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Graft copolymerization studies
Part II. Models related to polyethylene terephthalate

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Abstract

The chemistry of free radical graft copolymerization, initiated with *t*-butoxy radicals, has been investigated using ethylene glycol dibenzoate and diethylene glycol dibenzoate as models for polyethylene terephthalate (PET). Although diethylene glycol dibenzoate is more reactive than ethylene glycol dibenzoate the site of grafting from the polymer is determined by the concentration of ethylene glycol and diethylene glycol residues and the relative reactivity at these positions. Hence grafting occurs most frequently at the ethylene glycol positions. This study also suggests that PET is less reactive than the polyolefins LLDPE and polypropylene and that PET chain scission is possible using high *t*-butoxy radical concentrations in the presence of adventitious oxygen at relatively low temperatures.

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

1. Introduction

Free radical grafting of vinyl monomers from polyethylene terephthalate (PET) may help to introduce polarity and/or functionality from the polyester that otherwise has a lack of chemically reactive groups [1]. This approach has the additional attraction of being readily applied in many existing industrial processes [2,3]. The generally accepted radical-initiated graft copolymerization mechanism involves Eqs. (1)–(4), where I· is the primary radical, P–H the polymer backbone and M is the monomer. The relative rates of Eqs. (2) and (3), in competition with Eq. (4), are of critical importance for successful graft copolymerization [4].

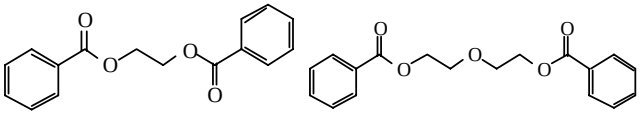
$$I_2 \rightarrow 2I\cdot \quad (1)$$

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

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

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

As in previous related studies on linear low-density polyethylene (LLDPE) and polypropylene (PP) [5], we have chosen firstly to examine model systems to gain data that can then be applied to conventional PET-graft formation. Ethylene glycol dibenzoate (5) and diethylene glycol dibenzoate (6) were chosen as models for PET because the polymer can contain glycol ether residues [6,7]. Di-*t*-butyl peroxalate was chosen as the initiator since it yields *t*-butoxy radicals at low temperatures [8]. These radicals exhibit an enhanced propensity for hydrogen abstraction [9–11], compared to other primary radicals [12], over addition to monomer.



(5) **(6)**

This paper reports on the reaction of ethylene glycol dibenzoate and on the mixture of ethylene glycol dibenzoate and diethylene glycol dibenzoate toward *t*-butoxy radicals. The significance of these results to radical facilitated grafting from PET is presented.

2. Experimental

The general experimental data is reported elsewhere [13].

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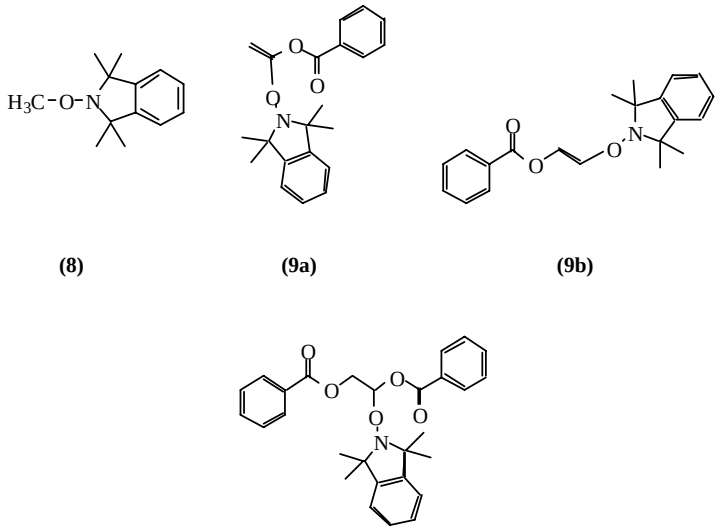


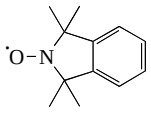
(8) **(9a)** **(9b)**

(10)

Fig. 1. Products from the reaction of ethylene glycol dibenzoate and *t*-butoxy radicals in the presence of (**7**).

