

Microstructure of solution-chlorinated polyethylene by ^{13}C nuclear magnetic resonance

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Solution-chlorinated polyethylene prepared by a modified method has been characterized using ^{13}C nuclear magnetic resonance (n.m.r.) and differential thermal analysis (d.t.a.). The results show that the residual paraffin segments, melting point and crystallinity decrease rapidly with increasing chlorine content. The prepared polymer seems to have a homogeneous chlorine distribution.

Keywords Solution-chlorinated polyethylene; microstructure; ^{13}C nuclear magnetic resonance; differential thermal analysis

INTRODUCTION

Chlorination is a widely used method for modifying polyethylene. The properties of chlorinated polyethylene (CPE) are determined by degree of chlorination, molecular weight, microstructure of the chain and technique used for chlorination. The attached chlorine atom destroys the ordered arrangement of the polyethylene chain so that the crystallinity of the polymer decreases. With increasing chlorine content of CPE to above 15% by weight, the polymer changes from a crystalline plastic to a typical rubber. The polymer is sticky and tough, and has high elasticity. When the chlorine content is above 50% chlorine by weight, CPE becomes hard, the glass transition temperature is above 35°C, and the material is a polar plastic.

Chlorination can be carried out in the homogeneous phase (solution) or heterogeneous phase (suspension). In the latter the product usually has a decreasing chlorine distribution from the surface to the core of the suspended particles. If the chlorination proceeds at a temperature lower than the melting point of polyethylene, the crystalline region will not be chlorinated. Solution chlorination is a different technique by which the reaction takes place homogeneously along the dissolved molecular chain. This reaction is easy to handle in the laboratory but difficult industrially because of the technical problems in recovery of solvent and removal of the residual solvent from the product.

There are several works on the microstructure of CPE¹⁻⁴. The chlorination was shown to be a hindered-type substitution: a substituent chlorine atom would prohibit the further substitution of hydrogen attached on the same carbon atom. When the chlorine content exceeds 50 wt%, sequences with more than four adjacent methylene groups disappear and the $-\text{CCl}_2-$ group appears. The sequence distribution is also different between suspension and solution CPE samples.

In this work a modified method for photochlorination

of high-density polyethylene has been reported. Instead of carbon tetrachloride⁵ (b.p. 76°C) and tetrachloroethylene⁶ (b.p. 121°C), chlorobenzene (b.p. 132°C) is used as solvent so that the reaction can proceed at above the melting point of high-density polyethylene when the polymer will be dissolved thoroughly. The light from a tungsten lamp is acceptable for photo-initiation without the necessity for ultra-violet or fluorescent lamps.

The physical properties have been measured. The structure of the chain has been studied using ^{13}C n.m.r. and differential thermal analysis (d.t.a.). The results are discussed in terms of the mechanism of the substitution reaction.

EXPERIMENTAL

Photochlorination of polyethylene

The reaction took place in a three-necked flask in an oil bath. The flask was equipped with a stirrer, a reflux condenser and two gas inlet tubes (nitrogen and chlorine). Commercial high-density polyethylene (10 g, nominal $M_n = 10\,000$) was dissolved in chlorobenzene (200 ml, A.R.) at 135°C. The solution was stirred during the reaction. It was photo-initiated using the light from a tungsten lamp (60 W) under a nitrogen atmosphere. Chlorine gas was bubbled into the flask with a flow rate of 28 ml min⁻¹. By adjusting the reaction time, products with different chlorine contents were obtained. The reaction usually lasted from 2 to 10 h. The resulting products were cooled and precipitated into 10 times excess of methanol (A.R.) and washed twice with methanol. The precipitate was soaked in methanol overnight to extract the residual chlorobenzene and dried in a vacuum oven at 1 mmHg at 50°C for 2 weeks.

