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2,3-Dimethyl-2,3-diphenylbutane mediated grafting of vinyltriethoxysilane to polyethylene: a novel radical initiation system

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Abstract

The melt grafting of vinyltriethoxysilane (VTEOS) to polyethylene using 2,3-dimethyl-2,3-diphenylbutane (bicumene) as a radical initiator is demonstrated and compared to conventional peroxide-initiated processes. A bicumene-initiated modification of high density polyethylene at 290 °C provided no benefits in terms of selectivity when compared to a standard peroxide-based process operating at 180 °C. However, the selectivity of linear low-density polyethylene modification was influenced by chain scission, which counteracted the molecular weight effects of macroradical combination. Reactive extrusion data as well as studies of bicumene decomposition kinetics suggest that initiation occurs through an auto-oxidation mechanism that is facilitated by the interaction of cumyl radicals with oxygen.

Keywords: Melt grafting; Vinylsilane; Bicumene

1. Introduction

Chemical modification of polyolefins by radical-mediated grafting chemistry is a robust method of generating value-added products from commodity materials [1,2]. These processes employ relatively inexpensive reagents, require little or no solvent, and are readily adapted to conventional polymer processing equipment [3]. A leading commercial example is the graft-modification of polyethylene with vinyltrialkoxysilane to yield moisture-curing resins that bond to siliceous fillers [4].

Conventional grafting processes are initiated by oxygen-centered radicals derived from the decomposition of organic peroxides (reaction r_1, Scheme 1). Hydrogen atom abstraction from the polymer (r_2) initiates a graft propagation cycle involving both VTEOS addition (r_3) and hydrogen abstraction (r_4). The main drawback of radical-mediated processes is the change brought about to the material's molecular weight distribution. Fragmentation (r_6) of materials such as polypropylene results in a loss of molecular weight and a corresponding increase in melt flow index (MFI). Radical combination (r_7) is of primary concern in the modification of linear, ethylene-based polymers because it results in significant increases in molecular weight (decrease in MFI). While an ideal grafting process would functionalize the resin without affecting MFI (Fig. 1), typical polyethylene and polypropylene modifications do not demonstrate this selectivity for grafting over molecular weight alteration [5].

The widespread use of oxygen-centered radical initiators reflects their favorable balance between hydrogen atom abstraction, fragmentation, and monomer addition tendencies. On the other hand, resonance stabilized, carbon-centered species such as cyanoalkyl radicals are relatively ineffective grafting initiators, due to their limited propensity for hydrogen abstraction [6]. Similar arguments apply to the cumyl radicals generated from 2,3-dimethyl-2,3-diphenylbutane (bicumene) homolysis. Nevertheless, Urawa et al. have disclosed evidence of maleic anhydride grafting to polyolefins using this compound as a radical initiator [7] and we have recently discovered the ability of bicumene to initiate the grafting of vinyltriethoxysilane (VTEOS) to polyethylene at temperatures above 225 °C. Given previous accounts of the unsuitability of resonance-stabilized radicals for polyolefin modifications [2], the graft initiation mechanism supported by cumyl radicals is of fundamental

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Peroxide Initiation

$$\mathrm{ROOR} \xrightarrow{k_d} 2\,\mathrm{RO}\bullet \ldots\ldots\ldots\ldots\ldots\ldots\ldots (r_1)$$

$$\mathrm{RO}\bullet + \mathrm{P} \xrightarrow{k_{fp}} \mathrm{ROH} + \mathrm{P}\bullet \ldots\ldots\ldots\ldots (r_2)$$

Graft Propagation

$$\mathrm{P}\bullet + \mathrm{VTEOS} \xrightarrow{k_p} \mathrm{P\text{-}Silane}\bullet \ldots\ldots\ldots (r_3)$$

$$\mathrm{P\text{-}Silane}\bullet + \mathrm{P} \xrightarrow{k_t} \mathrm{P\text{-}Silane} + \mathrm{P}\bullet \ldots (r_4)$$

Chain Transfer

$$\mathrm{P}\bullet + \mathrm{P} \xrightarrow{k_{ct}} \mathrm{P} + \mathrm{P}\bullet \ldots\ldots\ldots\ldots\ldots\ldots\ldots (r_5)$$

