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Free radical graft reactions onto polyolefins: studies on model compounds

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In order to understand the mechanism of free radical graft reactions onto high molecular weight polyolefins, squalane and related small molecules have been examined. Characterization of polyolefins with less than 5% grafted functionality is extremely difficult, and has been one of the major reasons for using smaller molecules in mechanistic studies. In this paper the free radical bromine graft reactions onto squalane, methylhexane and nonane in the presence or absence of an initiator are discussed. Multiple brominations were preferred at the same site, because of the acidic proton alpha to the bromide moiety. Material characterization by modern techniques as well as a possible radical reaction pathway have been suggested. Copyright © 1996 Elsevier Science Ltd.

(Keywords: graft reactions; free radical mechanism; bromination)

INTRODUCTION

Functionalization of saturated polyolefins requires a radical reaction pathway. However, radical reactions on polyolefins are complicated due to poor selectivity, chain scission and other related side reactions. Thus, characterization of less than 5% grafted polyolefin materials is extremely difficult and has been one of the major reasons for using smaller molecules in mechanistic studies. In order to understand the mechanism of free radical graft reactions onto high molecular weight polyolefin, squalane and related small molecules have been the targets for quite some time[1-4].

Squalane can be seen as a model compound for ethylene–propylene copolymer. In the context of polyolefin and hydrocarbon degradations, thermocracking of squalane, phytane and pristane was reported at 250°C for 24 h and was analysed by high resolution capillary gas chromatography (h.r.c.g.c.)[1]. Interestingly, the author reported that the tertiary protons in the middle of the molecule have a better radical population compared to those at the chain ends.

Currently, there is a lot of interest in maleated polyolefins, due to its commercial importance as a compatibilizer in immiscible polymer blends. Mechanistic studies of grafting maleic anyhdride (MAH) onto polyolefin using graft reactions onto *n*-eicosane and squalane have been reported[2,3]. One of the limiting factors in grafting MAH onto hydrocarbons is its insolubility in hydrocarbons. Homogeneous graft reactions were found at low MAH concentrations (< 0.02 M) and at 140–165°C[2,3].

Recently, such grafting reactions and reaction mechanisms have been studied in an extruder[4]. That is, MAH has been grafted onto squalane under varied extruder reaction conditions to optimize conditions for grafting MAH onto high density polyethylene. They found that mixing plays an important role as the grafting reaction is diffusion-limited. Increasing initiator concentration increases grafting, and crosslinking is the limiting factor. A low percentage of MAH is favourable for grafting reactions. Similarly, 2-(dimethylamino)ethylmethacrylate has been grafted onto squalane[5]. The authors concluded that the optimal conditions were: temperature above 160°C, 5.0 wt% monomer concentration, 1.0 wt% initiator concentration and reaction time 10–20 min.

Halogenation has been extensively studied for the functionalization of polyolefins due to its inherent low cost and high reactivity during reactive extrusion procedures. Chlorination is an exothermic reaction in polyolefin functionalization, and has poor selectivity, often leading to various chlorinated products. In the halogenation of polyolefin, the reactivities of the C–H, C–X (where X = halogen) and X–X bonds are of extreme importance.

A significant amount of work has been done on halogenation (bromination in particular) of alkanes[6,7]. Such free radical studies including bromination of alkanes, via initiation of visible and u.v. radiation at low temperatures are summarized in text books[8].

We have previously studied functionalization of polyolefins[9-13], reaction mechanism[14] and activation energy calculations of squalane[15]. In this paper, we report mechanistic studies on halogenation of polyolefins using model compounds. The model compounds, squalane (1), 3-methylhexane (2) and nonane (3) were chosen considering primary vs secondary vs tertiary carbons. In addition, using these model compounds, reaction progress can be studied easily, by analysis of the halogenated products formed along with any unsaturated and chain scission products.

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EXPERIMENTAL

Fourier transform infra-red (*FT*i.r.) spectra were recorded on a Nicolet 520 *FT*i.r. spectrometer. Thermogravimetric analysis (t.g.a.) was carried out on a Mettler TA 4000 instrument at a heating rate of 20°C min^{-1}. Proton nuclear magnetic resonance (^{1}H n.m.r.) spectra were recorded on a Varian VXR-300 (300 MHz) instrument and ^{13}C n.m.r. spectra were run on the same instrument (75.4 MHz) in $CDCl_3$. Carbon, hydrogen and nitrogen (CHN) analysis was carried out using an in house Leco CHN analyser.

Bromine in all the samples was measured using UniQuant X-ray fluorescence spectroscopy (UniQuant XRF) method. Total bromine in the sample was determined using wavelength-dispersive X-ray fluorescence spectrometry. Prior to such bromine analysis, a standard run with known sample was carried out and calibrated using combustion analysis method. In addition, analysis of bromine by UniQuant-XRF was in agreement with that of the combustion method for a few randomly selected samples.

The high temperature gas chromatography (HTGC) was conducted in a Carlo Erba HR GC 5300 Mega series instrument with the following experimental conditions: column 12 m × 0.53 mm × 0.15 μ SGE HT5; initial oven temperature 40°C; initial hold 1 min; program rate 5°C min^{-1}; final oven temperature 430°C; final hold 50 min; injector cold O.C; FID temperature 440°C; carrier gas He; column flow 7.2 ml min^{-1}; sample size 2.5 μl.

Gas chromatography with atomic emission detector (GCAED) was run in a Hewlett-Packard instrument, with a 5890 series 2 chromatograph and a 5921A atomic emission detector, and the following experimental set up: column 15 m × 0.25 mm × 0.1 μ dimethyl silicone (aluminium-clad); initial oven temperature 40°C min^{-1}; program rate 1 was 10°C min^{-1}; final oven temperature 1 was 250°C; program rate 2 was 2°C min^{-1}; final oven temperature 2 was 350°C; injector temperature 250°C; injector split with the ratio 1:140; column flow 0.7 ml min^{-1}; block temperature 350°C; transfer line temperature 350°C; carrier gas He; column head pressure 10 psi; sample size 1 μl; bromine line 478 nm.

Gas chromatography/mass spectrometry (g.c.-m.s.) was performed on a Finnigan SSQ710 quadruple mass spectrometer connected to a Varian 3400 gas chromatograph and an ICIS data system running on a DecStation 3100. The gas chromatography column used was a J. + W. Scientific DB5MS 30M × 0.25 mm i.d. ×0.25 μm phase thickness. One μl sample was injected into an injection port set for a 1:100 split at 300°C. The gas chromatography oven was held at 35°C for 5 min, ramped at 4°C min^{-1} to 150°C, ramped at 15°C min^{-1} to 290°C and held there for 15 min, for a total run time of 58 min. The mass spectrometer was configured in electron ionization mode with 70 eV electron energy, 150°C ion source temperature, and 0.5 s scans from m/z 34 to 600, with 9 kV post acceleration energy into an electron multiplier detector set for −1000 V bias.

Direct probe mass spectrometry was performed on a Finnigan TSQ70 quadruple mass spectrometer connected to a Finnigan VMS data system. 50 μg sample was deposited into a glass sample cup, and heated in the mass spectrometer ion source at 10^{-7} torr from 30 to 400°C in 15 min. The mass spectrometer was configured in electron ionization mode with 70 eV electron energy, 250°C ion source temperature, and 2 s scans of the first quadruple from m/z 34 to 1200, with 15 kV post-acceleration energy into an electron multiplier detector set for −1500 V bias. The last two quadruples were configured in r.f.-only mode.

Squalane, 3-methylhexane, nonane, t-butylbenzene, bromine, dicumylperoxide were used as received from Aldrich. As presence of light can initiate these bromination reactions, we tried to minimize contact of visible and u.v. radiation by covering the reaction flasks with aluminium foil. However, we did not totally exclude light during experiments. Prior to starting the reactions, solvent was degassed, and a nitrogen atmosphere was used in each of the reactions. Reaction mixtures were diluted with methylene chloride prior to work up. Excess bromine was removed by washing with aq. 5 wt% sodium sulfite solution. The solution was dried over sodium sulfate and the solvent was removed under vacuum using a rotovaporator at 40°C.