2.1. Substrates

Di-*t*-butyl peroxalate was prepared by the method of Bartlett et al. [8] 1,1,3,3-Tetramethylisoindoline-2-oxy (**7**) [14], and 2-(1′-methyl)-1,1,3,3-tetramethylisoindoline (**8**) [15], were prepared according to published procedures. New compounds were identified by isolation by preparative HPLC and spectroscopic analysis. Ethylene glycol dibenzoate was prepared from ethylene glycol and benzoic acid using sulphuric acid as the catalyst. Diethylene glycol dibenzoate was prepared according to McElvain and Carney [16]. The chromatography solvents, methanol and water, were distilled and filtered before use.



(7)

2.2. Radical trapping experiments: general procedure

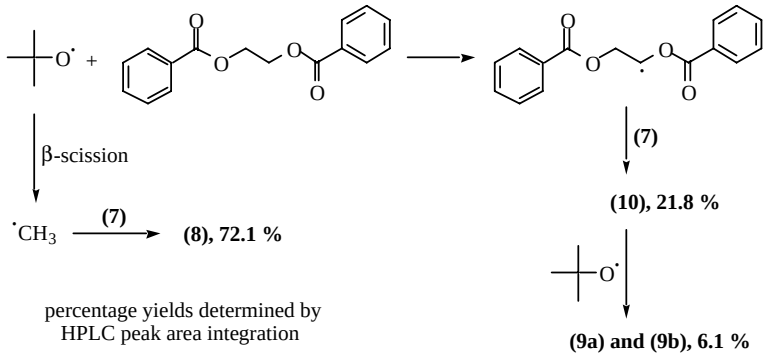
Reaction mixtures consisted of di-*t*-butyl peroxalate (0.05 mmol), 1,1,3,3-tetramethylisoindoline-2-oxy (0.11 mmol) and substrate (0.12–0.75 mmol) in benzene (0.5 ml). The solutions were degassed by successive freeze, pump and thaw cycles on a reduced pressure vacuum line [17], then heated at 60°C (±1°C), for 70 min (10 initiator half lives) [8]. 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 [18].

For preparative scale experiments the amount initiator, radical trap and solvent were scaled up by a factor of 6.6 and substrate (0.85 mmol) was added. Eluded HPLC fractions were concentrated under reduced pressure until the appearance of a white precipitate was observed. Solutions were then diluted with water and extracted with benzene. The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure yielding the alkoxyamines (**9**), (**10**) and (**11**) as viscous yellow oils.

The compounds are listed in order of elution from the HPLC column along with the spectroscopic data.

2-(1′-Benzoyloxy-1′-ethene)-1,1,3,3-tetramethylisoindoline (**9a**) and *2-(2′-benzoyloxy-1′-ethene)-1,1,3,3-tetramethylisoindoline* (**9b**). δ_H 1.47 (s, 24H, ring methyls), 6.90–6.95 (m, 2H, H1′, H2′ (**9b**)), 7.14–7.17 (m, 4H, H4, H7), 7.27–7.33 (m, 11H, H5, H6, ArH, H2′ (**9a**)), 7.46–7.51 (m, 2H, H_{meta}), 7.57–7.62 (m, 1H, H_{para}), 7.80–7.82 (m, 2H, H_{ortho}); δ_C 25.1, 29.3 (ring methyls), 67.9, (C1, C3), 113.9 (C2′ (**9a**)), 120.7 (C1′ (**9b**)), 121.5 (C4, C7), 127.4 (C5, C6), 128.3 (C_{meta}), 128.4 (C_{ipso}), 129.0 (C2′ (**9b**)), 130.1 (C_{ortho}), 132.4 (C_{para}), 137.6 (C1′ (**9a**)), 144.7 (C3a, C7a), 163.0 (C=O).