Characterization of CPE

The properties of CPE are listed in *Table 1*. The composition was obtained from elemental analysis. The

Table 1 Properties of CPE

CPE	Composition (weight fraction)			Molecular weights*			$d, 25^\circ\text{C}$ (g ml ⁻¹)	$\alpha, 25^\circ\text{--}45^\circ\text{C}$ $\times 10^4$ (K)	T_g (°C)
	C	H	Cl	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n			
1	0.546	0.083	0.369	1.10	1.58	6.96	1.159	6.25	-10
2	0.630	0.099	0.274	1.08	1.52	7.11	1.071	13.24	-8
3	0.454	0.062	0.480	1.20	1.80	6.67	1.301	4.43	26
4			0.357	1.15	1.89	6.08	1.127	8.73	-10
5	0.641	0.101	0.245				1.062	12.25	-10
8	0.712	0.115	0.165				1.015	9.10	
11			0.224				1.066	12.30	-12
12			0.210				1.036	11.57	
15			0.447	1.70	1.81	9.38	1.311	5.66	27
16			0.516	1.98	2.53	7.83	1.416		39
17			0.498	1.82	2.08	8.78	1.365	3.85	32
18			0.456	2.02	2.29	8.81	1.319	4.93	28
19			0.441	1.79	2.09	8.56	1.304	5.47	25
20	0.349	0.037	0.621	2.42	2.58	9.41	1.487	3.72	78

* Relative to polystyrene standard

molecular weights were determined with g.p.c. relative to polystyrene standard. The density was measured using equal density titration⁷. The thermal expansion coefficient α was calculated from the densities at two temperatures (25° and 45°C). T_g was evaluated from dynamic mechanical measurements, the quoted values being peak points of the $\tan \delta$ curves.

¹³C n.m.r. measurements

A Bruker WM 250 FT n.m.r. spectrometer was used to obtain the ¹³C n.m.r. spectra of the polymers. The resonance frequency for ¹³C is 62.9 MHz on the instrument.

Samples were dissolved in a 75/25 w/w *o*-dichlorobenzene/*d*₆-benzene mixture and hexamethyldisiloxane (HMDS) was added as an internal shift reference. Sample concentrations were normally around 15 wt%. The solvent system permitted an adequate polymer solubility and sufficient deuterium concentration to operate the spectrometer field lock system. All spectra were run at 80°C to improve solubility and resolution, by reducing the solution viscosity. Broad-band proton decoupling was used for all spectra.

The resulting spectra are shown in Figure 1.

D.t.a. measurements

Measurements were made on a Du Pont 990 machine using a sample weight of around 10 mg. The sample was scanned at a rate of 10°C min⁻¹ between -60° and 160°C. The samples moulded at 140°C were used for measurements.

RESULTS AND DISCUSSION

¹³C n.m.r. measurements

The analysis is composed of two aspects, following the papers published by Keller and Mugge¹.

Determination of the constitution. The contents of -CH₂-, -CHCl- and -CCl₂- groups (in mol%) of the CPE samples, which are designated as X, Y and Z, respectively, are determined from:

$$X = F_0 / \sum_{i=0}^2 F_i \quad (1)$$

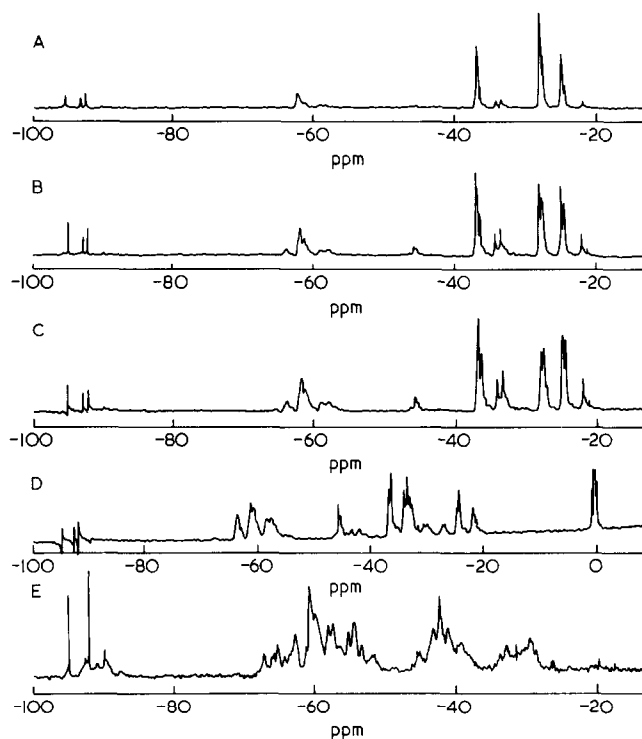


Figure 1 ¹³C n.m.r. spectra of CPE samples: spectrum A, CPE 2; B, CPE 4; C, CPE 1; D, CPE 3; and E, CPE 20