Typical solution reaction

(Procedure for experiment reported in Entry 2, *Table 2*.) While stirring degassed tertiary-butylbenzene (50 ml), squalane (10.0 ml (8.10 g, 0.01915 mol)) was added and heated to 100°C. While still stirring continuously, bromine (1.0 ml (3.102 g, 0.0194 mol)) was added and the mixture stirred for 10 min. This was followed by the addition of dicumyl peroxide (0.5 g, 0.001849 mol) and stirring continued for 1.5 h. The reaction was stopped by pouring the solution into a vigorously stirring water (200 ml). The organic layer was separated and consecutively washed with water (3 × 100 ml), aqueous 5% sodium bisulfite (3 × 100 ml) and water (3 × 100 ml). The resulting solution was dried over anhydrous sodium sulfate (30 g) and filtered. The brominated solution was used for further analysis without any purifications. Bromine (wt%) 0.97%.

*General procedure followed for neat reaction (*Table 2, Table 5 *and* Table 7*)*

(Procedure for experiment reported in Entry 4, *Table 2*.) While stirring a solution of squalane (10.0 ml (8.10 g, 0.01915 mol), and bromine (1.0 ml (3.102 g, 0.0194 mol)) at 100°C, dicumyl peroxide (0.5 g, 0.001849 mol) was added with positive nitrogen pressure. The reaction mixture was stirred for 30 min, followed by the addition of dicumyl peroxide (0.5 g, 0.001849 mol) and stirred for 1 h. The reaction was quenched by diluting it with dichloromethane (200 ml). The organic layer was consecutively washed with water (3 × 100 ml), aq. 5% sodium bisulfite (3 × 100 ml) and water (3 × 100 ml). The resulting solution was dried over anhydrous sodium sulfate (30 g) and filtered. The solvent was removed under vacuum using a rotovaporator at 40°C. Yield 9.31 g (76.3%); t.g.a. (5% wt loss in nitrogen atm.) 174°C; g.p.c. $M_w = 500$, $M_n = 480$; bromine (wt%) 2.07%.

RESULTS AND DISCUSSION

In this study, we concentrated on grafting reactions using bromine. It is easy to analyse bromine by elemental analysis and other analytical methods. Bromine atoms are more specific as hydrogen abstracting radicals, and less energetic than chlorine atoms. Hydrogen abstraction by bromine radicals is typically endothermic, except for extremely weak C–H bonds. H–Br bond formation is ~ 16 kcal mol^{-1} less than H–Cl bond formation (considering the same molecule). In addition, bromine being a better leaving group than chlorine, brominated polyolefin could be further modified with greater ease.

Grafting reactions on polymers are known and are as old as the invention of natural rubber. However, these reactions need an additional source – an initiator, either chemical or photo/visible frequency radiations. However, the Br–Br bond has a low bond dissociation energy (46.1 kcal mol^{-1} at 25°C)[16,17] and is very close to the peroxide (O–O) bond dissociation energy (*Table 1*).

Bromination of squalane

Initially, bromination of squalane was carried out in *t*-butylbenzene at 100°C. Typically, the neat reaction (without any solvents) mimics the extruder reaction. Thus, we carried out neat reactions at 55, 100 and 170°C (*Table 2*). Reactions were carried out both in the presence and in the absence of dicumylperoxide (DCP). Control reactions of squalane with DCP were also carried out. Wt% bromine grafted, thermal stability and molecular weights as determined by g.p.c. are tabulated in *Table 3*.

Table 1 Bond dissociation energy

Bond	Dissociation energy[9,10] (kcal mol^{-1} at 25°C)
C–H Methyl	102
1°	97
2°	95
3°	90
CH_2CH–H (Vinylic)	105
CH_3–CH_3 (1°–1°)	90
CH_2CHCH_2–H (Allylic)	88
CH_3–CH_2C (1°–2°)	76
CH_3–$CH(CH_3)C$ (1°–3°)	73
C–Br	68
Br–Br	46
O–O	35

Table 2 Reactions on squalane

Entry No.	Reaction conditions	Product yield (%)
1	Squalane (as is)[a]	
2	Br_2 1 ml, DCP 0.5 g, t-BB[b] 50 ml, 100°C, 1.5 h	–[c]
3	Br_2 1 ml, DCP 2 × 0.5 g, t-BB 50 ml, 100°C, 1.5 h	–[c]
4	Br_2 1 ml, DCP 2 × 0.5 g, 100°C, 1.5 h	76.30
5	DCP 2 × 0.5 g, 100°C, 1.5 h	81.56
6	Br_2 1 ml, 55°C, 1.5 h	70.58
7	Br_2 1 ml, 100°C, 1.5 h	79.18
8	Br_2 1 ml, 55°C, 1.5 h[d]	63.11
9	Br_2 1 ml, 100°C, 1.5 h[d]	73.20
10	Br_2 1 ml, 170°C, 10 s[d]	64.01
11	170°C, 2 h	75.92
12	DCP 2 × 0.51 g, 170°C, 1.5 h	65.68

[a] Experiments 2–12, 10 ml squalane was used. In all the reactions, 1 equivalence of squalane to 1 equivalence of bromine was used. Reaction was carried out with positive nitrogen pressure, water condenser was used to avoid bromine escape. After the neat reactions were carried out, it was diluted with dichloromethane, washed consecutively with excess of water, sodium bisulfite, water and dried over anhydrous sodium sulfate. Organic solvent was removed before the analysis. No bromine was used in Experiments 5, 11 and 12

[b] t-BB = t-butylbenzene

[c] Reaction was carried out in t-butylbenzene and analysed directly without measuring the yield

[d] The reaction mixture was stirred in a closed system

Bromination of squalane at 55°C is low. In the case of a closed system, the level of bromination at elevated temperatures was not affected, even though bromine boils off at 59.5°C. Thus, the reaction between gaseous bromine and liquid squalane phase takes place effectively. One can expect bromination to be steady above a certain temperature as dehydrobromination and debromination would take place. Our objective here is to take the reaction temperature to extruder reaction conditions. For example, when a typical extruder reaction at 170°C for ~ 10 s was carried out in a closed system, amount of bromine grafted onto squalane was found to be 2.88 wt%. The effect of temperature on bromination of squalane is shown in *Figure 1*.

Even though we have used a 1/1 molar ratio of substrate to bromine, we obtained lightly substituted products, due to the fact that there was no unsaturation in the starting material. The overall bromine content in the product is tabulated in *Table 3*. Considering each molecule to have only one bromine, the bromination level is observed to be 1–3 bromine atoms in every 20 molecules. However, due to multi-bromination taking place within a molecule, it could be far less than expected bromine in each squalane.