2-(Ethylene glycol-1′,2′-dibenzoate)-1,1,3,3-tetramethylisoindoline (**10**). (Found: MH^+, 460.2122. $C_{28}H_{30}NO_5$ requires MH^+, 460.2125); *m*/*z* 460 (MH^+), 190 (MH^+–$CH(OC(O)(C_6H_5)CH_2(OC(O)(C_6H_5))$); δ_H 1.36 (s, 3H, ring methyls), 1.41 (s, 3H, ring methyls), 1.42 (s, 3H, ring methyls), 1.63 (s, 3H, ring methyls), 4.51–4.55 (m, 1H, H2′), 4.70–4.74 (m, 1H, H2′), 6.83 (dd, 1H, J 2.0, 4.4, H1′), 7.06–7.09 (m, 2H, H4, H7), 7.20–7.23 (m, 2H, H5, H6), 7.44–7.50 (m, 4H, H_{meta}), 7.56–7.61 (m, 2H, H_{para}), 8.06–8.12 (m, 4H, H_{ortho}); δ_C 25.2, 25.4, 29.4 and 29.5 (ring methyls), 63.4 (C2′), 67.5, 68.3 (C1, C3), 99.7 (C1′), 121.4, 121.6 (C4, C7), 127.3, 127.4 (C5, C6), 128.4 (C_{meta}),



Scheme 1.

129.6 (C_{ipso}), 129.8, 129.9 (C_{ortho}), 133.2, 133.3 (C_{para}), 144.2 (C3a, C7a), 165.1, 166.0 (C=O).

2-(Diethylene glycol-2′,2″-dibenzoate)-1,1,3,3-tetramethylisoindoline (**11**). *m/z* 504 (MH^+); δ_H 1.38 (s, 6H, ring methyls), 1.52 (s, 3H, ring methyls), 1.60 (s, 3H, ring methyls), 4.07–4.15 (m, 1H, H1″), 4.27–4.34 (m, 1H, H1″), 4.46–4.52 (m, 4H, H2′, H2″), 5.31 (t, 1H, J 4.8, H1′), 7.05–7.13 (m, 2H, H4, H7), 7.19–7.26 (m, 2H, H5, H6), 7.35–7.45 (m, 4H, H_{meta}), 7.50–7.60 (m, 2H, H_{para}), 8.01–8.07 (m, 4H, H_{ortho}); δ_C 25.1, 25.4 (ring methyls), 29.0 and 29.9 (ring methyls), 64.1, 64.5 (C2′, C2″), 67.7 (C1, C3), 68.1 (C1′), 105.3 (C1′), 121.4, 121.7 (C4, C7), 127.3, 127.4 (C5, C6), 128.3, 128.4 (C_{meta}), 129.7 (C_{ortho}), 129.7, 129.9 (C_{ipso}), 133.0, 133.1 (C_{para}), 144.5, 144.8 (C3a, C7a), 166.2, 166.5 (C=O).

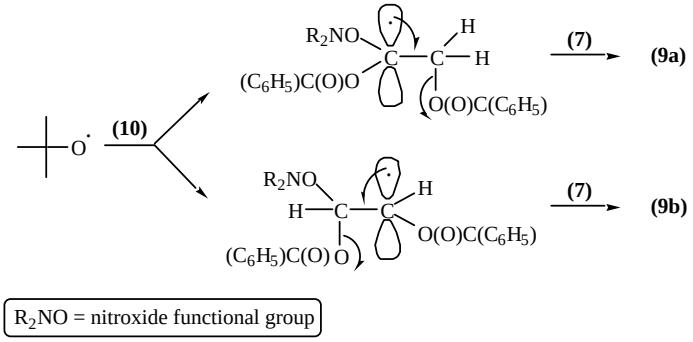
3. Results

The competing reactions in graft copolymerization 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 [10]. The radical trapping technique, developed by Rizzardo and Solomon [19], enables reaction between the *t*-butoxy radicals with the model compounds to be investigated. The method relies on the near diffusion controlled rate (10^7–10^9 l mol^{-1} s^{-1}) [20], at which nitroxide reagents combine with alkyl radicals affording relatively stable alkoxyamines. The nitroxide trapping reagent 1,1,3,3-tetramethylisoindoline-2-oxy (**7**) [14] was used in the present study.

