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Polymer 41 (2000) 3137–3145

polymer

Graft copolymerisation studies
Part 1. Models related to polyolefins

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Received 25 May 1999; received in revised form 19 July 1999; accepted 28 July 1999

Abstract

The chemistry of free radical graft copolymerisation, initiated with *t*-butoxy radicals, has been investigated using 3-methylpentane and 2,4-dimethylpentane as models for LLDPE and PP, respectively. The tertiary C–H reaction site of 3-methylpentane is twice as reactive as the secondary position. However, the site of grafting from the polymer is determined by the concentration of tertiary and secondary reaction sites and the relative reactivity at these positions and hence grafting occurs most frequently from the secondary C–H reaction sites. Abstraction from 2,4-dimethylpentane is solvent dependent and occurs most readily at the tertiary position. Therefore, grafting will be predominantly concentrated at the tertiary C–H site. The models also indicate that PP is less reactive than LLDPE. Competition reactions between 3-methylpentane and the monomers methyl methacrylate, styrene or 4-vinylpyridine suggest that the nucleophilicity of the monomer influences the competing abstraction–monomer initiation reactions. Evidence for grafting methyl methacrylate from 3-methylpentane is also presented. This study also provides evidence of the incorporation of peroxide linkages into the graft even when standard deoxygenating techniques are used.

Keywords: Free radical grafting; *t*-Butoxy radicals; Model compounds

1. Introduction

The properties of polyolefins may be extended by chemical modification introducing polarity and/or functionality from the polymer backbone [1,2]. Free radical grafting of vinyl monomers from polyolefins is one of the oldest and cheapest approaches with the additional attraction of being readily applied in many existing industrial processes [3,4]. The generally accepted radical facilitated graft copolymerisation mechanism involves the Eqs. (1)–(4), where I· is the primary radical, P–H is the polyolefin backbone and M is the monomer. The relative rates of (2) and (3), in competition with (4), are of critical importance for successful graft copolymerisation [5]:

$$I_2 \rightarrow 2I\cdot \quad (1)$$

$$I\cdot + P\text{–}H \rightarrow P\cdot + I\text{–}H \quad (2)$$

$$P\cdot + M \rightarrow P\text{–}M\cdot \quad (3)$$

$$I\cdot + M \rightarrow I\text{–}M\cdot \quad (4)$$

The analysis of graft modified polyolefins is complicated [6] and we have chosen firstly to examine model systems to gain data that can then be applied to conventional polyolefin-graft formation. 3-Methylpentane and 2,4-dimethylpentane were chosen as the substrates to model the commercial polyolefins linear low density polyethylene (LLDPE) and polypropylene (PP), respectively. The chosen monomers were methyl methacrylate (MMA), styrene and 4-vinylpyridine. Di-*t*-butyl peroxalate was chosen as the initiator since it yields *t*-butoxy radicals at low temperatures [7]. These radicals exhibit an enhanced propensity for hydrogen abstraction [8–10] compared to other primary radicals [11] over addition to monomer.

This paper reports on the reaction of 3-methylpentane and 2,4-dimethylpentane toward *t*-butoxy radicals. Competition reactions between 3-methylpentane and the vinyl monomers toward *t*-butoxy radicals are also reported and the evidence for grafting methyl methacrylate from 3-methylpentane is discussed. The significance of these results to radical facilitated grafting from LLDPE and PP is presented. The theoretical implications of the data have been discussed elsewhere [12].

2. Experimental

The general experimental data is reported elsewhere [12].

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0032-3861/00/$ - see front matter
PII: S0032-3861(99)00529-7

2.1. Substrates

Di-*t*-butyl peroxalate was prepared by the method of Bartlett et al. [7]. 1,1,3,3-Tetramethylisoindoline-2-oxy (**5**) [13] and 2-(1′-methyl)-1,1,3,3-tetramethylisoindoline (**6**) [14] were prepared according to published procedures. The products (**7**)–(**13**) [12] and methyl methacrylate [15] and styrene [16] initiation products were identified by comparison with authentic samples. New compounds were identified by isolation by preparative HPLC and spectroscopic analysis.

3-^{13}C-Methyl-pentane was prepared in three steps. 3-^{13}C-Methyl-3-pentanol was prepared from 3-pentanone, 99 at.% ^{13}C, ^{13}C-iodomethane (Aldrich), and lithium metal according to the procedure of Pearce et al. in 63% yield [17]. The alcohol was heated in the presence of $CuSO_4$ affording a mixture of 1-^{13}C-2-ethylbutene, *cis*- and *trans*-3-^{13}C-methyl-2-pentene in 72% [18]. Hydrogenation of the alkene mixture gave the desired product as a clear liquid in 56% yield.

3-Methylpentane (TCI General Reagents) and 2,4-dimethylpentane (Aldrich), were used as supplied. Styrene (Aldrich), 4-vinylpyridine (Aldrich) and MMA (Aldrich), were passed through a plug of basic alumina then distilled immediately before use. The chromatography solvents, methanol and water, were distilled and filtered before use.