Fragmentation

$$\mathrm{P}_{m+n}\bullet \xrightarrow{k_f} \mathrm{P}_m\bullet + \mathrm{P}_n^{=} \ldots\ldots\ldots\ldots\ldots\ldots (r_6)$$

Termination

$$\mathrm{P}\bullet + \mathrm{P}\bullet \xrightarrow{k_{tc}} \mathrm{P} - \mathrm{P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (r_7)$$

$$\mathrm{P}\bullet + \mathrm{P}\bullet \xrightarrow{k_{td}} \mathrm{P}^{=} + \mathrm{P} \ldots\ldots\ldots\ldots\ldots\ldots (r_8)$$

Scheme 1.

interest. Furthermore, given that bicumene is activated by temperatures well above those of alkyl peroxides in common use, it is conceivable that the selectivity of a bicumene-based system may differ from conventional processes.

In this report we present melt grafting data to demonstrate the effect of bicumene concentration and residence time on the VTEOS graft content and MFI of modified polyethylene. An appropriate measure of grafting selectivity is developed and subsequently applied to evaluate the performance of bicumene relative to common organic peroxides. Studies of bicumene decomposition and homolysis kinetics are discussed in terms of plausible graft-initiation mechanisms.

2. Experimental

2.1. Materials

Dicumylperoxide (DCP, 98%, Sigma-Aldrich), 2,5-dimethyl-2,5-di(*t*-butylperoxyl)hexane (Lupersol-101, 45% on $CaCO_3$, Atochem), 2,3-dimethyl-2,3-diphenylbutane (bicumene, Perkadox-30, 95%, Akzo Nobel), cyclooctane (99% Sigma-Aldrich), 1,2,4-trichlorobenzene (99%, Sigma-Aldrich) and benzenethiol (97%, Sigma-Aldrich) were used as received. Vinyltriethoxysilane (97%, VTEOS) and ethyltriethoxysilane (96%) was used as received from Sigma-Aldrich and stored under nitrogen. High-density polyethylene (14.7 MFI@190 °C, 5 kg load), linear low-density polyethylene (24 wt%/7.3 mol% octene, 5.6 MFI@190 °C, 5 kg load) and tetradecane (99%, Acros) were used without purification.

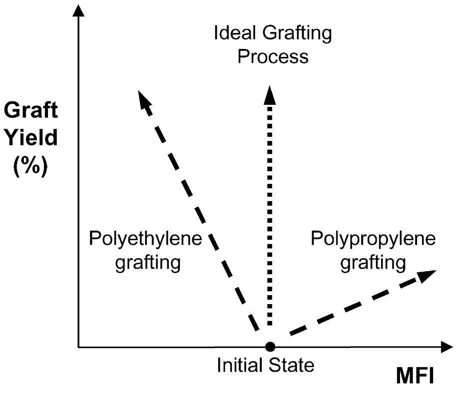


Fig. 1. Typical selectivity of radical-mediated polyolefin modification.

2.2. Bicumene decomposition kinetics

A solution of bicumene (10 g, 0.042 mol) in 1,2,4-trichlorobenzene (100 g, 0.55 mol) was combined with the desired quantity of additive (benzenethiol, cyclooctane). Approximately 0.3 ml of solution was sealed within a 0.35 ml Wheaton vial and placed in an aluminum heating block at the desired temperature (± 1 °C) for a given time interval, after which the sample was cooled and analyzed by ^{1}H NMR. Normalized ^{1}H NMR integration of spectra recorded in $CDCl_3$ provided the relative concentration of the following compounds to within ±5%: 1.39 δ (bicumene, 12H, s), 2.24 δ (α-methylstyrene, 3H, s), 1.35 δ (cumene, 6H, d).

