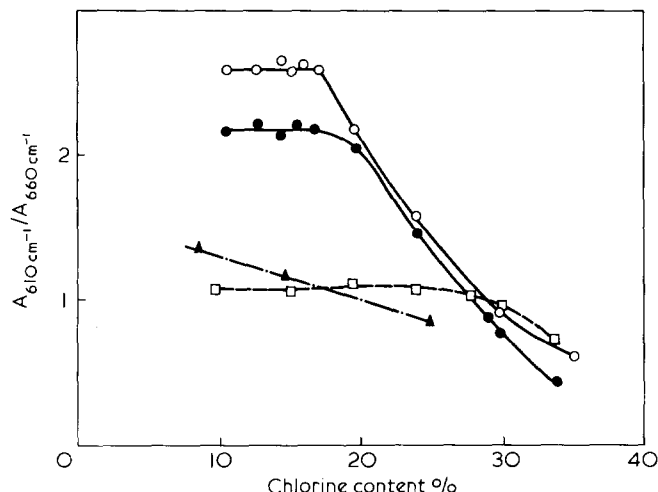

Figure 2 A_{610}/A_{660} ratio as function of chlorine content for various chlorinated polyethylene films. (●) compression moulded high density polyethylene film A, 9 μm; (O) blow extruded high density polyethylene film B, 9 μm; (▲) blow extruded high density polyethylene film C, 24 μm; (□) blow extruded low density polyethylene film D, 100 μm

RESULTS AND DISCUSSION

The i.r. absorption spectra of the chlorinated films prepared by chlorination of the 9 μm thick film A [unoriented high density polyethylene (HDPE)], in the 500–800 cm^{-1} region, are shown in *Figure 1*. The changes in the relative intensities of the 610 and 660 cm^{-1} absorption bands due to increase in the degree of substitution, should be noted. The effect of the degree of substitution on the i.r. spectra in the 600–700 cm^{-1} region was analysed for samples obtained by chlorination of four different polyethylene films. The ratio $r = A_{610cm^{-1}}/A_{660cm^{-1}}$ was calculated for each sample. Plots of r vs. %Cl are shown in *Figure 2*. Values of r remain virtually constant up to 18% of chlorine content for samples prepared by chlorination of the compression moulded (A) and of the blow extruded (B) 9 μm thick films

of HDPE. However, at higher degrees of substitution of these films, they start to decrease sharply. For samples obtained by chlorination of the 100 μm thick, low density polyethylene (LDPE), film D, the plateau region of r is maintained up to ~30% of Cl content. Although the shape of the r vs. %Cl curves is analogous for samples obtained by chlorination of the thin (9 μm) HDPE films A and B and of the 100 μm thick LDPE film D, the actual values of the absorbance ratios differ considerably. The 'plateau' value of r is ~1.1 for samples of the D series while it is 2.2 and 2.6 for the A and B series, respectively.

The dependence of r on %Cl for samples obtained by chlorination of the 24 μm thick HDPE film C shows a different relationship between r and %Cl than for the other three series. In this case values of r decrease in a linear fashion from 1.3 at 10% Cl to 0.8 at 25% Cl.

The absorption bands at 660 cm^{-1} and at 610 cm^{-1} that appear in the spectra of chlorinated polyethylenes were assigned[8,9] to the C–Cl stretching modes and were related to the *gauche* and to the extendended *trans–trans* sequences, respectively. It was pointed out[7] that such assignment is correct only if the concentration of vicinal dichlorides may be neglected, because the 660 cm^{-1} band overlaps with the 642 cm^{-1} band, characteristic of the C–Cl stretching mode of the *trans* sequences of vicinal chlorides.

N.m.r. analysis was used in order to check the concentrations of vicinal chlorides n the investigated samples. ^{1}H n.m.r. chemical shifts of the CH(Cl) protons are strongly shifted downfield as a result of chain substitution in their vicinity. Hence, the analysis of the ^{1}H-n.m.r. spectra enables estimation of the distribution of substituted groups along the polymeric chains of the chlorinated compounds. According to Saito *et al.*[17] the chemical shifts of CH*(Cl) protons in the –CHCl(CH$_2$)$_m$CH*Cl(CH$_2$)$_n$CHCl– sequences are shown in *Table 1*.