$$Y = F_1 / \sum_{i=0}^2 F_i \quad (2)$$

$$Z = F_2 / \sum_{i=0}^2 F_i \quad (3)$$

where F_0 , F_1 and F_2 are the corrected intensities (area) under -CH₂-, -CHCl- and -CCl₂- resonances, respectively. $F_i = F_i(\text{expt})/N_i$. $F_i(\text{expt})$ is the experimental value. N_i is the relative intensity factor. $N_0 = N_1 = 1.5 \pm 0.2$ and $N_2 = 1$, obtained from the measurement of chlorinated poly(vinyl chloride) at the analogous condition. When the chlorine content is higher than 50 wt%, the resonances of -CH₂- and -CHCl- begin to overlap, and we need a

further correction for the intensities:

$$F_{0,\text{corr}} = (F_0 + F_1)/(I_{\text{corr}}^{-1} + 1) \quad (4)$$

$$F_{1,\text{corr}} = I_{\text{corr}}^{-1}(F_0 + F_1)/(I_{\text{corr}}^{-1} + 1) \quad (5)$$

where

$$I_{\text{corr}}^{-1} = 0.47I^{-1} + 0.34 \quad (6)$$

and

$$I = F_1/F_0 \quad (7)$$

Equation (6) is obtained from calibrating the I^{-1} of the ^{13}C n.m.r. spectra with the corresponding ratio of the ^1H n.m.r. spectra.

After obtaining X , Y and Z , the molar degree of chlorination can be calculated.

$$\bar{\alpha} = (Y + 2Z)/2 \quad (8)$$

The original definition of $\bar{\alpha}$ is

$$\bar{\alpha} = N_{\text{Cl}}/(N_{\text{Cl}} + N_{\text{H}}) \quad (9)$$

where N_{Cl} and N_{H} are the numbers of Cl and H atoms in the chain, respectively. $\bar{\alpha}$ should be between 0 and 1, and is connected with the weight degree of chlorination in wt%, G_x :

$$G_x = M_{\text{Cl}}\bar{\alpha}/[M_{\text{Cl}} - M_{\text{H}}]\bar{\alpha} + M_{\text{H}} + M_{\text{C}}/2 = g_x \times 100\% \quad (10)$$

where M_{Cl} , M_{H} and M_{C} are the atomic weights. Thus, $\bar{\alpha}$ and G_x can be determined from the n.m.r. spectra.

G_x can also be determined from the chemical analysis. Thus, $\bar{\alpha}$ can be calculated from G_x if we rewrite (10):

$$\bar{\alpha} = g_x(M_{\text{H}} + M_{\text{C}}/2)/[M_{\text{Cl}} - g_x(M_{\text{Cl}} - M_{\text{H}})] \quad (11)$$

The two series of results for $\bar{\alpha}$ and G_x can be compared.

Determination of chlorine distribution. From the statistics⁸ the probabilities of finding $-\text{CH}_2-$, $-\text{CHCl}-$ and $-\text{CCl}_2-$ groups in a random substitution are

$$\pi_0 = X(\bar{\alpha}) = (1 - \bar{\alpha})^2 \quad (12)$$

$$\pi_1 = Y(\bar{\alpha}) = 2\bar{\alpha}(1 - \bar{\alpha}) \quad (13)$$

$$\pi_2 = Z(\bar{\alpha}) = \bar{\alpha}^2 \quad (14)$$

The conditional probabilities of finding the corresponding groups in the circumstances where the presence of a substituent on a given repeat unit affects the probability of a second substituent on the same repeat unit but not the