2.2. Radical trapping experiments: general procedure

Reaction mixtures consisted of di-*t*-butyl peroxalate (0.05 mmol) and 1,1,3,3-tetramethylisoindoline-2-oxy (0.11 mmol) in 3-methylpentane or 2,4-dimethylpentane (5.50 mmol). Reactions were also performed in benzene (0.5 ml). Competition reactions consisted of di-*t*-butyl peroxalate (0.05 mmol), 1,1,3,3-tetramethylisoindoline-2-oxy (0.11 mmol), 3-methylpentane (1.00–20.00 mmol) and monomer (1.00 mmol) in benzene (0.50 ml). The solutions were degassed by successive freeze, pump and thaw cycles on a reduced pressure vacuum line, [19] then heated at 60 ± 1°C, for 70 min (10 initiator half lives) [7]. Quantitative product analysis was established by directly injecting the reaction mixtures into the reverse-phase HPLC system. Integrated HPLC peak areas were converted directly into percentage yields based on extinction coefficients of the UV chromophores at 270 nm [20].

2.2.1. 2[2′-t-Butoxy-1′-(4-pyridine)ethoxy]-1,1,3,3-tetramethylisoindoline[1]

(Found: MH^+, 369.2548. $C_{23}H_{33}N_2O_2$ requires MH^+, 369.2544); *m/z* 369 (MH^+), 190 (MH^+–$CH(C_5H_4N)CH_2OC(CH_3)_3$); δ_H 0.89 (s, 3H, ring methyls), 1.17 (s, 9H, $OC(CH_3)_3$), 1.28 (s, 3H, ring methyls), 1.49 (s, 3H, ring methyls), 1.66 (s, 3H, ring methyls), 3.41 (dd, 1H, J 4.8, 4.9, H2′), 3.80 (dd, 1H, J 7.6, 2.3, H1′), 4.85 (dd, 1H, J 5.1, 2.4, H2′), 6.98–7.34 (m, 9H, ArH); δ_C 25.2, 25.4 (ring methyls), 27.4 ($OC(CH_3)_3$), 29.5, 29.7 (ring methyls), 64.7 (C2'), 67.0, 68.3 (C1, C3), 73.3 ($OC(CH_3)_3$), 87.2 (C1′), 121.4, 121.6 (C4, C7) 122.9 (ArC), 127.2 (C5, C6), 144.8, 145.1 (C3a, C7a), 149.5 (ArC), 150.6 (ArC).

2.2.2. 2[2′-(1″-Ethyl-1″-methyl-propylperoxy)-1′-phenylethoxy]-1,1,3,3-tetramethylisoindoline (12)

(Found: MH^+, 412.2817. $C_{26}H_{38}NO_3$ requires MH^+, 412.2853); *m/z* 412 (MH^+), 190 (MH^+–$CH(C_6H_5)CH_2OOC(CH_3)(CH_2CH_3)_2$); δ_H 0.72 (s, 3H, ring methyls), 0.88 (t, 6H, J 7.5, H3″), 1.15 (s, 3H, C1″–CH_3), 1.24 (s, 3H, ring methyls), 1.50 (s, 3H, ring methyl), 1.56 (q, 4H, J 7.5, 4.7, H2″), 1.68 (s, 3H, ring methyls), 4.01 (dd, 1H, J 3.7, 7.4, H2′), 4.40 (dd, 1H, J 8.8, 2.2, H1′), 5.02 (dd, 1H, J 3.7, 5.2, H2′), 6.95–7.38 (m, 9H, ArH); δ_C 8.0 (C3″), 21.2 (C1″–CH_3), 25.2, 25.3 (ring methyls), 28.9 (C2″), 29.2, 29.5 (ring methyls), 66.8 (C2′), 68.2 (C1, C3), 84.4 (C1″), 85.8 (C1′), 121.3, 121.6 (C4, C7), 127.0 (C5, C6), 127.8 (ArC), 127.9 (ArC), 128.1 (ArC), 141.1 (ArC), 145.1, 145.3 (C3a, C7a).

2.2.3. 2[2′(1″-Ethyl-1″-methyl-propylperoxy)-1′-(4-pyridine)ethoxy]-1,1,3,3-tetramethylisoindoline (14)

δ_C 8.0 (C3″), 21.1 (C1″–CH_3), 25.2, 25.4 (ring methyls), 28.9, 29.0 (C2″), 29.6 (ring methyls), 67.1 (C2′), 68.3 (C1, C3), 84.5 (C1″), 85.0 (C1′), 121.4, 121.6 (C4, C7), 122.6 (ArC), 127.2 (C5, C6), 144.6, 144.9 (C3a, C7a), 149.7 (ArC), 150.0 (ArC).

The NMR data for (**11**) and (**13**) are not reported because of the complicated nature of the spectra due to the presence of three chiral carbons affording eight diastereoisomers.