Characterization of lightly brominated model compounds turned out to be quite complex (*Table 4*), as

Table 3 Brominated squalane product analysis

Entry No.	Bromine (%)	G.p.c. M_w	G.p.c. M_n	G.p.c. PD	T.g.a. (°C, 5 wt% loss in N_2 atm.)
1	0	483	479	1.01	220
2	0.97	510	510	1.01	–
3	1.10	515	510	1.02	–
4	2.07	500	480	1.05	174
5	0	350	170	2.03	181
6	0.35	495	460	1.08	215
7	2.32	505	470	1.08	219
8	0.36	490	450	1.08	232
9	2.34	450	420	1.08	206
10	2.88	630	440	1.42	222
11	0	470	450	1.05	214
12	0	690	520	1.33	215

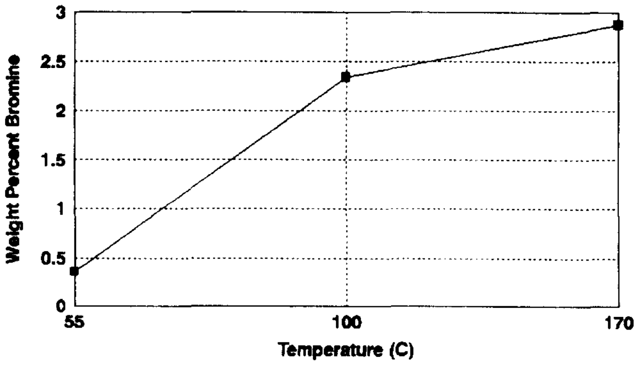


Figure 1 Effect of temperature on bromination of squalane

Table 4 Number of brominated products and bromine concentrations upon squalane bromination

	Bromine concentration observed[a]						
Entry No.	1-1.5[b] wt%	2-24[c] ppm	24-28[d] ppm	30-33[d] ppm	34-36[d] ppm	36-50[d] ppm	Total wt%
1	0	0	0	0	0	0	0
2	0.5	5,363	404	30	80	0	1.09
	(1)	(10)	(10)	(1)	(2)	(0)	(24)
3	0.59	8,323	355	19	19	0	1.46
	(1)	(20)	(11)	(1)	(1)	(0)	(34)
4	2.47	32,936	1,722	98	223	0	5.97
	(1)	(21)	(13)	(3)	(2)	(0)	(40)
5	0	0	0	0	0	0	0
6	0.28	0	60	0	31	0	0.29
	(1)		(2)	(0)	(1)	(0)	(4)
7	3.45	0	2,485	210	399	117	3.75
	(1)		(15)	(3)	(2)	(1)	(22)
8	0.32	0	161	0	39	0	0.34
	(1)		(6)	(0)	(1)	(0)	(8)
9	2.69	0	1,500	107	307	186	2.90
	(1)		(15)	(3)	(2)	(1)	(22)
10	2.40	399	1,743	36	72	0	2.63
	(1)	(10)	(14)	(1)	(2)	(0)	(28)

[a] Peaks were grouped according to 'Retention Time (in min)' as seen in GCAED. Number of brominated peaks found are expressed in parentheses. The entry numbers correspond to those in *Table 2* and *3*

[b] HBr as detected by g.c.-m.s.