Table 3 Correlation between pentads and chemical shifts

-CCl ₂ - sequence		-CHCl- sequence		-CH ₂ - sequence	
Pentad	δ (^{13}C)	Pentad	δ (^{13}C)	Pentad	δ (^{13}C)
11201	-88.5 . . . -89.3	10101	-54.4 . . . -54.9	10001	-21.0
10200	-89.9	10100	-58.1	10000	-24.2
01210	-96.6	00100	-61.3	00000	-27.4
		01100	-63.1	11001	-29.8
				01001	-33.0
				01000	-36.2
				11010	-41.7
				01010	-44.9

substitution probability on any other repeat unit are

$$\pi_0 = X(\bar{\alpha}, \lambda) = (1 - \lambda)^{-2}[1 + \lambda^2 - 2\bar{\alpha}(1 - \lambda) - 2\lambda(1 - 2\bar{\alpha} + 2\bar{\alpha}\lambda)^{1/2}] \quad (15)$$

$$\pi_1 = Y(\bar{\alpha}, \lambda) = (1 - \lambda)^{-2}[-4\lambda + 2\bar{\alpha}(1 - \lambda)(1 + \lambda) + 4\lambda(1 - 2\bar{\alpha} + 2\bar{\alpha}\lambda)^{1/2}] \quad (16)$$

$$\pi_2 = Z(\bar{\alpha}, \lambda) = (1 - \lambda)^{-2}[2\lambda - 2\bar{\alpha}\lambda(1 - \lambda) - 2\lambda(1 - 2\bar{\alpha} + 2\bar{\alpha}\lambda)^{1/2}] \quad (17)$$

where $\lambda < 1$ means that the reaction is a hindered substitution, $\lambda = 0$ is that the probability of finding $-\text{CCl}_2-$ group is zero, and $\lambda > 1$ means that the substituent Cl atom increases the chance for the second H atom on the same C atom to be substituted by another Cl atom. When $\lambda = 1$ the reaction is a random substitution: equations (15)–(17) reduce to equations (12)–(14).

With ^{13}C n.m.r. we are interested in analysing the sequence structure up to five repeat units (pentads). For example, the probabilities of finding some of them are listed in Table 2, where 0, 1 and 2 refer to $-\text{CH}_2-$, $-\text{CHCl}-$ and $-\text{CCl}_2-$ groups, respectively. The middle 0 in Table 2 can be replaced by 1 and 2. Thus if we know $\bar{\alpha}$ and λ , the theoretical probabilities of finding these pentads can be calculated and compared with the experimental values.

From the spectra of model compounds we know the correlation between the pentads and the related chemical shifts of CPE polymers, which are listed in Table 3¹.

The molar degree of chlorination $\bar{\alpha}$ and the weight degree of chlorination G_x determined by ^{13}C n.m.r. are seen in Table 4. They are compared with the values obtained from chemical analysis. It can be seen that the relative error Δ between the two methods is reasonable because each method was estimated to have a relative error of 5%:

$$\Delta = (G_{x,\text{sp}} - G_{x,\text{chem}})/G_{x,\text{chem}} \quad (18)$$

The molar fraction contents of $-\text{CH}_2-$, $-\text{CHCl}-$ and $-\text{CCl}_2-$ groups (X , Y and Z) determined from spectra are plotted against $\bar{\alpha}$ in Figure 2. Also plotted are the theoretical curves from equations (12)–(17). Our data at low chlorine contents are close to the theoretical curves of hindered-type substitution.