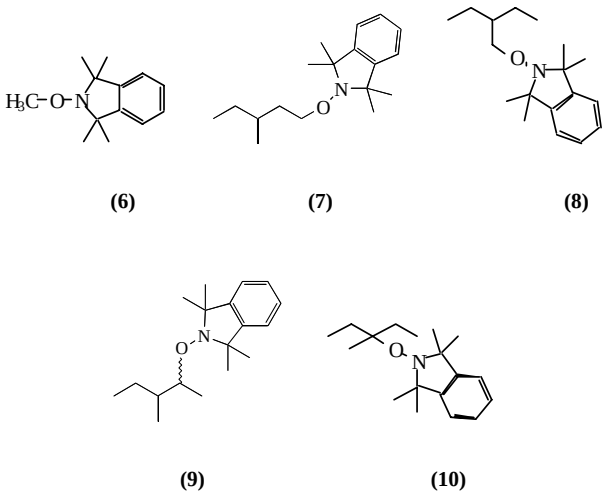
2.3. Grafting experiments: general procedure

Reaction mixtures consisted of di-*t*-butyl peroxalate (0.50 mmol), 3-methylpentane (0, 1.10 and 50.0 mmol), MMA (10.0 mmol) and benzene (5.0 ml). Reactions were also performed using 25% by mass of 15% ^{13}C-3-methylpentane (12.5 mmol). The solutions were degassed [19] then heated at 60 ± 1°C, for 70 min. Concentration of solution under reduced pressure afforded a viscous solution. Precipitation from cold light petroleum afforded a mixture of 3-methylpentane-*graft*-poly(MMA) and poly(MMA) as a fine white powder.

3. Results

The competing reactions in graft copolymerisation involving *t*-butoxy radicals, monomer and polymer are shown in Eqs. (1)–(4). A further competing reaction is the β-scission of *t*-butoxy radicals to form methyl radicals and the extent of this alternative pathway is a measure of substrate reactivity [9]. The radical trapping technique, developed by Rizzardo and Solomon [21] enables reaction between the *t*-butoxy radicals with the model compounds, monomer and

[1] Product from the reaction of di-*t*-butyl peroxalate and 4-vinylpyridine in the presence of the radical trapping agent.

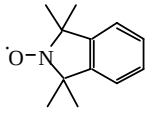


(6) **(7)** **(8)**

(9) **(10)**

Fig. 1. Products from the reaction of 3-methylpentane and *t*-butoxy radicals in the presence of (**5**).

the competing reaction to be investigated. The method relies on the near diffusion controlled rate (10^7–10^9 l mol^{-1} s^{-1}) [22] at which nitroxide reagents combine with alkyl radicals affording relatively stable alkoxyamines. The trapping technique has therefore found wide use in the isolation of reactive radical intermediates [11]. The nitroxide trapping reagent 1,1,3,3-tetramethylisoindoline-2-oxy (**5**) [13] was used in the present study.



3.1. Reaction of di-t-butyl peroxalate with 3-methylpentane

The decomposition of di-*t*-butyl peroxalate in 3-methylpentane and (**5**) gave a mixture of six alkoxyamine products. These include the methoxyamine (**6**) [14] from *t*-butoxy radical β-scission, and the four positional isomers (**7**)–(**10**), including the diastereoisomers of (**9**) (Fig. 1).

The product distribution reflects the relative amounts of hydrogen abstraction from 3-methylpentane in neat solution (Table 1). The distribution is not modified by dilution in benzene [12]. The values are determined from the ratio of each product formed to the sum of (**7**)–(**10**). Abstraction from the tertiary and secondary C–H reaction sites accounts for almost 90% of the total distribution with comparable yields obtained from these two positions. Since in the model there are two secondary C–H sites for each tertiary position, approximately twice as much reaction is expected at the tertiary reaction site. The position of grafting is however determined by the concentration of tertiary and secondary reaction sites and the relative reactivity at these positions.

Table 1
The relative amounts of hydrogen abstraction from 3-methylpentane using *t*-butoxy radicals in neat solution. ([3-Methylpentane] = 7.7 mol l^{-1})

Product	Site of abstraction	Relative yield (%)[a]
(**7**)	Acyclic primary	8.1 ± 0.1
(**8**)	Branch primary	3.2 ± 0.1
(**9**)	Secondary	45.0 ± 0.8
(**10**)	Tertiary	43.7 ± 0.7

[a] Percentage yield determined by HPLC.

3.2. Reaction of di-t-butyl peroxalate with 3-methylpentane and MMA

Solomon and co-workers have reported the reaction of MMA [15,20] styrene [16] and several other monomers toward *t*-butoxy radicals in the presence of a radical trapping agent to study primary radical initiation. Therefore, a study of a mixed system of di-*t*-butyl peroxalate, 3-methylpentane and MMA can be used to model radical facilitated grafting. During this study varying amounts of 3-methylpentane were used whilst maintaining the amount of initiator and monomer constant in benzene.

The distribution of (**7**)–(**10**) is not modified by dilution in MMA. Reaction of equimolar concentrations of 3-methylpentane and MMA gives similar amounts of (**7**)–(**10**) (51.2% as determined by HPLC), and monomer initiation derived products. As is to be expected, formation of (**7**)–(**10**) is favoured at high substrate concentrations. However, the amount of (**7**)–(**10**) produced begins to plateau above five molar equivalents of the model compound due to the near quantitative favouring of hydrogen abstraction. The decline in the monomer initiation derived products mirrors the formation of (**7**)–(**10**) (Fig. 2a). This suggests that five molar equivalents of 3-methylpentane to methyl methacrylate is the optimum concentration ratio for this example as further increasing the amount of substrate will only afford more material that is not attacked by *t*-butoxy radicals (Fig. 2b).