[c] Brominated scission products

[d] Post squalane brominated scission products

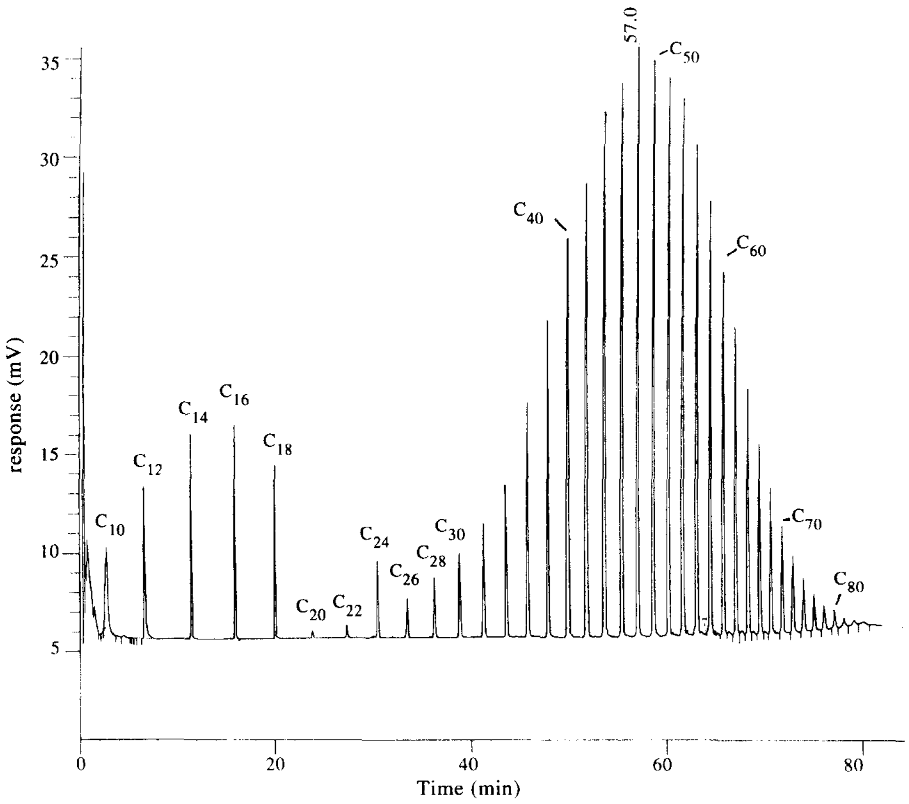


Figure 2 A standard high temperature gas chromatogram up to C_{80} hydrocarbon

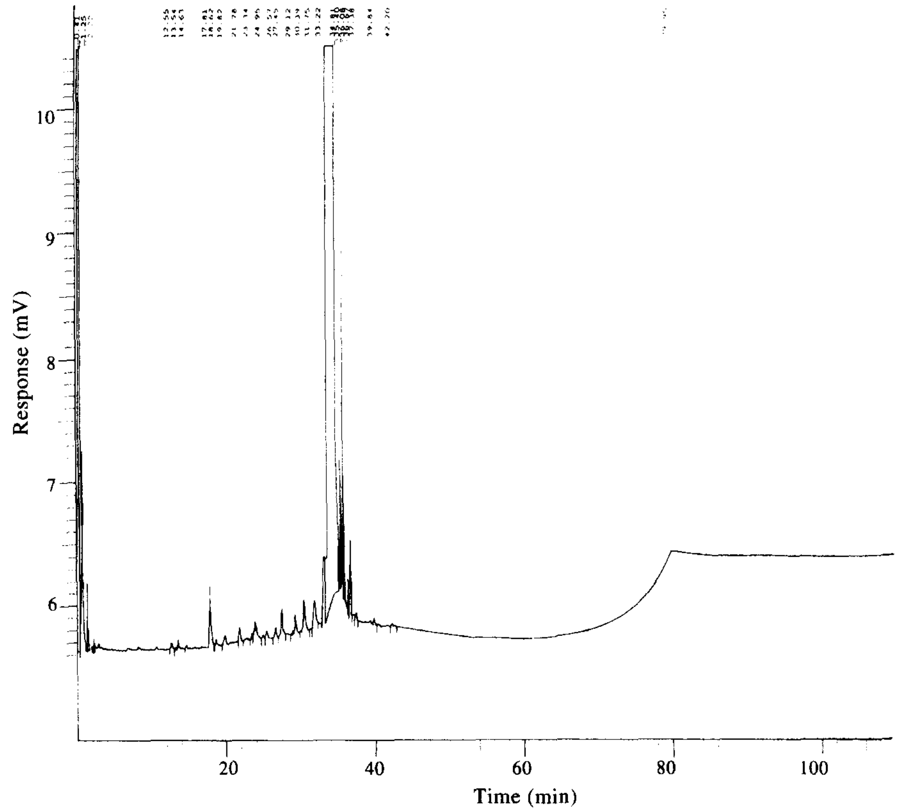


Figure 3 A high temperature gas chromatogram of squalane

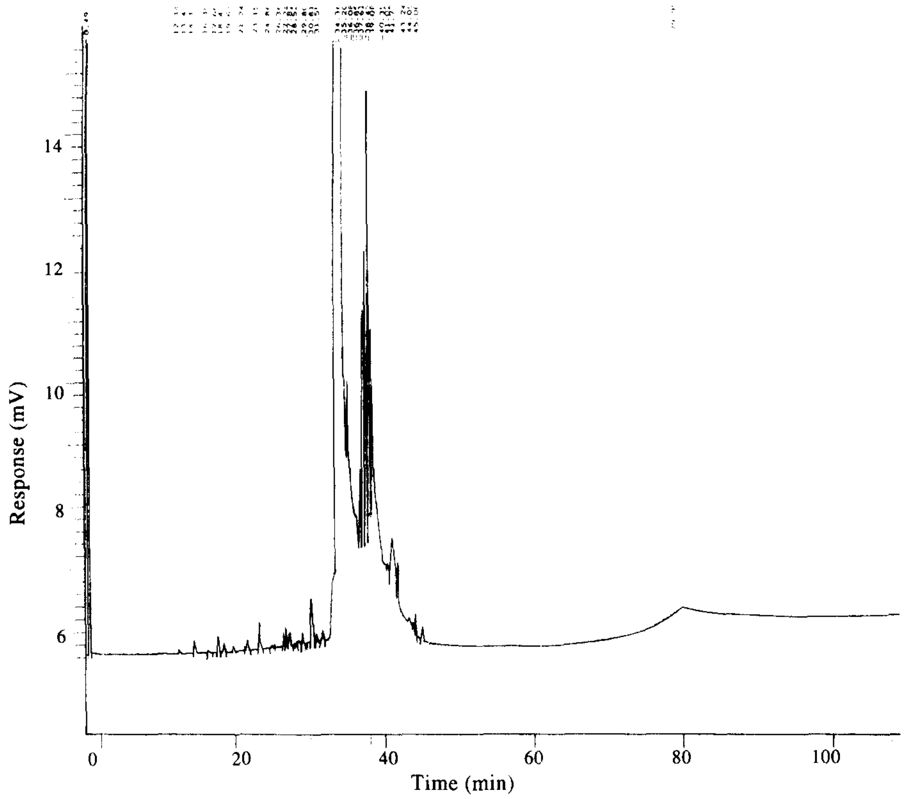


Figure 4 A high temperature gas chromatogram of a typical brominated squalane

expected, in the case of polyolefins. Bromination of squalane primarily occurs at the tertiary carbon, however, minor components of secondary carbon bromination and formation of unsaturated molecules have been observed by ^1H and ^{13}C n.m.r. For quantitative analysis, we used a combination of HTGC, GCAED and mass spectrometric detector (g.c.-m.s.) techniques.

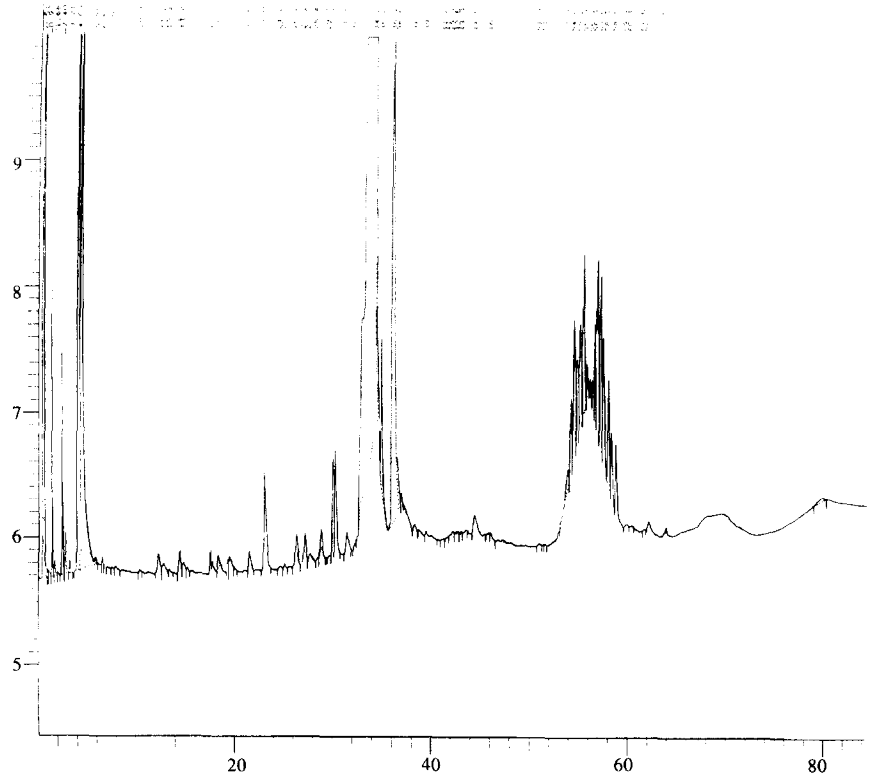


Figure 5 A high temperature gas chromatogram of squalene after treatment with dicumylperoxide

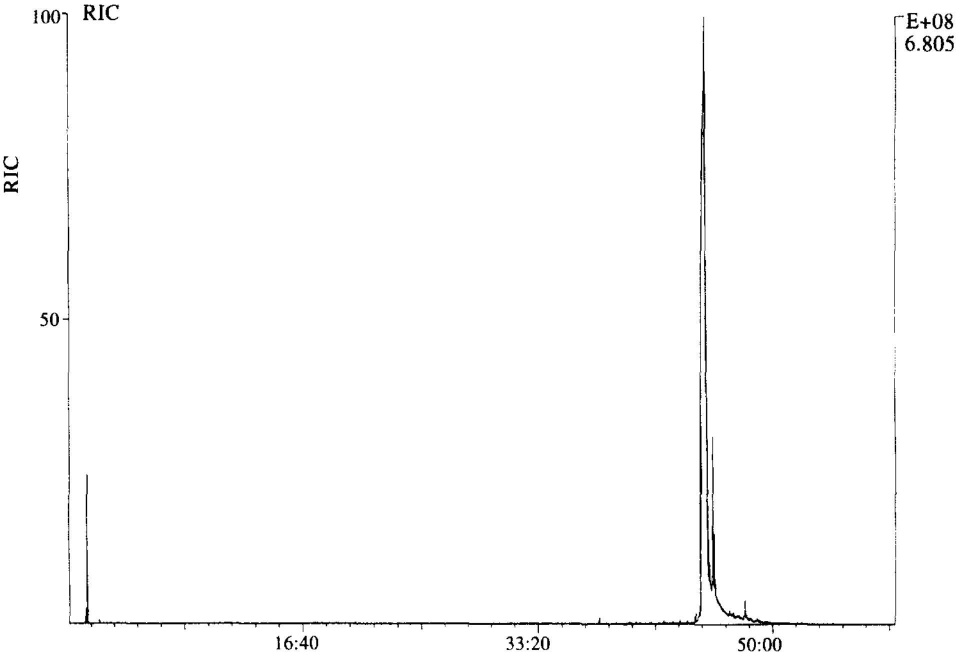


Figure 6 A full g.c.-m.s. spectrum of brominated squalane (Entry 7, *Table 2*)

A standard run of HTGC up to C_{80} hydrocarbons is given in *Figure 2*. *Figure 3* shows the squalane that we used as a substrate. A typical product, after bromination is given in *Figure 4*. Each was subjected to further analysis and the molecular weight and molecular formula deduced. As expected, crosslinking of squalane in the presence of dicumyl peroxide and in the absence of bromine was observed (*Figure 5*). As there was a large number of brominated species, we grouped the peaks into six groups, depending on the number of carbons, and the results were tabulated in *Table 4*.