Table 2 Probabilities of finding some pentads

Pentads	Random substitution	Conditional substitution
00000	$(1 - \bar{\alpha})^8$	$X^4(\bar{\alpha}, \lambda)$
10000	$4\bar{\alpha}(1 - \bar{\alpha})^7$	$2X^3(\bar{\alpha}, \lambda)Y(\bar{\alpha}, \lambda)$
01000	$4\bar{\alpha}(1 - \bar{\alpha})^7$	$2X^3(\bar{\alpha}, \lambda)Y(\bar{\alpha}, \lambda)$
10001	$4\bar{\alpha}^2(1 - \bar{\alpha})^6$	$X^2(\bar{\alpha}, \lambda)Y^2(\bar{\alpha}, \lambda)$
01010	$4\bar{\alpha}^2(1 - \bar{\alpha})^6$	$X^2(\bar{\alpha}, \lambda)Y^2(\bar{\alpha}, \lambda)$
11000	$16\bar{\alpha}^2(1 - \bar{\alpha})^6$	$4X^2(\bar{\alpha}, \lambda)Y^2(\bar{\alpha}, \lambda)$
11001	$16\bar{\alpha}^3(1 - \bar{\alpha})^5$	$2X(\bar{\alpha}, \lambda)Y^3(\bar{\alpha}, \lambda)$

Table 4 $\bar{\alpha}$ and G_α from ^{13}C n.m.r. and chemical analysis

Sample	$\bar{\alpha}$		G_α		Δ
	N.m.r.	Chem.	N.m.r.	Chem.	
CPE 1	0.1160	0.1138	37.4	36.9	+0.01
2	0.0651	0.0739	24.9	27.4	-0.09
3	0.1641	0.1779	45.9	48.0	-0.04
4	0.0958	0.1081	32.9	35.7	-0.08
20	0.3084	0.3094	62.0	62.1	0

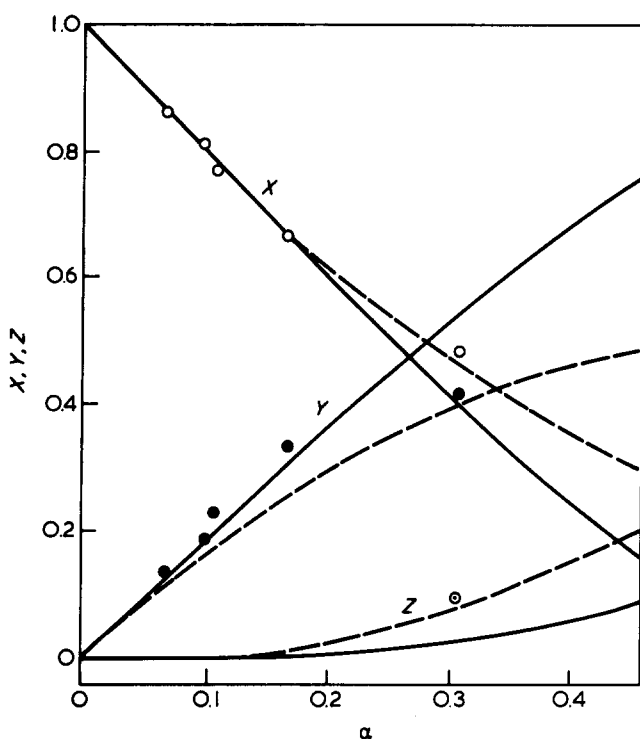


Figure 2 Experimental values of X, Y and Z as a function of the molar degree of chlorination α . Theoretical curves: ---, random substitution; —, hindered substitution with $\lambda=0.2$

The sequence distribution was also determined. Three pentad fractions F_{00000} , F_{01000} and F_{10000} with higher accuracy are plotted in Figures 3 and 4 and compared with the theoretical curves calculated from the equations in Table 2. The results also show the characteristics of hindered-type substitution of our chlorination when the chlorine content is lower than 50 wt%. The theoretical curves cannot fit the experimental data even at $\lambda=0$, where the probability of finding $-\text{CCl}_2-$ group is zero. We considered the model that the intimate neighbour is influenced by the μ parameter⁸, but this did not improve the discrepancy.

Comparing the results of F_{00000} with the literature^{1,2}, we can draw the conclusion that our sample has a more homogeneous chlorine distribution along the chain because F_{00000} decreases rapidly with $\bar{\alpha}$. Calculation shows that F_{00000} should be zero at $\bar{\alpha}=0.100$ ($G_\alpha=34.0$) if chlorine is homogeneously distributed along the chain.