Vicinal chlorides at 4.7–5.1 ppm may, therefore, be easily distinguished from the isolated CH(Cl) at 3.9–4.7 ppm. Inspection of *Figure 3* reveals that at 18 and 16% of chlorine content, the vicinal chlorides represent less than 1% of all –CHCl– groups, in samples obtained by chlorination of films B and D, respectively. However, in samples obtained by chlorination of film C, the presence of vicinal chlorides is becoming significant already at 8.9% of chlorine (~10% of vicinal chlorides).

The experimental findings indicate that in samples of the C series, the concentrations of vicinal chlorides are much higher than expected on statistical grounds. It was previously shown[18,19] that the kinetics of the heterogeneous reactions may be diffusion controlled or 'diffusion free'* on a macroscopic scale, depending on the geometric and morphological parameters of the films. A 'diffusion-free' character of the chlorinations conducted

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* The term 'diffusion free' is used to indicate that the reaction rates are not diffusion controlled[18a]

Table 1 Chemical shifts of CH*Cl protons in CHCl(CH$_2$)$_m$CH*Cl (CH$_2$)$_n$CHCl

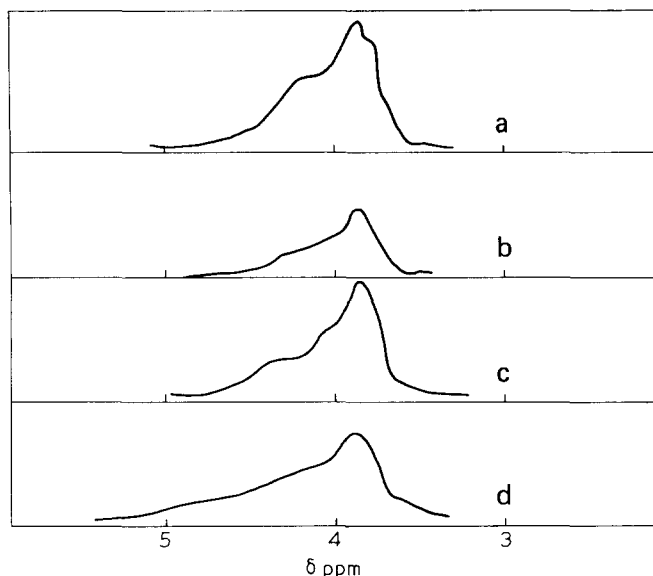| δ (ppm)	3.9	4.2	4.5	4.7	5.1
m	⩾3	2	1	0	0
n	⩾3	⩾3	1	⩾2	0

Figure 3 N.m.r. spectra at 90 MHz of the chlorinated films B, C, D in deuterated bromobenzene at 110°C. (a) Film B, chlorine content 17.8%; (b) film D, chlorine content 15.7%; (c) film D, chlorine content 27.8%; (d) film C, chlorine content 8.9%

on the 9 μm thick films was implied by kinetic evidence[19]. For a LDPE film the critical dimension at which the kinetics became diffusion controlled was found to be around 130 μm. When a heterogeneous reaction is diffusion controlled, steep concentration profiles may be obtained in the modified polymeric network. Thus, the local degrees of substitution must be much higher than the average one. This means that the distribution of the substituted groups along the polymeric chains will differ from that predicted on statistical grounds. The experimental evidence, indicating that the fraction of vicinal chlorides in samples prepared by chlorination of film C is indeed much higher than expected from the overall amount of the chlorinated groups (cf. *Figure 3d*) confirms, therefore, the diffusion controlled character of the reactions conducted on these 24 μm thick films.

The diffusion across the highly chlorinated layers is very slow because their free volume is considerably decreased. Hence, further chlorination of the inner region of such films becomes extremely slow. Even after very long chlorination times the overall chlorine content of the chlorinated film C did not exceed 27%, while 35% of Cl content could be easily arrived at for the analogous but thinner films A and B.