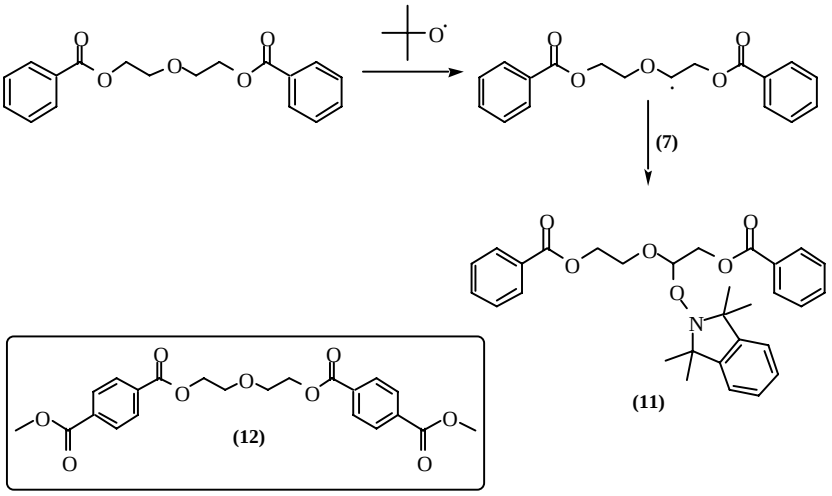
3.1. Reaction of di-t-butyl peroxalate with ethylene glycol dibenzoate

The decomposition of di-*t*-butyl peroxalate in a benzene solution of ethylene glycol dibenzoate (13.5 molar equivalents) and (**7**) gave a mixture of four alkoxyamine products. These include the methoxyamine (**8**) [15], from *t*-butoxy radical β-scission, the unsaturated isomers (**9a**) and (**9b**) and the positional isomer **10** (Fig. 1). The unsaturated isomers were isolated and characterized as a mixture of products because they could not be resolved by HPLC. Products derived from aromatic substitution were not detected in this study. Similarly, Solomon and coworkers [21,22] have shown that *t*-butoxy radicals react exclusively with the methyl group of toluene.

The products shown in Fig. 1 can be translated into the series of reaction pathways outlined in Scheme 1 (the reaction of ethylene glycol dibenzoate and *t*-butoxy radicals in the presence of (**7**)). Thermal decomposition of (**10**) did not yield the unsaturated isomers, however, heating the alkoxyamine in the presence of di-*t*-butyl peroxalate affords (**9a**) and (**9b**) and the yield of these products was found to increase by adding more initiator to solution. This suggests that *t*-butoxy radicals initiate hydrogen abstraction from



Scheme 2.



Scheme 3.

(**10**). Scheme 2 shows a possible mechanism to explain the formation of (**9a**) and (**9b**). *t*-Butoxy radical initiated abstraction geminal to the nitroxide moiety of (**10**) yields an alkyl radical that most likely possesses a planar structure in which the radical is sp^2 hybridized and the unpaired electron is in a p-orbital [23]. The radical intermediate can then facilitate elimination of a benzoyloxy radical affording (**9a**). Abstraction of the hydrogen near the nitroxide affords the *trans*-isomer (**9b**) through the transient radical intermediate.

3.2. Reaction of di-t-butyl peroxalate with a mixture of ethylene glycol dibenzoate and diethylene glycol dibenzoate

Similar experiments with a 99:1 molar ratio of ethylene glycol dibenzoate and diethylene glycol dibenzoate gave a mixture of five alkoxyamine products. These include (**8**), (**9a**), (**9b**), (**10**) and the positional isomer (**11**) (Scheme 3, the reaction of diethylene glycol dibenzoate and *t*-butoxy radicals in the presence of (**7**)). Abstraction β to the ether oxygen atom was not detected in this study. This is most likely due to: (a) the much lower concentration of diethylene glycol dibenzoate in solution; and (b) electron attracting effect of the ether oxygen atom, β to the C–H reaction site [24], which discourages attack by electrophilic *t*-butoxy radicals [25].