G.c.-m.s. Analysis of all the samples showed the number of alkanes of lower molecular weight than squalane, with 2–3 isomers of many carbon numbers. Squalane was the major constituent in all samples (> 99%). One such example (*Table 2*, Entry 7) has

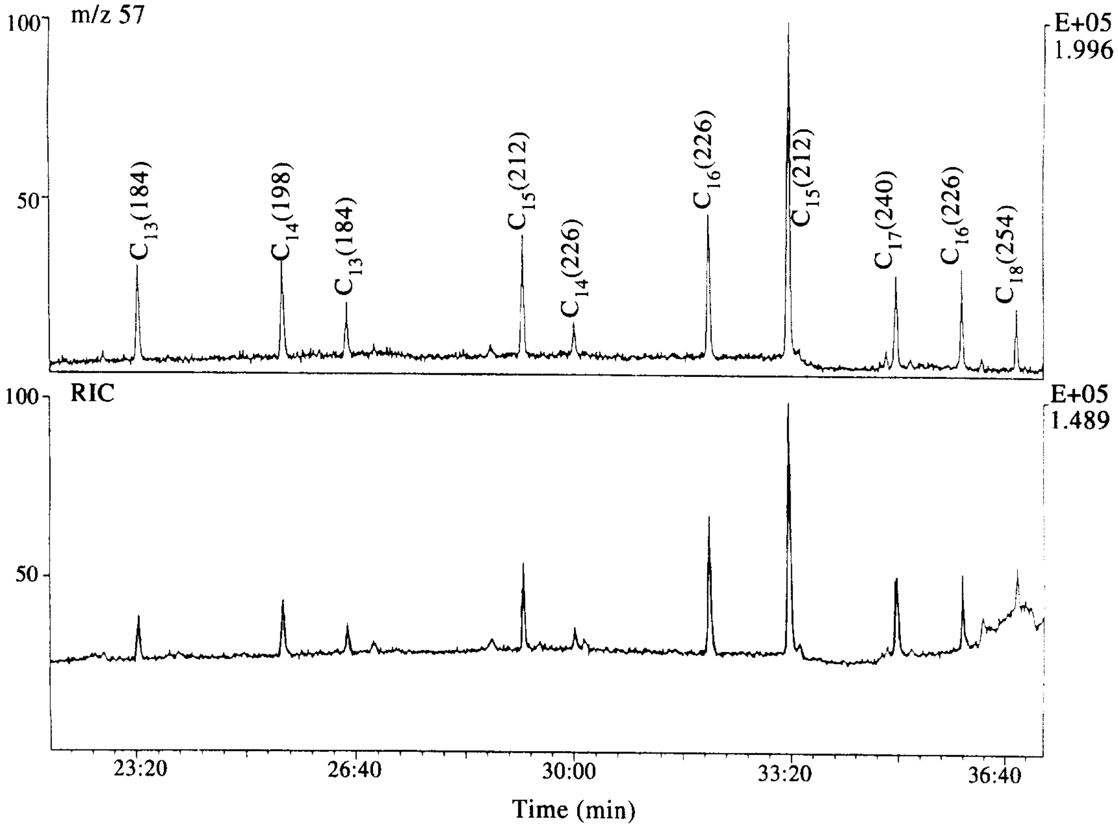


Figure 7 Expanded g.c.-m.s. spectrum of brominated squalane (Entry 7, *Table 2*); peak match to alkane major peak (*m/z* 57)

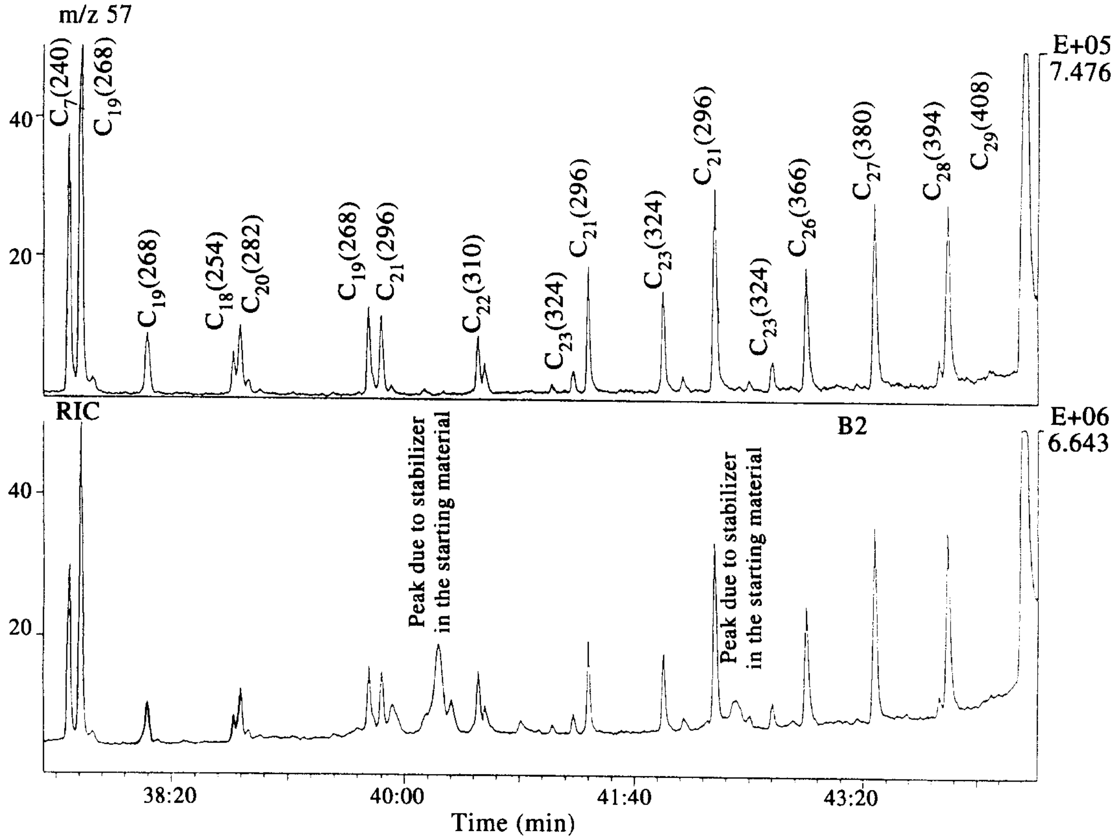


Figure 8 Expanded g.c.-m.s. spectrum of brominated squalane (Entry 7, *Table 2*); peak match to alkane major peak (*m/z* 57)

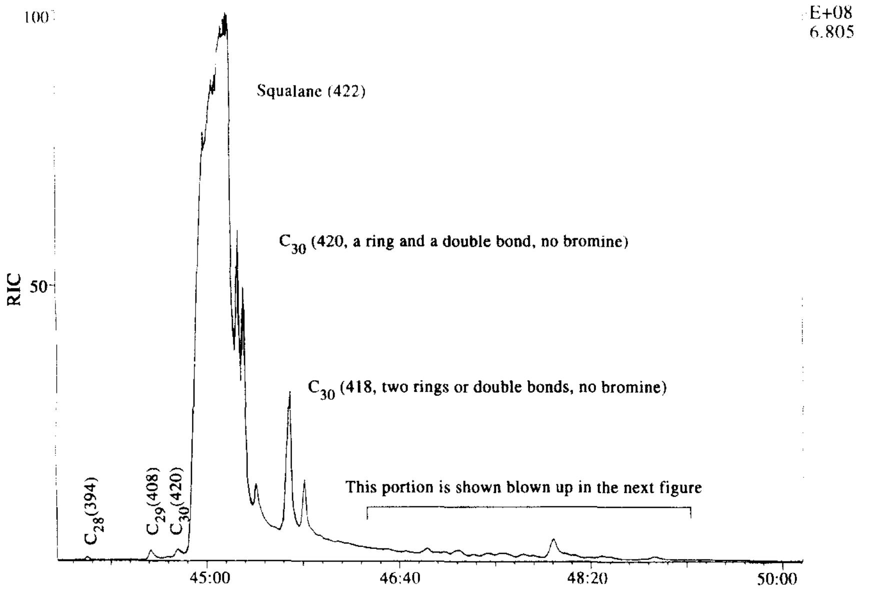


Figure 9 Expanded g.c.-m.s. spectrum of brominated squalane (Entry 7, *Table 2*) showing post-squalane products