2.3. Bicumene decomposition in tetradecane

A solution of bicumene (3.28 g, 0.0138 mol) in tetradecane (50 ml) was refluxed (253 °C) for 4.5 h under continuous sparging with a minimal flow of air. A portion of the resulting mixture was fractionated by flash chromatography (alumina, hexanes eluent) to give a clear, colorless product that ^{1}H NMR, FT-IR and ^{13}C NMR analysis confirmed to be acetophenone and cumyl alcohol. Further confirmation of these compounds was gained by gas chromatography–mass spectrometry analysis of the unfractionated mixture (GC–MS, Hewlett–Packard 5890 Series II, HP 5972 MS detector, electron impact ionization, Supelco SPB-1 capillary column, injector temperature: 275 °C, oven temperature profile: 70 °C hold 8 min, ramp to 140 °C at 8 °C/min, hold 17 min). Required for acetophenone *m/e* 120.2 found 120.0; required for cumyl alcohol *m/e* 136.2, found 136.0.

2.4. Single screw extrusion grafting

Polyethylene pellets (500 g) were tumble-mixed with the desired initiator prior to adding VTEOS (25 g, 0.131 mol) and tumbling for a further 20 min. The resulting masterbatch was charged through a gravity-feed hopper to a Haake Rheomex 259 single screw extruder that was driven and controlled by a Haake Polylab. The extruder had a 2.54 cm barrel diameter and a length/diameter ratio of 25:1. The first zone of the extruder barrel was held at 150 °C throughout the work, while the second and third zones were maintained at the desired process temperature. The screw speed was varied throughout the range of (5, 10, 15, 20 and 25) rpm, which corresponded to polymer residence times of (18, 9, 6, 5 and 4) min, respectively. The product was extruded through a strand die and cooled by a forced air stream prior to storing within a desiccator.

2.5. Analysis

Graft modified resins (1 g) were purified by dissolving in boiling xylene (20 ml) and precipitating with acetone (100 ml), followed by filtering and drying under vacuum for 24 h at 25 °C. Films of 0.03 mm thickness were pressed and analyzed for silane graft content by an infra-red spectroscopic method based on an integration of the 744–825 cm^{-1} resonance of the silane relative to a 1978–2098 cm^{-1} internal standard region [5]. The instrument (Nicolet Avatar 360 FT-IR ESP spectrometer) was calibrated using polyethylene samples of known ethyltriethoxysilane content. MFI was measured with a Tinius Olsen apparatus at 190 °C with a 5 kg load. MFI values are reported as grams of resin extruded in 10 min. ^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker AC-400 spectrometer, with chemical shifts reported in ppm relative to chloroform (7.24 δ).

3. Results

3.1. Kinetics of bicumene-initiated modification of HDPE

Bicumene initiates VTEOS grafting efficiently over an uncommonly large range of operating temperatures. This is shown in Figs. 2 and 3, which illustrate the silane graft content and MFI for HDPE modifications performed at 240 and 290 °C, respectively. Not surprisingly, the processing of VTEOS/HDPE masterbatches in the absence of bicumene had little effect on the resin. No activity was observed in the absence of initiator at 240 °C, while a marginal VTEOS conversion and MFI reduction was observed at 290 °C, presumably due to the generation of radical activity through thermo-mechanical and/or oxidative pathways. The addition of 0.10 wt% bicumene to the system heightened the radical grafting activity significantly, yielding an ultimate VTEOS conversion of 38% at 240 °C within 20 min of residence time. Similarly, 71% silane conversion was achieved within 10 min at 290 °C. Significant MFI reductions were incurred at both temperatures, indicating that radical combination was an influential macroradical termination pathway.

Given the recognized inefficiency of resonance-stabilized radicals for hydrogen abstraction, the high conversions shown in Figs. 2 and 3 are somewhat surprising. To gain further insight into the initiation mechanism, a study of reactive extrusion using bicumene in the absence of VTEOS was undertaken. Under an air atmosphere, 0.10 wt% of bicumene reduced the MFI of the polymer to the same extent whether or not VTEOS was present in the system (Figs. 2 and 3), indicating that bicumene does not require monomer to facilitate polymer macroradical chemistry.