D.t.a. measurements

D.t.a. results support the conclusion drawn from ^{13}C n.m.r. Figure 5 shows the thermograms of some chlori-

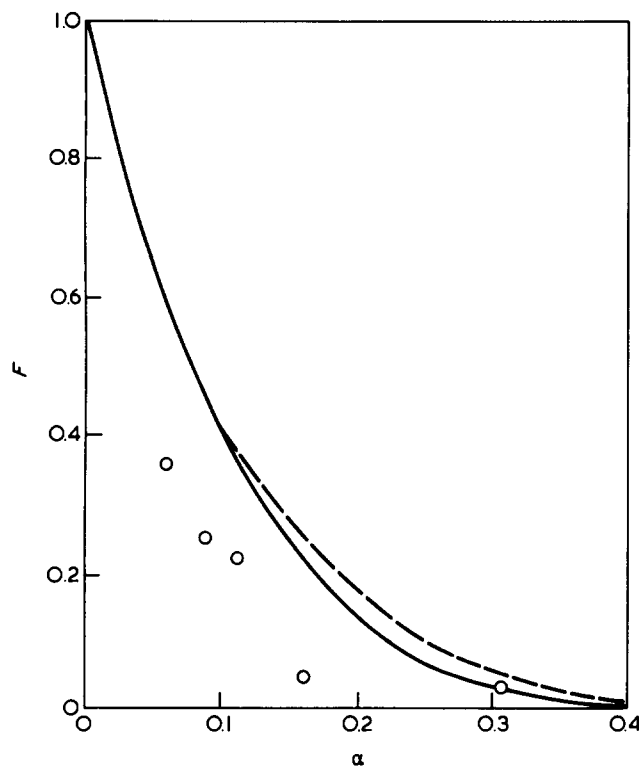


Figure 3 Molar fraction of pentad 00000 determined by ^{13}C n.m.r. Theoretical curves as in Figure 2

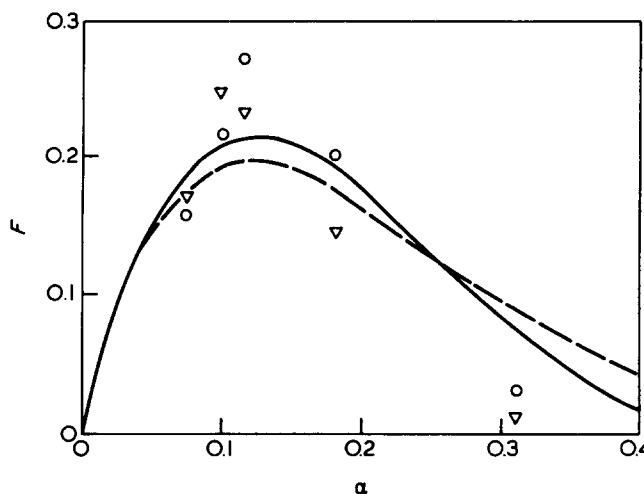


Figure 4 Molar fractions of pentads 01000 (O) and 10000 (V) determined by ^{13}C n.m.r. Theoretical curves as in Figure 2

nated polyethylenes. It can be seen that for CEP 3 a normal T_g transition occurs at 10°C while for others there are endothermic peaks. These can be considered as the melting points of the residual crystalline parts in CPE, which correspond to paraffins with appropriate numbers of carbons. The higher the melting point, the longer the $-\text{CH}_2-$ segment length. For example the melting points of CPE 4, 2 and 8 are 0°, 40° and 73°C, which correspond to the paraffins with 14, 21 and 35 carbons, respectively. The melting points of CPE are plotted against chlorine contents in Figure 6. It can be seen that starting from pure high-density polyethylene ($T_m=137^\circ\text{C}$ by d.t.a. at $10^\circ\text{C min}^{-1}$ heating rate in this experiment) the melting point decreases linearly with chlorination. A similar phenomenon was reported for suspension-chlorinated