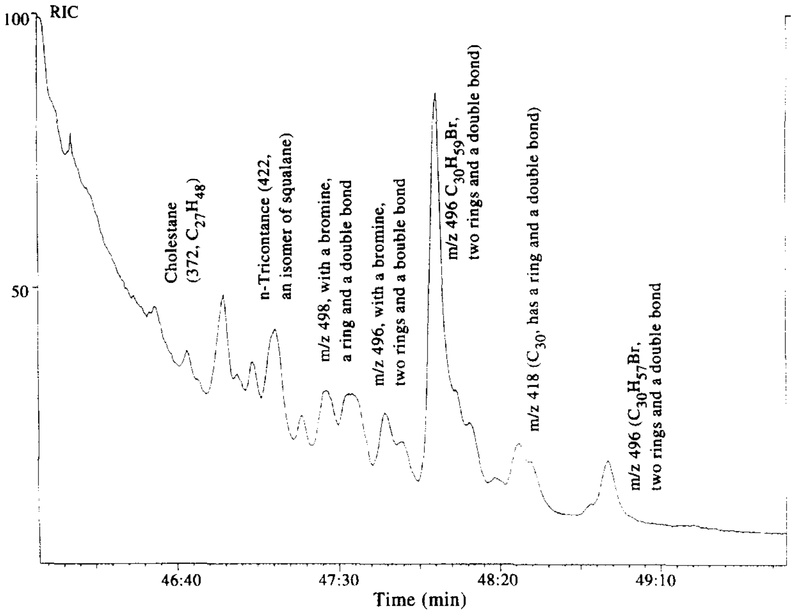


Figure 10 Peak assignment of post-squalane products in g.c.-m.s. spectrum of brominated squalane (Entry 7, *Table 2*)

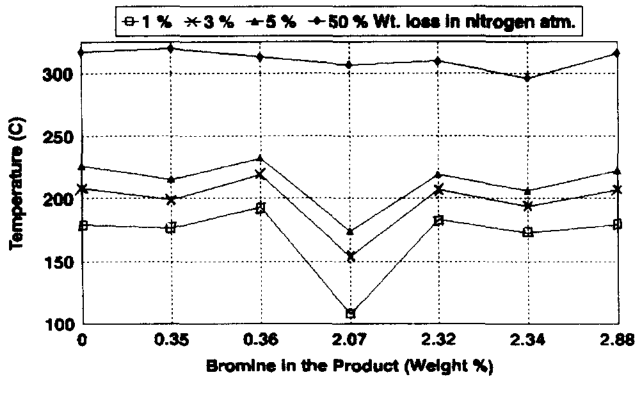
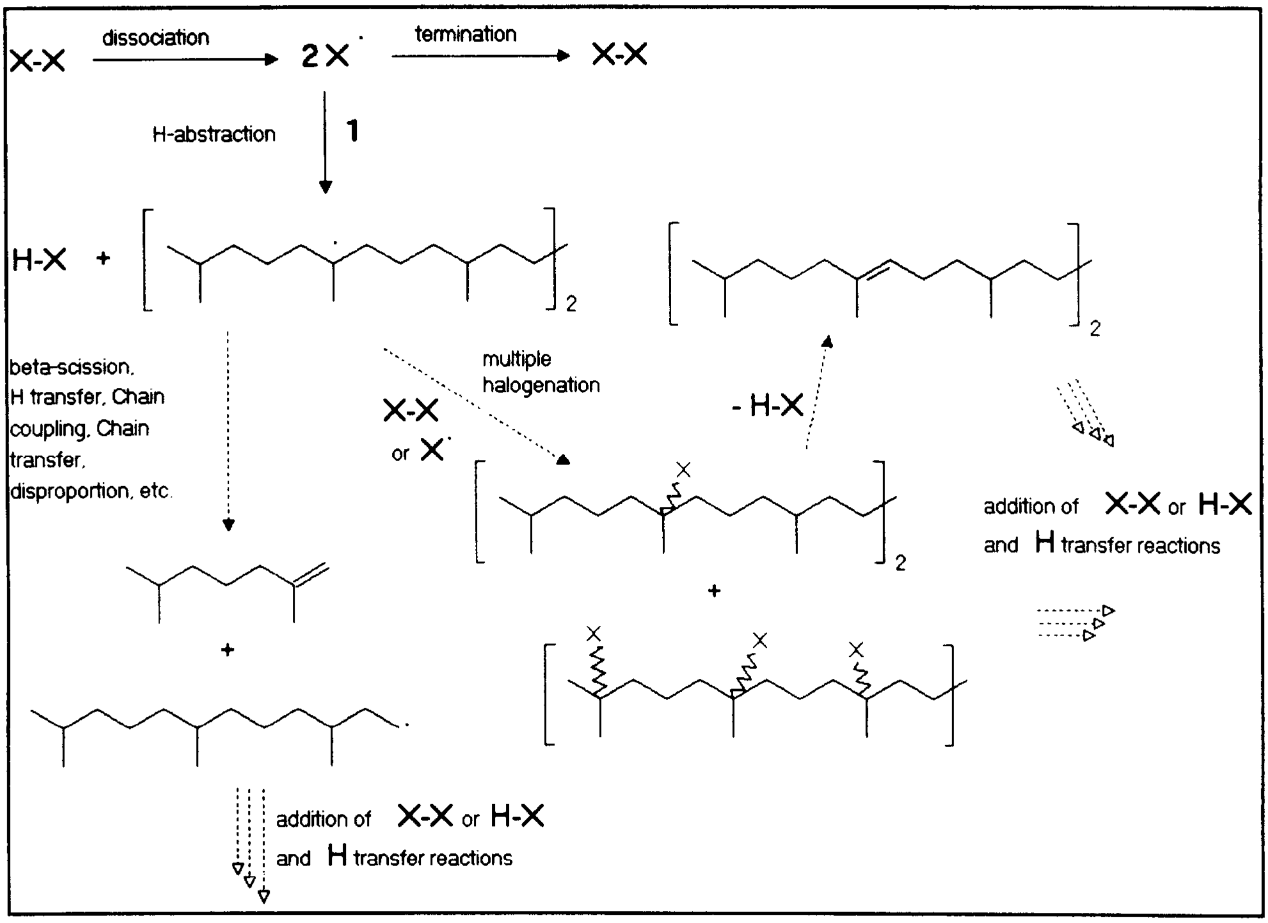


Figure 11 Thermal stability of brominated squalane

been shown in *Figures 6–10*, wherein, several hydrogen-deficient compounds have also been identified. Several brominated compounds have also been qualitatively identified, which was further supported by GCAED results. A combination of HTGC, GCAED, and g.c.-m.s. results shows multiple bromination occurring on all the model compounds. In the presence of a radical initiator, DCP, brominated aromatic compounds have been detected by g.c.-m.s.

The thermal stability (1, 3, 5 and 50% weight loss in nitrogen atmosphere) of all the reaction products were studied using t.g.a. Interestingly, there was no considerable deviation observed from the starting material (*Figure 11*). This indicates no considerable decomposition or degradation while grafting reactions, except in one experiment (Entry 4, *Tables 2* and *3*). Molecular



Scheme 1 Proposed reaction mechanism of bromination of squalane

Table 5 Reactions on 3-methylhexane

		Product analysis				
Entry No.	Reaction conditions	Product yield (%)	Bromine (%)	M_w	M_n	PD
1	3-Methylhexane (as is)[a]		0	–	–	–
2	Br_2 1.059 ml, DCP 2 × 0.56 g, 55°C, 1.5 h	56.89	3.90	2400	540	4.44
3	Br_2 1.059 ml, 55°C, 1.5 h	27.49	1.80	630	630	1.00
4	Bromine 1.059 ml, DCP 0.56 g, 55°C, 1.5 h	35.04	1.43	200	150	1.39
5	DCP 2 × 0.56 g, 55°C, 1.5 h	35.21	0	–[b]	–	–

[a] Experiments 2–5, 3 ml 3-methylhexane was used. T.g.a. (°C, 5 wt% loss in N_2 atm) of product in entry 2 was 164 and that of starting material (entry 1) was 53

[b] G.p.c. was run, but could not get a conclusive value due to the low molecular weight of the product

weight determination of the products using gel permeation chromatography (g.p.c.) supported the HTGC and GCAED results.