3.3. Reaction of 3-methylpentane and MMA towards t-butoxy radicals: ^{13}C NMR study

The reaction of di-*t*-butyl peroxalate, 3-methylpentane and MMA was also investigated without the nitroxide agent to determine if there is evidence for grafting the monomer from 3-methylpentane. Polymerisations were performed using five molar equivalents of 3-methylpentane to monomer, previously established as the optimum conditions for abstraction, and 10 molar equivalents of monomer. The amount of initiator and monomer was kept constant whilst varying the amounts of 3-methylpentane.

Fig. 3 shows the downfield region of the ^{13}C NMR spectra for the 3-methylpentane-*graft*-poly(MMA) and poly(MMA) mixture. The C_α (quaternary carbon atom), C_β (secondary carbon), methyl and methoxy carbon signals of the homopolymer are shown in Fig. 3a. The signal at 27 ppm is assigned to the methyl carbons of the *t*-butoxy end group.

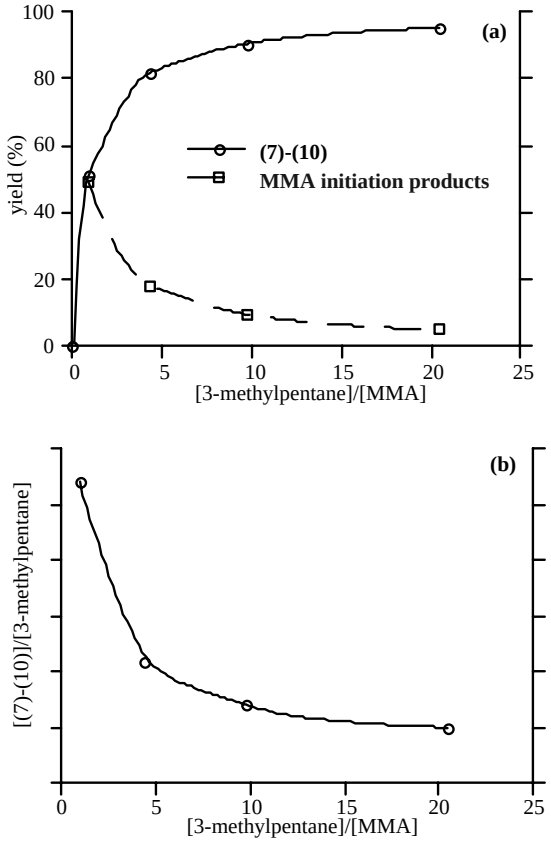


Fig. 2. (a) Yields of (**7**)–(**10**) and MMA initiation products; (b) (**7**)–(**10**) to 3-methylpentane concentration versus 3-methylpentane to MMA concentration.

The quaternary *t*-butoxy carbon resonance is upfield at 72 ppm [23]. Table 2 shows some of the more distinguishable chemical shifts of the 3-methylpentane-*graft*-poly (MMA) end groups. These assignments are based on the chemical shifts of aliphatic methyl ester derivatives [24].

The concentration of the *t*-butoxy end group is monitored by comparing the signal intensity at 27 ppm with the height of the C_α signal. The height of these two signals is similar for the control homopolymer sample. Addition of excess monomer affords a small reduction in the concentration of the *t*-butoxy end group (Fig. 3a). A much more noticeable reduction is found on addition of excess substrate (Fig. 3b). This is most likely due to an increase in the amount of graft obtained (compare intensity of 3-methylpentane end groups in Fig. 3a and b), although it is not possible from the spectra presented in this paper to determine the amount of graft and initiator derived end groups.

The addition of 25% by mass of 15% 3-^{13}C-methylpentane gave signals that were easier to detect and therefore assign (Fig. 3c). For example, the signal at 31.5 ppm located between the envelope at 31 and 32 ppm is good evidence for grafting from the branched methyl unit of 3-methylpentane. By comparing the height of the C4′ signal of the tertiary grafted product (24 ppm), with the C5′ signals of the secondary product (14 and 15 ppm), we tentatively predict that approximately twice as much reaction is expected at the tertiary position. This correlates with the radical trapping study. However, the concentration of tertiary and secondary reaction sites and the relative reactivity at these positions determine the grafting site from the polymer.

Preliminary ^{13}C NMR experiments on the crude reaction mixture also show evidence for the dimerisation of the 3-methylpentanyl radicals particularly at high substrate concentrations. Similar products were not detected in the model trapping study because near diffusion controlled trapping of the alkyl radicals affords (**7**)–(**10**) in almost quantitative yields based on the initiator [12]. Even though the formation of the dimerisation products was not investigated in detail, such alternative reaction pathways can compete with MMA-grafting resulting in a reduction in the amount of graft produced. This is illustrated by the reduction in the yield of the 3-methylpentane-*graft*-poly(MMA) and poly (MMA) mixture from 65 to 22% using the excess of substrate.