At sufficiently high degrees of substitution the concentrations of vicinal chlorides must of course become significant in all samples. The n.m.r. spectra shown in *Figures 3* and *4* indicate that an increasingly large fraction of vicinal chlorides is formed in the B and D series when their degree of substitution exceeds 18 and 28%, respectively. Note that such overall degrees of substitutions correspond to ~45 and 38% of chlorine substitution in the amorphous phase of the HDPE and LDPE films, respectively, since the crystallites were found to be completely unaccessible to chlorination under conditions prevailing in such experiments[16,20].

The sharp decline of the A_{610}/A_{660} ratio above 18% Cl for samples obtained from films A and B ($\alpha^c \approx 60\%$), and above 30% Cl for samples obtained from film D ($\alpha^c \approx 27\%$) is, therefore, due to the contribution of the stretching

mode of vicinal chlorides to the absorption peak centred at ~660 cm^{-1} and not to the *trans*-to-*gauche* conformational changes. The conformational features of the chlorinated samples may, however, be deduced from values of r in the 'plateau' regions of these series, where the contributions due to the vicinal chlorides are negligible.

It may be assumed that the molar absorbance is virtually identical for the C–Cl stretching modes of the chlorinated *trans* and *gauche* segments[10,11,21]. Thus, the values of $r = 2.6$, 2.15 and 1.1, obtained for the 'plateau' regions of these three series, imply that 28%, 32% and 48% of the substituted segments are in *gauche* conformations for the B, A and D, series, respectively.

For the unoriented amorphous phase of polyethylene the concentration of CH_2 groups in *gauche* (g and g') conformations may be estimated, if one assumes that it has the same distribution of conformations as a supercooled liquid. The potential energy difference between *trans* and *gauche* conformations of CH_2 segments was found to be 800 cal mol^{-1}.[22] Hence, the Boltzmann distribution of the conformational sequences at room temperature corresponds to 33% of the *gauche* sequences. This value is close to the ~32% of the substituted *gauche* sequences indicated by i.r. for the chlorinated samples prepared from the unoriented (compression moulded) film A. The lower fraction of the *gauche* sequences (~28%) in samples prepared from the blow extruded film B is consistent with the observation that the orientation of the amorphous phase leads to an increase in the concentration of the *trans* conformational sequences. Glenz and Peterlin[2] reported that at draw ratio $\lambda = 10$ the concentration of *gauche* sequences in cold drawn polyethylene films decreases by 40%, i.e. down to ~20%. Orientation due to blow extrusion may be expected to be less pronounced than that induced by extensive cold drawing. Hence, an estimate of 28% of *gauche* sequences seems to be plausible for the blow extruded film. Thus, for the HDPE samples the conformation of the polymeric segments does not seem to be affected by their substitution, though the equilibrium distribution of various conformers must be quite different for polyethylene than for the product of its chlorination.

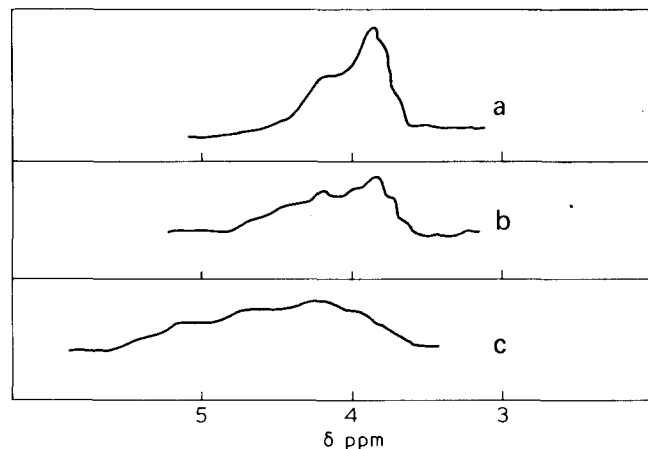The behaviour of the LDPE systems is different. The high fraction of the chlorinated sequences in *gauche* con-