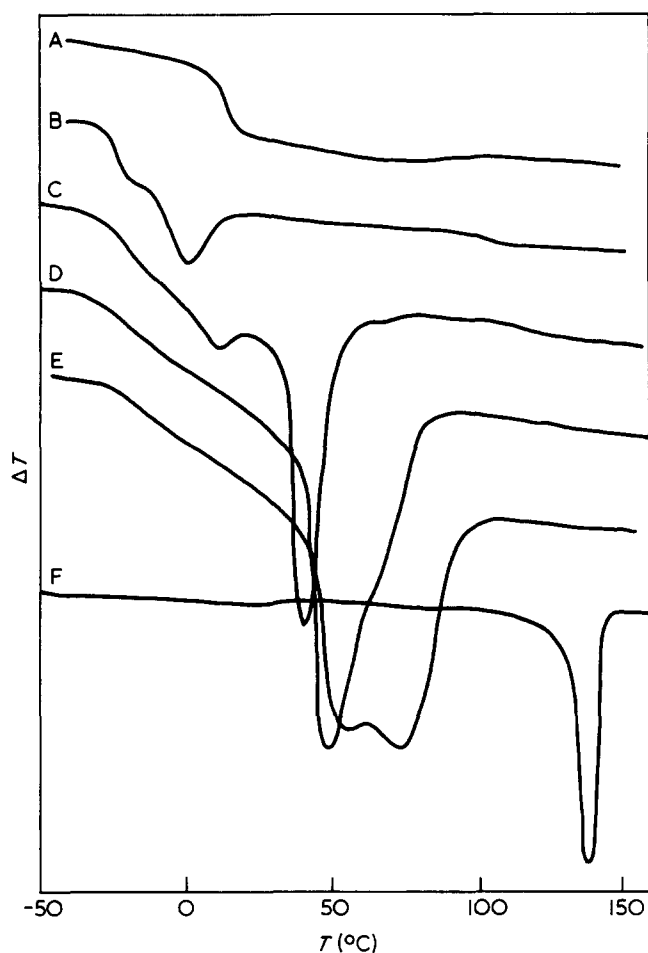


Figure 5 D.t.a. of CPE samples: curve A, CPE 3; B, CPE 4; C, CPE 2; D, CPE 12; E, CPE 8; F, high-density polyethylene

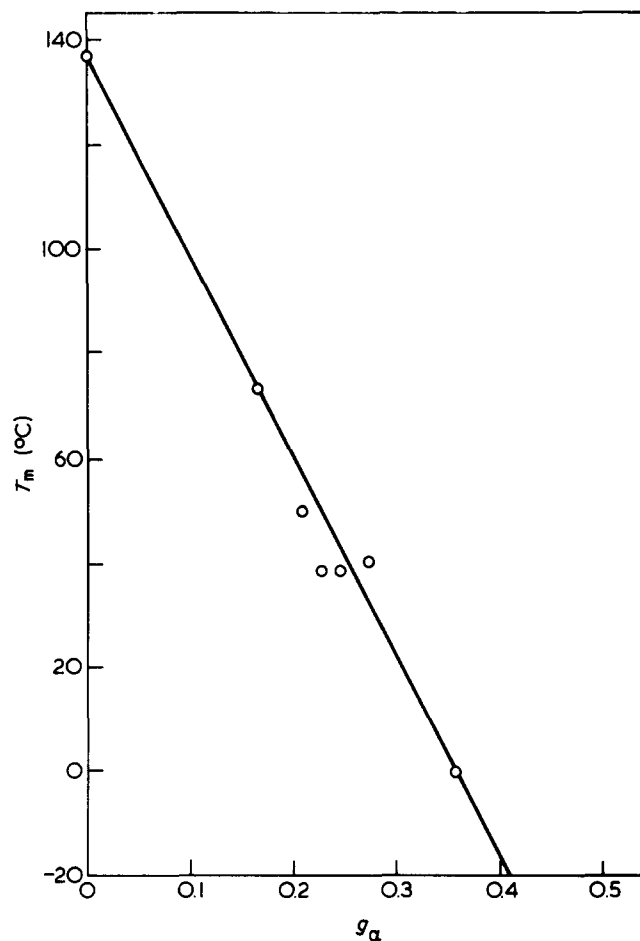


Figure 6 The melting points of residual paraffin segments in CPE as a function of chlorine content of polymers

polyethylenes³; however, there is a difference between the two systems. When suspension CPE samples with different degrees of chlorination were used the endothermic peaks occurred over the same temperature range ($\sim 95^\circ\text{C}$), which shows that it can leave a long length of $-\text{CH}_2-$ segments without chlorination (~ 54 carbons).