3.4. Reaction of di-t-butyl peroxalate with 3-methylpentane and styrene, 4-vinylpyridine

The decomposition of di-*t*-butyl peroxalate in a mixture of 3-methylpentane, styrene or 4-vinylpyridine and (**5**) gave a mixture of (**6**), (**7**)–(**10**), the respective styrene, [16] 4-vinylpyridine[2] initiation products and (**11**)–(**14**) (Fig. 4). The distribution of (**7**)–(**10**) is not modified by dilution in the respective solvents. Reaction of equimolar concentrations of 3-methylpentane and 4-vinylpyridine afforded (**7**)–(**10**) in 45.9% yield whilst styrene gave less abstraction (31.3% by HPLC), suggesting that addition to monomer is more favoured. Hydrogen abstraction is the most likely reaction at high 3-methylpentane concentrations but as with the example of MMA this will afford more substrate that does not react with *t*-butoxy radicals.

Conventional deoxygenation techniques were used in this study, but even so a small amount of oxygen was obviously present as reflected in the formation of the products (**11**)–(**14**) [Scheme 1 (Reaction of 3-methylpentane, styrene or 4-vinylpyridine towards *t*-butoxy radicals in the presence of (**5**) and adventitious oxygen)]. Adventitious oxygen in degassed solutions has been previously reported [25–27]. Carbon-centred radicals react with oxygen at or near diffusion controlled rates affording alkylperoxy radicals [28]. Nitroxides do not react with oxygen centred radicals enabling tail addition of the peroxy radical to styrene and 4-vinylpyridine. This gives monomer grafted from 3-methylpentane through the intermediary of peroxide functionality.

Peroxide incorporation is not detected in the presence of MMA. The reason for this is unclear. However, it is known that peroxy radical addition to MMA is slower than to

[2] Studies performed in these laboratories suggest that *t*-butoxy radicals only add to the ‘tail’ of 4-vinylpyridine.

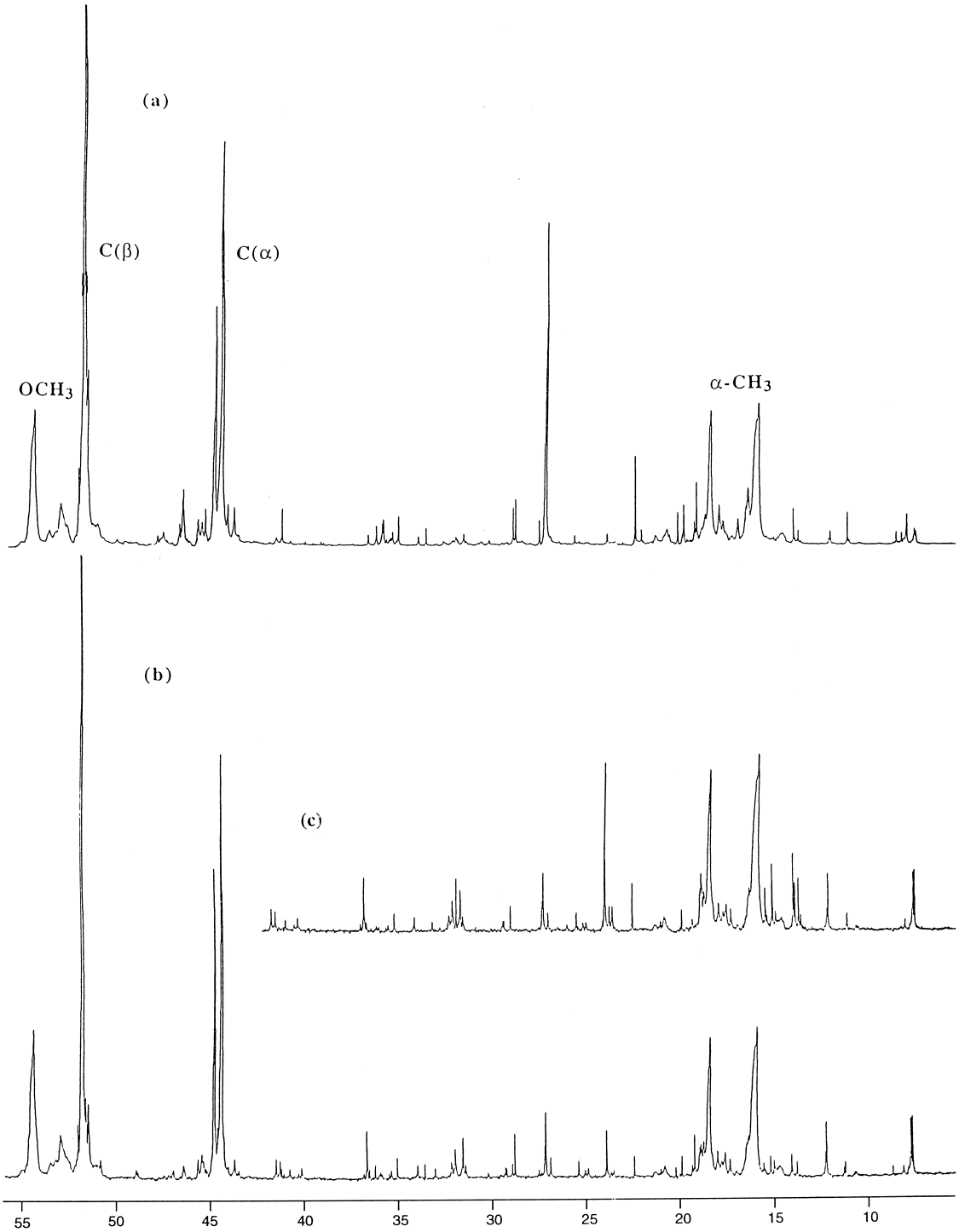
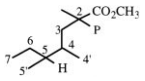
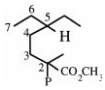