These conditions were chosen because commercial PET typically contains approximately 1–2.5 mol% of glycol ether residues such as (**12**) [26,27]. This irregularity in the structure of the polyester results from the in

Table 1
Relative amounts of (**8**)–(**11**) produced with varying concentrations of a 99:1 molar ratio of ethylene glycol dibenzoate and diethylene glycol dibenzoate ([(**5**) and (**6**)] = 0.25, 0.50, 1.00, 1.50 mol l^{-1}; [di-*t*-butyl peroxalate] = 0.10 mol l^{-1})

[(**5**) and (**6**)]/[di-*t*-butyl peroxalate]	Relative yield (%)[a]			
	(**8**)	(**9**)	(**10**)	(**11**)
2.5	82.6	9.9	7.0	0.5
5.0	79.9	8.3	11.1	0.8
10.0	77.7	5.3	15.5	1.4
15.0	73.4	4.2	20.5	1.9

[a] Percentage yield determined by HPLC.

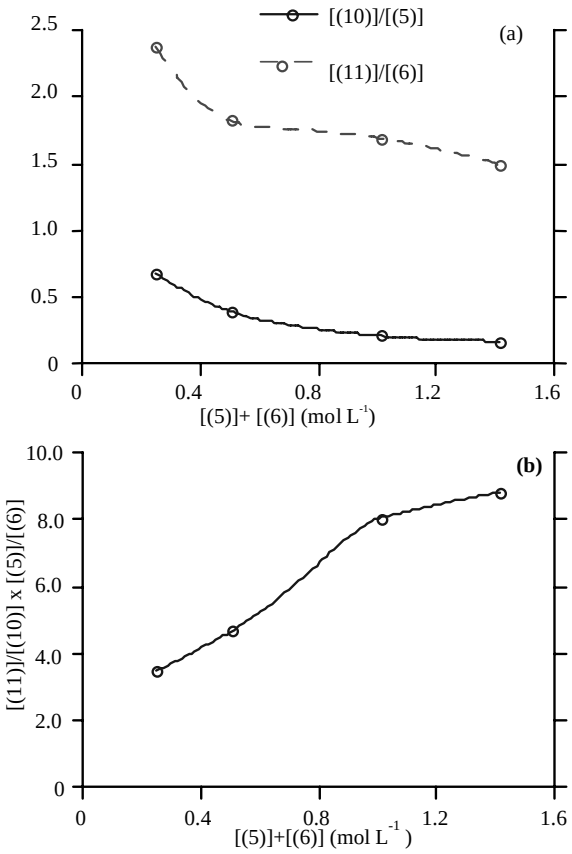


Fig. 2. Concentration of (a) (**10**) to ethylene glycol dibenzoate and (**11**) to diethylene glycol dibenzoate; (b) (**11**) to (**10**) as a function of the respective substrate concentrations versus the total substrate concentration.

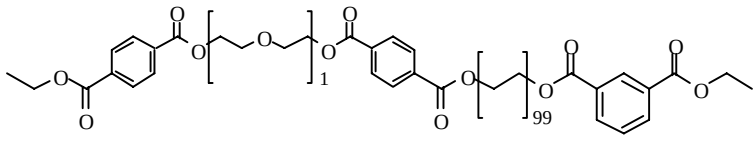


Fig. 3. Repeat unit of PET containing 1 mol% of glycol ether residues.

situ etherification side reaction of ethylene glycol, or perhaps of hydroxyethyl end groups, during the esterification reaction between terephthalic acid (or its esters), and ethylene glycol [6].