Halogenation in polyolefins is known to occur initially in the amorphous region, followed by gradual halogenation into the crystalline region. Consequently, halogenated products are known to be blocky in nature. In addition, we believe from these model studies that monobromination creates an acidic proton in the hydrocarbon molecule. This leads to multiple bromination on the same site. Alternatively, at elevated temperatures debromination or dehydrobromination is possible. This leads to unsaturation. At the same time, addition reactions by bromine and HBr at these sites would lead to a blocky nature in the polymer. A tentative mechanism has been proposed which is supported by ^1H and ^{13}C n.m.r., HTGC, GCAED and g.c.-m.s. results (*Scheme 1*).

Bromination of 3-methylhexane

3-Methylhexane is a much smaller molecule than squalane, with formula weight 100. The results observed (*Table 5*) were similar to those of squalane, with the exception of the increase in molecular weight of the products. An increase in the thermal stability of products was also observed. Thus, the crosslinking reaction seems to predominate along with multiple bromination

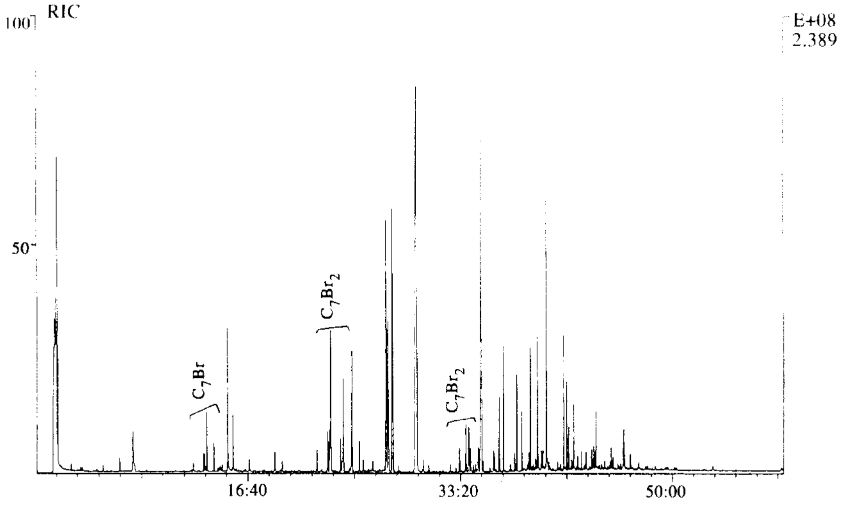


Figure 12 G.c.-m.s. spectrum of brominated 3-methylhexane in presence of dicumylperoxide

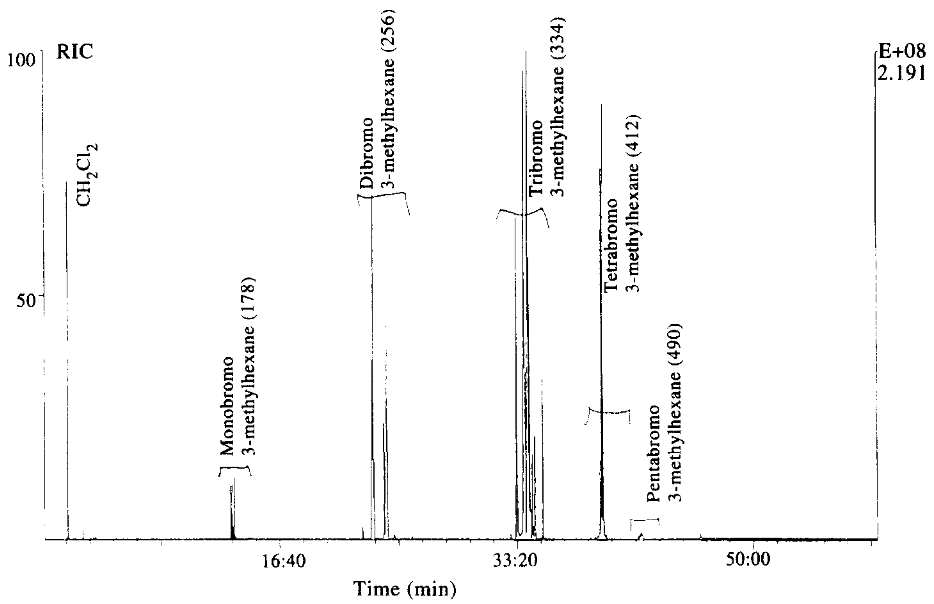


Figure 13 G.c.-m.s. spectrum of brominated 3-methylhexane in absence of dicumylperoxide

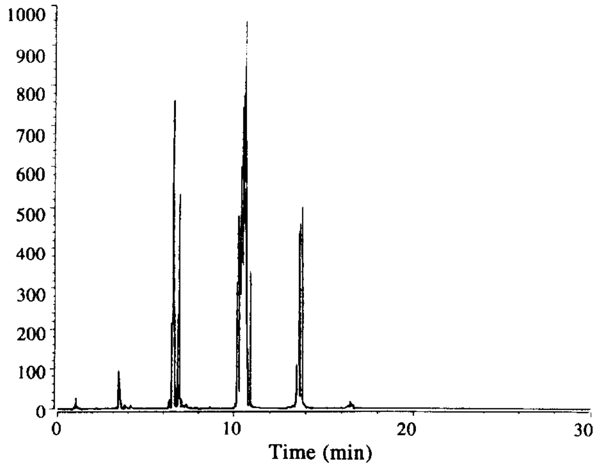


Figure 14 GCAED spectrum of brominated 3-methylhexane in absence of dicumylperoxide

reaction in 3-methylhexane. Considering each molecule has only one bromine, the bromination level is observed to be 1–2 bromine atoms in every 40 molecules of 3-methylhexane. However, due to multi-bromination taking place, it could be far less than expected bromine in each 3-methylhexane molecule.

It is clear from *Figures 12* and *13* that the presence of dicumyl peroxide complicates analysis of the product. In addition to the multiple brominated 3-methylhexane products, DCP and brominated cumene derivatives are also detected in the product. Interestingly, in the absence of DCP, g.c.-m.s. and GCAED spectra (*Figures 13* and *14*) appear to be the same, even though peaks appeared at different retention times due to the different g.c. columns. A combination of g.c.-m.s., GCAED and XRF (quantitiation of total bromine content) analysis led to quantitation of the different bromomethylhexanes present in the crude product (*Table 6*). The n.m.r. spectra of

Table 6 3-Methylhexane bromination quantitation of brominated products[a]

Group No.	Retention time (min)	Empirical formula	Amount[b] (ng)	Weight (%)	Area (%)
1	3–5	$C_7H_{13}Br$	129.6	3.3	2.3
2	6–8	$C_7H_{12}Br_2$	996.2	25.4	23.2
3	9–12	$C_7H_{11}Br_2$	2223.3	56.7	58.6
4	12.5–15.5	$C_7H_{10}Br_4$	553.0	14.1	15.4
5	16–17.5	$C_7H_9Br_5$	19.9	0.5	0.6

[a] Quantitation of the product described in *Table 5*, Entry 2. The group number corresponds to the group marked in *Figure 14*

[b] Total bromine present in the product was 3.9 wt%

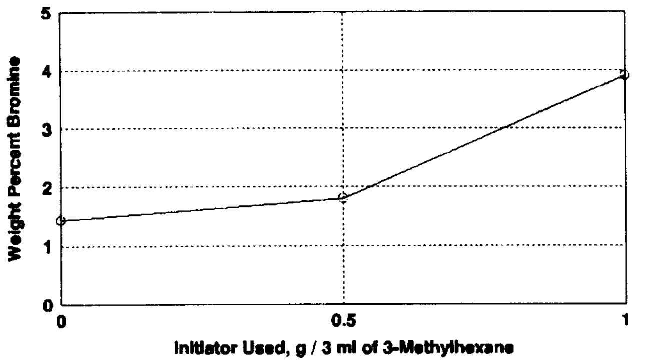


Figure 15 Effect of initiator concentration on bromination of 3-methylhexane

products to 3-methylhexane were compared. These comparisons confirmed the bromination; the presence of C$\underline{H}$-Br (δ 5–3.8) and C$\underline{H}_2$C-Br (δ 2.5–1.5) were detected. Integration of these peaks vs starting material 3-methylhexane provides an estimate of conversion, which were in accord with the more accurate GCAED determinations. Unlike squalane, in the case of 3-methylhexane, increasing DCP concentration increases bromine grafting (*Figure 15*).