Fig. 3. Portion of 400 MHz ^{13}C NMR spectra of a mixture of 3-methylpentane-*graft*-poly(MMA) and poly(MMA) prepared from (a) 10 molar equivalents of MMA to 3-methylpentane; (b) 5 molar equivalents of 3-methylpentane to MMA; and (c) 5 molar equivalents of 25% by mass of 15% 3-^{13}C-methyl-pentane (inset).

styrene [29] and this could allow the alternative pathway of abstraction, by the peroxy radical, to be preferred. Because of the low oxygen content, it is not possible to reliably determine if there is an increase in the amount of (**7**)–(**10**) produced by this alternative pathway and the formation of hydroperoxides was not detected.

Fig. 5 shows the total yield of (**11**) and (**12**) as a function of the 3-methylpentane to styrene concentration. The amount of these products is very much less than (**7**)–(**10**) and is reduced even further at high substrate concentrations. Hence, the amount of peroxide units in the graft can be virtually eliminated. Reliable information could not be

Table 2
Chemical shifts of 3-methylpentane-*graft*-poly(MMA) end groups (P = poly(MMA))

	Chemical shifts (ppm)						
	C_2	C_4	C_5	C_6	C_7	$C_{4'}$	$C_{5'}$
	40–42	31–32	37	8	–	24	–
	40–42			31–32	12		14 and 15
	40–42	31.5			12	–	–

extracted from the 4-vinylpyridine model experiments because (**13**) and (**14**) are detected in very low amounts.

3.5. Relative rate of hydrogen abstraction to monomer initiation: k_a/k_i ratios

The k_a/k_i ratio, where k_a and k_i are the hydrogen abstraction and monomer initiation rate coefficients respectively, for the 3-methylpentane and MMA competition reactions is determined from the slope of Fig. 6 (Table 3). This method does not give any information about absolute rates [15].

3.6. Reaction of di-t-butyl peroxalate with 2,4-dimethylpentane

Previous studies performed in these laboratories suggest that 2,4-dimethylpentane is sterically less accessible to attack by *t*-butoxy radicals [12]. This is most likely due to the hydrocarbon possessing a 2,4-dimethyl arrangement. Because of the similarity in structure to the polymer, we consider this is a more suitable model for PP. The results of the 3-methylpentane radical trapping experiments including the effect of monomer during competitive abstraction–initiation and the presence of peroxy linkages are however still applicable to this model.

Similar experiments with 2,4-dimethylpentane replacing 3-methylpentane gave a mixture of four alkoxyamine products. These include (**6**), and the positional isomers (**15**)– (**17**) (Fig. 7). Table 4 shows the product distribution. Abstraction from the tertiary C–H position accounts for approximately two-thirds of the total product distribution and is not modified in benzene. In contrast, abstraction from the secondary and primary C–H reaction sites is solvent dependent [12].

4. Discussion

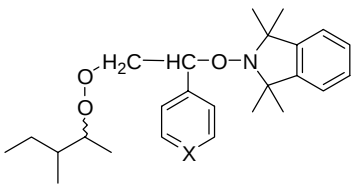
This paper has focused on model compounds to study *t*-butoxy radical initiated grafting from LLDPE and PP. Extrapolation of the results of the model study enables predictions about (i) the site of polyolefin grafting, (ii) the relative reactivity of the polyolefins and (iii) competition between graft copolymer and homopolymer formation to be made.

4.1. Site of grafting from LLDPE and PP

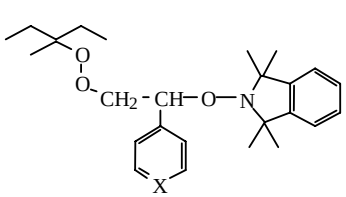
The site of grafting from LLDPE is determined by the concentration of secondary (2°) and tertiary C–H (3°) reaction sites, and the relative reactivity at these positions. The site of 2°:3° grafting is predicted to be 12:1 for a 10% copolymer of 1-octene and ethylene [30,31] for example. Therefore, the greater number of secondary groups results in predominant grafting at these points offsetting the greater reactivity of the tertiary C–H reaction sites. To a much smaller extent, some grafting is expected from the branch methyl group of LLDPE.

Although the site of grafting is not affected by the reaction medium, [12] the grafting ratio is expected to change with copolymer composition. For example, the site of 2°:3° grafting is predicted to be 22:1 for a 5% copolymer of 1-octene and ethylene. In contrast, reducing the chain length of α-olefin does not significantly alter the grafting ratio. The findings of this paper are in contrast to reports claiming that abstraction and hence grafting occurs exclusively from the tertiary C–H position of polyethylene [32].