The heats of fusion $\Delta H_f(\text{sample})$ were obtained from the areas of the endothermic peaks. The absolute value was calculated directly using the calibrated heating rate of the instrument. The overall calibration has been checked by measuring the heat of fusion of indium: ΔH_f measurements have an accuracy of $\pm 10\%$ or better.

The crystallinity was calculated by

$$\text{crystallinity} = \Delta H_f(\text{sample}) / \Delta H_f(\text{ideal}) \quad (19)$$

For completely crystalline polyethylene⁹ $\Delta H_f(\text{ideal}) = 69 \text{ cal g}^{-1}$. Considering the molecular weight dependence of heat of fusion of paraffins, $\Delta H_f(\text{ideal}) = 40 \text{ cal g}^{-1}$ was taken for other CPE samples¹⁰. The crystallinity so calculated is shown in Figure 7 as a function of chlorine content in CPE. It can be seen that the crystallinity decreases rapidly with chlorination, and disappears at $G_\alpha = 0.37$. This is in contrast with the result from suspension CPE: there crystallinity persists until the polymer contains 56 wt% chlorine, which corresponds to the chlorine content of poly(vinyl chloride).

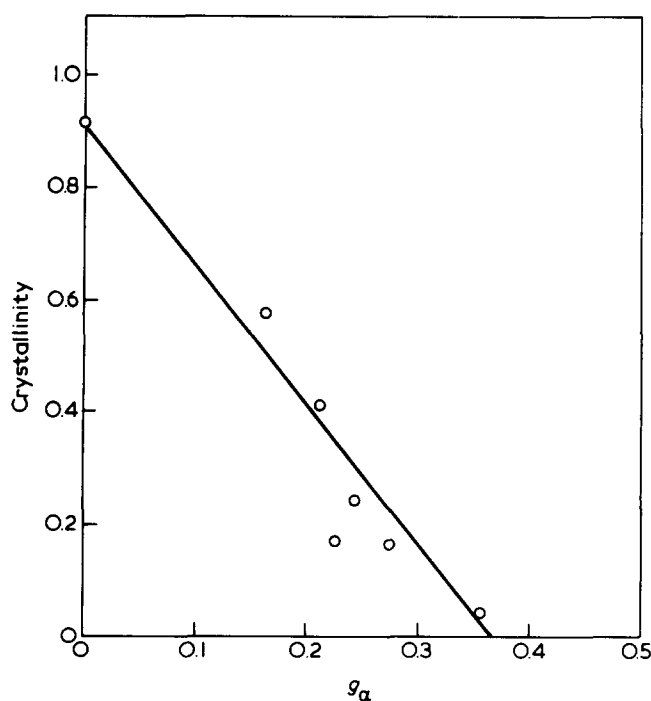


Figure 7 Crystallinities of CPE samples as a function of chlorine content of polymers

CONCLUSIONS

CPE has been prepared by photochlorination in solution at 135°C in which chlorobenzene is used as solvent and the light from a tungsten lamp is used as an initiator.

¹³C n.m.r. measurement shows a hindered-type substitution when chlorine content is lower than 50% by weight. Segments of five successive -CH₂- units decrease rapidly with chlorination.

D.t.a. measurement shows that both the melting point of residual paraffin segments and crystallinity in CPE decrease with increasing chlorine content. The crystallinity disappears when chlorine content is greater than 37 wt%.

The prepared polymer has a more homogeneous chlorine distribution than reported in the literature.

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