Table 1 shows the relative amounts of (**8**)–(**11**) produced with varying concentrations of the model compounds. There is a small reduction in the amount of (**8**) produced with increasing the substrate concentration. The poor solubility of the model compounds in the reaction medium, however, prevented the addition of more substrate to favour hydrogen abstraction. The yield of (**10**) is less than that of the unsaturated isomers using 2.5 molar equivalents of substrate. The amount of (**10**) produced, however, increases with substrate concentration whilst there is a simultaneous reduction in the yield of (**9**). This is in line with the earlier suggestion that formation of the unsaturated isomers is favoured at low substrate or high initiator concentrations. Although (**11**) is detected in very low yields, this is most likely due to the small amounts of diethylene glycol dibenzoate in solution.

Fig. 2a shows the yield of (**10**), including (**9**), and (**11**) per mole of ethylene glycol dibenzoate and diethylene glycol dibenzoate, respectively. The plot suggests that increasing the total substrate concentration affords more material that is not attacked by *t*-butoxy radicals even though there is an overall increase in the yield of the respective products. Over the concentration range investigated diethylene glycol dibenzoate is 3.5–9 times more susceptible to *t*-butoxy radical attack suggesting enhanced reactivity α to the ether oxygen atom (Fig. 2b). We therefore suggest that the UV and thermal instability of PET-containing glycol ether residues [26–28] is most likely due to the greater reactivity of these groups.

Qureshi [29] similarly reported enhanced reactivity α to the ether oxygens of a series of diethylene glycol bis-carbonates which are structurally like diethylene glycol dibenzoate. Similar findings have also been reported by other authors for acyclic ethers [30–34]. The greater reactivity is most likely due to stereoelectronic effects [24] because the oxygen lone pair donates electron density to the adjacent carbon antibonding orbitals thereby increasing the possibility of attack by electrophilic *t*-butoxy radicals [25]. The extent of conjugative delocalization may be reduced for PET because the polymer has restricted movement [24]. Besides stereoelectronics, the presence of glycol ether residues may also reduce steric crowding that can restrict *t*-butoxy radical attack.

3.3. Substrate reactivity: k_a/k_d ratios

The relative reactivity of diethylene glycol dibenzoate toward *t*-butoxy radicals is determined to be 0.29 from the ratio of the amount of (**10**), including (**9**), to (**8**) produced where k_a and k_d are the hydrogen abstraction and *t*-butoxy radical β-scission rate coefficients, respectively, and [R–H] is the substrate concentration, Eq. (13) [35].

$$\frac{\text{Rate (abstraction)}}{\text{Rate}(\beta\text{-scission})} = \frac{[(\mathbf{10})]}{[(\mathbf{8})]} = \frac{k_a[t\text{-butoxy radical}][\text{R–H}]}{k_d[t\text{-butoxy radical}]} \quad (13)$$

This method does not give any information about absolute rates [21] or the relative rate of formation of (**9**). For the 99:1 molar ratio of model compounds the k_a/k_d ratio is determined to be 0.21 ± 0.12 in good agreement with ethylene glycol dibenzoate suggesting that the small amount of diethylene glycol dibenzoate does not affect the overall substrate reactivity. Therefore, the mixture of ethylene glycol and diethylene glycol dibenzoate is much less susceptible to *t*-butoxy radical attack compared to 3-methylpentane and 2,4-dimethylpentane (in benzene solution) [13].

4. Discussion

This paper has focussed on model compounds to study *t*-butoxy radical initiated grafting from PET. Extrapolation of the results of the model study enables predictions about (i) the site of PET grafting and (ii) the relative reactivity of PET compared to LLDPE and PP to be made. The formation of unsaturated isomers from the hemiacetal (**10**) also indicates the possibility of an alternative pathway for PET chain scission.

4.1. Site of grafting from PET

The relative reactivity of diethylene glycol (DEG) to ethylene glycol (EG) towards *t*-butanyl radicals, is approximately 6.1:1. Therefore, for a copolymer which contains 1 mol% of glycol ether residues we would expect the grafting to be in the ratio of 16:1 EG:DEG residues. That is the greater number of EG residues more than compensates for the lower reactivity.