The site of grafting from PP is determined by the relative reactivity at the respective reaction sites. Hence, the amount of reaction expected at the various sites is: 5.6 (3°):1.5 (2°):1 (1°) in neat solution; and 3.9 (3°):0.3 (2°):1 (1°) in benzene. The 3°: 2° graft ratio is improved in benzene most likely due to *t*-butoxy radical solvation [12]. However, more grafting is expected from the branching sites. Similar grafting patterns are expected using aromatic monomers such as styrene.

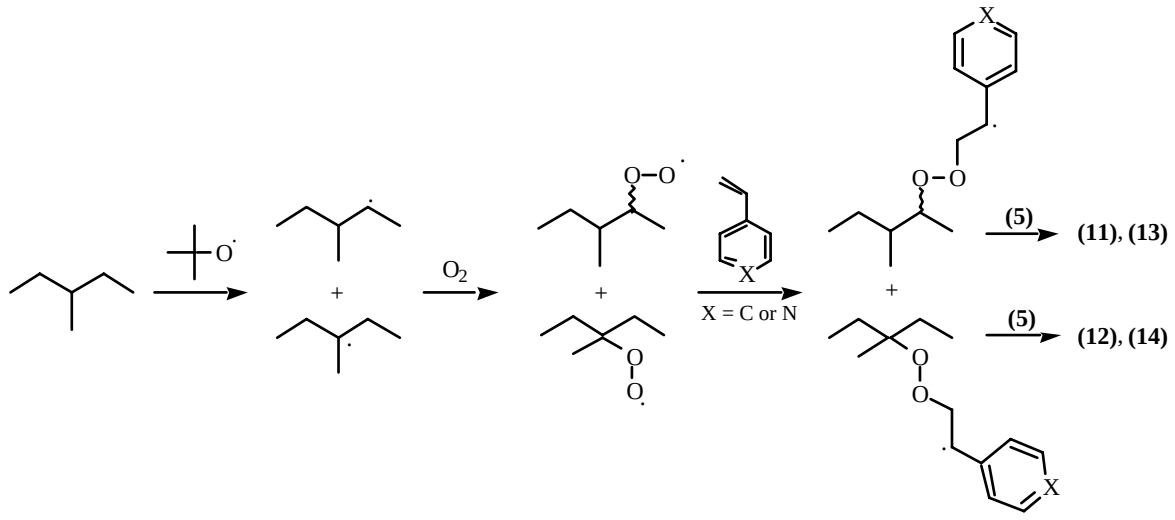


X = C **(11)**, N **(13)**



X = C **(12)**, N **(14)**

Fig. 4. Products from the reaction of 3-methylpentane, styrene or 4-vinylpyridine and *t*-butoxy radicals in the presence of (**5**) and adventitious oxygen.



Scheme 1.

These predictions illustrate the greater detail given by the nitroxide trapping technique compared to ESR studies on 2,4-dimethylpentane, PP [33] and oxidation studies on PP [34] that reported selective abstraction of the tertiary hydrogens.

Therefore, the results of this study suggest that the position of *t*-butoxy radical initiated grafting in LLDPE and PP is most likely different. For LLDPE, grafting will be mainly located at the secondary C–H reaction sites. For PP, grafting will be predominantly concentrated at the tertiary C–H positions, the extent of which varies with the reaction medium.

4.2. Relative reactivity of LLDPE and PP

Previously reported k_a/k_d ratios, [12] where k_a and k_d are the hydrogen abstraction and *t*-butoxy radical β-scission rate coefficients, respectively, have been recalculated to determine the relative polyolefin reactivity towards *t*-butoxy radicals (Table 5). This involves determining the ratio of the amount of abstraction from the model that represents the PP repeat unit for example, to the model compound as a whole. This ratio is then multiplied by the k_a/k_d ratio of the model. This approach assumes that the reactivity of the polymer and the model is similar. Niki and Kamiya however reported that polymers are less reactive than models because the coiled conformations retard primary radicals from approaching the reaction site [35]. Regardless, the values reported here reflect the relative reactivity of the respective polyolefins.

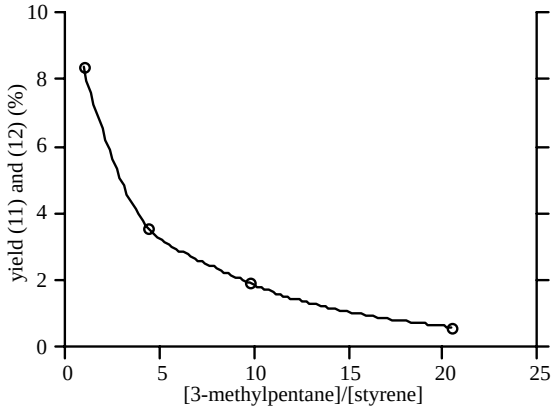


Fig. 5. Yield of (**11**) and (**12**) versus 3-methylpentane to styrene concentration.