Table 7 Reactions on nonane

Entry No.	Reaction conditions	Product analysis (%) Yield	Bromine
1	Nonane (as is)[a]	–	0
2	Br_2 3.28 ml, DCP 2 × 0.86 g, 100°C, 1.5 h	73.55	6.25
3	DCP 2 × 0.86 g, 100°C, 1.5 h	62.08	0
4	Br_2 3.28 ml, 100°C, 1.5 h	76.30	4.99

[a] Experiments 2–4, 10 ml nonane was used

Table 8 Bromine concentrations in brominated nonane

	Bromine concentration observed[a]				
Entry No.	6–8 (ng)	8–11.5 (ng)	11.5–14 (ng)	14–17.5 (ng)	Total (wt%)
2	825.0	722.7	310.1	1093.4	6.25
4	1959.8	370.8	45.1	14.2	4.99

[a] Peaks were grouped according to 'Retention Time (in min)' as seen in GCAED. The entry numbers corresponds to those in *Table 7*

Bromination of nonane

We expected nonane (with no tertiary carbon present) to show different bromination pattern. Surprisingly, bromine content in the product (*Table 7*) was observed to be higher than that of squalane and 3-methylhexane, even though later compounds have more reactive tertiary carbons. Interestingly, we did not observe any post-nonane products, either in g.p.c. or in HTGC. However, mono- to penta-bromononane were identified in g.c.-m.s. and GCAED. The wt% bromine obtained for different samples at different retention times has been calculated (*Table 8*).

^{1}H n.m.r. or brominated nonane and nonane is shown in *Figures 16* and *17*, wherein well separated product C$\underline{H}$–Br and C$\underline{H}_2$–CBr can be identified. Considering each molecule has only one bromine, the bromination level is observed to be 3–5 bromine atoms in every 40 molecules of nonane. However, due to multi bromina-

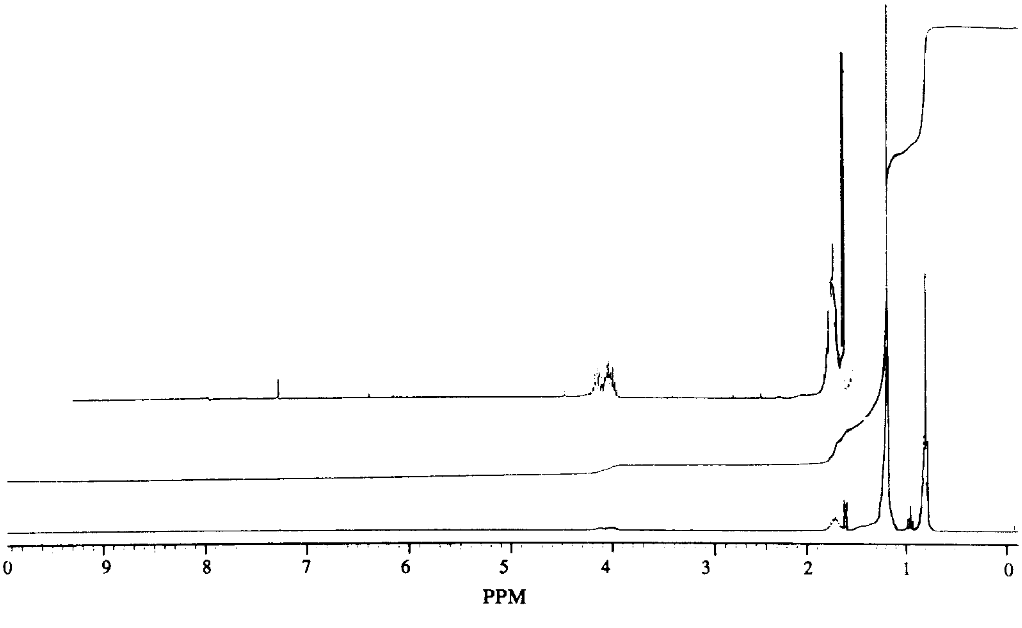


Figure 16 Proton n.m.r. spectrum of brominated nonane

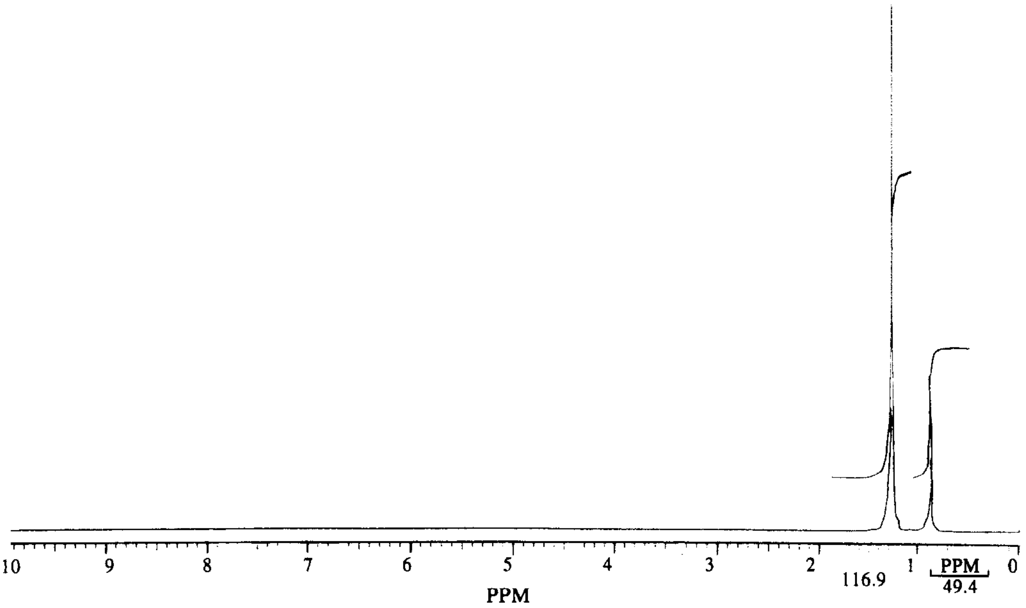


Figure 17 Proton n.m.r. spectrum of nonane

tion taking place, it could be far less than expected bromine in each nonane molecule.

CONCLUSION

Bromination on the model compounds squalane, 3-methylhexane and nonane clearly shows how enormously complicated radical grafting reactions in polyolefins could be. Product analysis by several techniques showed the presence of 8–40 brominated species depending on the reaction conditions and substrates (C_7 to C_{30} hydrocarbons). In the presence of DCP, bromination of model compounds led to large amounts of brominated aromatic compounds as side products originating from the initiator itself.

Free-radical bromination of hydrocarbons as carried out in the presence or absence of radical initiators at 55°C and above. We have also shown bromination in the absence of initiators can eliminate several side products. Multiple brominations were preferred at the same site and on a same molecule, because of the acidic proton alpha to the bromide moiety. Characterization of all the products have been carried out by novel techniques. A possible radical reaction pathway has been suggested (*Scheme 1*).

Molecular weight and thermal analysis showed that there was no termination via crosslinking in the case of squalane and nonane. However, formation of high molecular weight oligomers were observed in the case of 3-methylhexane.

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