4.2. Relative reactivity of PET

The relative reactivity of PET containing 1 mol% of glycol ether residues toward *t*-butoxy radicals is equal to

Table 2
The relative reactivity of LLDPE, PP and PET toward *t*-butoxy radicals in benzene solution

	k_a/k_d ratio
LLDPE (10% copolymer)	2.9 ± 0.5
PP	0.4 ± 0.1
PET	0.2 ± 0.1

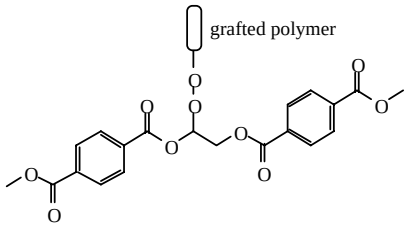
the previously reported k_a/k_d ratio for the 99:1 molar ratio of ethylene glycol and diethylene glycol dibenzoate because the mixture represents both the concentration and relative reactivity of the polymer repeat units (Fig. 3).

Although Niki and Kamiya [35] reported that polymers are less reactive than models, because the coiled conformations retard primary radicals from approaching the reaction site, in this study the assumption is made that the reactivity of model and polymer is similar.

The results suggest that PET is less reactive than PP and LLDPE (Table 2). Purposely 'doping' PET with diethylene glycol residues to increase the amount of graft is not a suitable option because these groups impart some undesirable properties to the polyester [26–28]. The lower reactivity of the polyester is most likely due to steric factors that reduce approach by *t*-butoxy radicals. The relatively small difference in reactivity between PET and PP model is due to the reduced reactivity of the tertiary and in particular secondary C–H reaction sites of PP [5] and *t*-butoxy radical solvation [13]. LLDPE does not have the same steric limitations [5,13]. Busfield [24] reported *t*-butoxy radicals initiate abstraction from ethylene glycol dimethylether a model for polyethylene oxide. Extrapolating the small molecule data to the polymer suggests that polyethylene oxide is more reactive than PET most likely due to the enhanced conjugative delocalization and reduced steric hindrance associated with the acyclic ether.

4.3. PET chain scission

Pohl [36] reported that the methylene units of PET are the main points of weakness during chain scission affording unsaturated by-products at 300°C. Allan et al. [37] reported that heating ethylene glycol dibenzoate at 400–550°C initiates chain scission at the ester linkage affording vinyl benzoate and benzoic acid as the principal reaction products. Similarly, the formation of (**9**) can be envisaged as an alternative pathway for PET chain scission at high initiator concentrations and relatively low reaction temperatures if the chemistry of peroxides such as (**14**) parallels (**10**). The model study on polyolefins illustrated that even when conventional deoxygenation techniques are used small amounts of oxygen may be present and grafting experiments with styrene and 4-vinylpyridine can result in peroxide linkages being incorporated into the graft [5]. Adventitious oxygen in degassed solutions has also been reported by other authors [38–40].



(14)

5. Conclusions

The results of the model study can be extended to develop an understanding for *t*-butoxy radical grafting from PET. The diethylene glycol residue is 3.5–9 times more reactive than ethylene glycol over the concentration range investigated. However, the greater reactivity of the diethylene glycol groups is offset by the concentration of the ethylene glycol reaction sites and hence grafting occurs most frequently from the ethylene glycol position from a 1 mol% copolymer of PET.

The amount of graft expected with PET is less than PP and LLDPE. Purposely doping PET with diethylene glycol residues to enhance the amount of graft obtained is not a suitable option because diethylene glycol units afford some undesirable properties to the polyester [26–28]. This study also suggests that polyester chain scission is possible using high *t*-butoxy radical concentrations in the presence of adventitious oxygen at relatively low temperatures. Furthermore in commercial operations, oxygen (air) is likely to be present. Hence, chain scission by further attack by the initiator at the C bearing the peroxide linkage is likely to lead to scission.

Acknowledgements

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