Because the polyolefins are insoluble in most organic solvents the relative substrate reactivity in neat solution is a model for melt grafting where solvent effects are not important. The results suggest that LLDPE is much more reactive than PP toward *t*-butoxy radicals, particularly in benzene. This is most likely due to the lower reactivity of the tertiary and in particular secondary hydrogens of PP and *t*-butoxy radical solvation [12]. The relative reactivity of LLDPE is not affected by the copolymer composition. However, Wong Shing et al. reported that LLDPE is less reactive than the model compound squalene because the polymer has a lower concentration of tertiary C–H reaction sites [6].

4.3. Competing graft copolymer and homopolymer formation

The results of this study suggest that experiments with LLDPE will give more graft formation, compared to PP, because of the greater reactivity of LLDPE toward *t*-butoxy radicals. Experiments with MMA will also give more grafting than styrene and 4-vinylpyridine because of the higher k_a/k_i ratio. This is most likely due to the relatively electrophilic nature of MMA that does not favour attack by the electrophilic *t*-butoxy radicals [36]. The reaction kinetics can also be modified to favour grafting by increasing the polyolefin concentration although this will result in more material that does not react with the *t*-butoxy radicals.

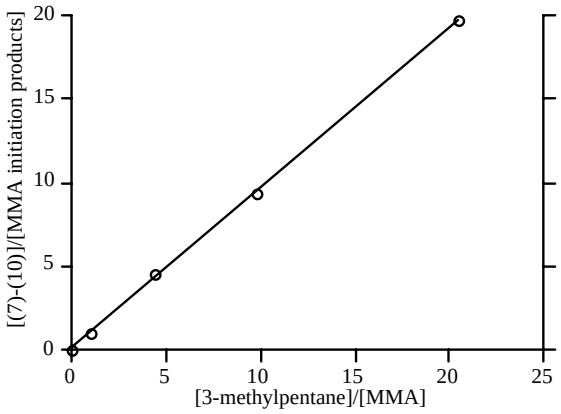


Fig. 6. The relative ratio of (**7**)–(**10**) to MMA initiation derived products versus 3-methylpentane to MMA concentration.

Table 3
Relative ratio of (**7**)–(**10**) to monomer initiation derived products. (k_a/k_i)

Monomer	k_a/k_i ratio
MMA	0.96
Styrene	0.53
4-vinylpyridine	0.84

Table 4
Relative amounts of abstraction from 2,4-dimethylpentane using *t*-butoxy radicals in neat and benzene solutions

Product	Site of abstraction	Relative yield (%)[a]	
		Neat[b]	Benzene[c]
(**15**)	Primary	23.9 ± 0.1	33.2 ± 0.1
(**16**)	Secondary	9.1 ± 0.2	2.6 ± 0.5
(**17**)	Tertiary	67.3 ± 0.1	64.3 ± 0.1

[a] Percentage yield determined by HPLC.
[b] [2,4-Dimethylpentane] = 6.8 mol l^{-1}
[c] [2,4-Dimethylpentane] = 4.2 mol l^{-1}.

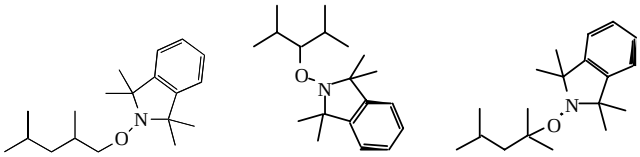
Table 5
The relative reactivity of LLDPE and PP toward *t*-butoxy radicals

	k_a/k_d ratio	
	Neat	Benzene
LLDPE (5% copolymer)	4.2 ± 0.1	2.9 ± 0.4
LLDPE (10% copolymer)	4.5 ± 0.1	2.9 ± 0.5
PP	1.8 ± 0.2	0.4 ± 0.1

Similarly, high polyolefin concentrations reduce the amounts of unwanted degradation points such as the peroxide links expected with styrene and 4-vinylpyridine.

5. Conclusions

The results of the model study can be extended to develop an understanding for *t*-butoxy radical initiated grafting from LLDPE and PP. The tertiary C–H reaction site of 3-methylpentane is twice as reactive as the secondary position. However, the greater reactivity of the tertiary position is offset by the concentration of secondary reaction sites and hence grafting occurs most frequently from the secondary position of LLDPE. Using 2,4-dimethylpentane as a model for PP suggests that grafting will be predominantly concentrated at the tertiary position although the grafting selectivity varies significantly in benzene due to *t*-butoxy radical solvation [12].



(15) **(16)** **(17)**

Fig. 7. Products from the reaction of 2,4-dimethylpentane and *t*-butoxy radicals in the presence of (**5**).

Besides grafting from LLDPE being more selective, the amount of graft produced is expected to be higher than for PP. However, the reaction kinetics can be altered to favour grafting by increasing the substrate concentration although this will result in more polymer that does not react with the *t*-butoxy radicals. Experiments with MMA are also expected to give more grafting. In contrast, experiments with styrene will result in unwanted peroxide links within the graft even when conventional deoxygenating techniques are used.

Further articles in this series will discuss the *t*-butoxy radical initiated grafting of MMA from PP.

Acknowledgements

We would like to thank the Australian Research Council for financial support and Dr Marcus J. Caulfield and Dr Greg Qiao for fruitful discussion during the preparation of this manuscript.

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