Figure 4 N.m.r. spectra at 90 MHz of the heterogeneously chlorinated high density polyethylene film B in deuterated bromobenzene at 110°C. (a) 17.8% Cl; (b) 24.2% Cl; (c) 37.8% Cl
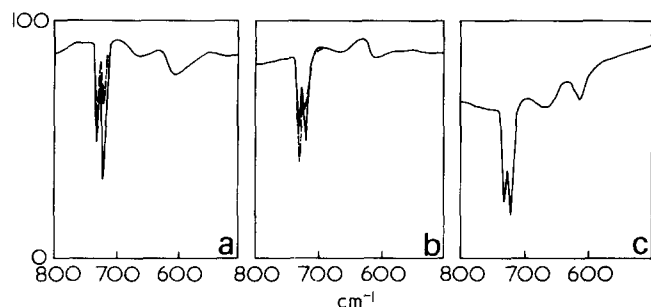
Figure 5 I.r. spectra of heterogeneously chlorinated high density polyethylene film B, (17.8% chlorine). Full and dotted lines denote light polarized perpendicular and parallel to the machine direction, respectively. Only full lines are shown when the two lines coincide. (a) Initial, thermally untreated film; (b) this film after thermal treatment in a press under isometric conditions (155°C, 200 psi); (c) this film after treatment in a silicone oil bath at 155°C

formation in the LDPE samples of the D series ($\sim 48\%$) cannot be attributed to a selective chlorination of the *gauche* sequences, since it was shown previously that both *gauche* and *trans* sequences are chlorinated indiscriminately under such conditions[7]. It seems, therefore, that a *trans* to *gauche* conformational transition must follow the chlorination reaction in such systems. Polymeric chains in the amorphous phase of low density polyethylenes are very mobile at room temperature[5]. Thus, conformational transitions in their amorphous phase can proceed quite easily and the distribution of conformational sequences may approach the equilibrium situation. 3-Chloropentane may be considered in first approximation as a low molecular weight model of the chlorinated LDPE. At room temperature, the equilibrium composition of its rotational isomers is comprised[22] of 68% of various *gauche* conformers and 32% of isomers having *trans* conformation in the vicinity of the CHCl group.

In high density polyethylenes the mobility of the polymeric segments is severely restricted by the adjacent crystalline regions. It was reported[5] that the energy of activation of their conformational transitions is as large as 13 kcal mol^{-1}. The probability of conformational transitions is even lower for the chlorinated high density polyethylenes, because of the strong induced dipole–dipole interactions. The thermodynamically unfavourable conformers, that can initially be formed during heterogeneously conducted chlorinations will, therefore, be 'frozen' in such systems. The conclusion based on the analysis of values of r pointing to a strong deviation from an equilibrium distribution of the conformers in the heterogeneously chlorinated HDPE films, is therefore supported by theoretical considerations. An additional confirmation of this conclusion was provided by the analysis of changes in the i.r. spectra of such samples induced by their recrystallization. The chlorinated HDPE films B were kept for 15 min at 155°C in silicone oil or in a press at 200 psi (restricted melting under isometric conditions). The thermally treated samples were quenched by immersion in cold water (at 20°C). Their polarized i.r. spectra in the 500–800 cm^{-1}

region are shown in *Figure 5*. It is evident that values of r decrease as a result of thermal treatment. However, a value of $r = 0.8$, which corresponds to 55% of the chlorine substituted sequences in *gauche* conformation, a value reasonably close to the one expected for thermodynamic equilibrium ($r = 0.7$), is obtained only in case of the dimensionally unrestricted thermal treatment in silicone oil. Conformational changes, which take place when the thermal treatment is performed under isometric conditions, are much more limited (*Figure 5b*). The limitation of conformational changes even at elevated temperatures, but under isometric conditions, is consistent with the observation that the orientation of the polymeric chains in the amorphous phase may also be preserved to a large extent during such treatment. The morphology and the orientation of the crystalline regions of the heterogeneously chlorinated high density polyethylenes, upon their recrystallization under isometric conditions, will be discussed elsewhere[23].

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