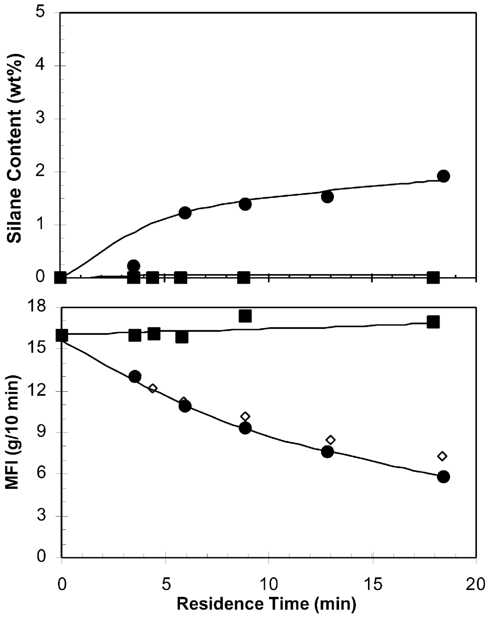


Fig. 2. Bicumene initiated modification of HDPE (T_1 = 150 °C, $T_2 = T_3$ = 240 °C; ■ no bicumene, 5 wt% silane; ● 0.10 wt% bicumene, 5 wt% silane; ◇ 0.10 wt% bicumene, no silane).

3.2. Selectivity of bicumene initiated modification of HDPE

The data shown in Figs. 2 and 3 are typical of a

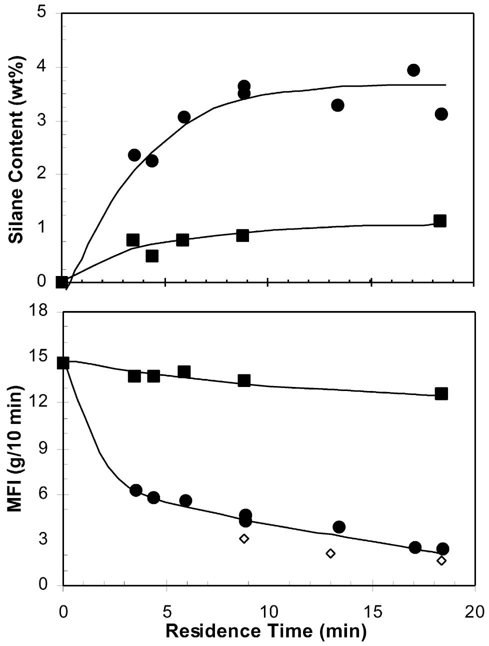


Fig. 3. Bicumene initiated modification of HDPE (T_1 = 150 °C, $T_2 = T_3$ = 290 °C; ■ no bicumene, 5 wt% silane; ● 0.10 wt% bicumene, 5 wt% silane; ◇ 0.10 wt% bicumene, no silane).

conventional HDPE modification in that the resin was cross-linked in addition to being graft-modified. Irrespective of the initiation mechanism, a bicumene-mediated process should be functionally similar to a peroxide process, because it is expected to operate with the same alkyl radical intermediates. Therefore, a significant improvement in selectivity on the basis of radical initiation was not anticipated. However, the potential for macroradical termination by cumyl radicals, as well as the temperature sensitivity of reactions such as VTEOS addition, hydrogen abstraction and radical fragmentation could produce unique selectivity effects in a bicumene-initiated system that are not observed in relatively low temperature, peroxide-based processes.

To address the question of whether bicumene was more selective for grafting over cross-linking than conventional peroxide initiators, a selectivity plot of silane graft content versus MFI was generated (Fig. 4). This representation of the data transforms residence time and reagent concentrations into implicit variables of process selectivity, thereby allowing bicumene to be compared directly to alternate initiation systems. In the HDPE modification experiments, the performance of bicumene was compared to that of 2,5-dimethyl-2,5-di(*t*-butylperoxyl)hexane (L-101). A comprehensive summary of all the data acquired in this study is provided in Tables 1 and 2.

It is clear from the HDPE selectivity plot that L-101 operating at 180 °C performed similarly to bicumene operating at 290 °C. Both initiation systems generated standard polyethylene modification behavior, as higher graft contents were achieved only at the expense of increased cross-link density. Although two bicumene experiments demonstrated a marginally lower MFI for a given silane graft content than were recorded for L-101, the effect cannot be declared statistically significant. As a result, it appears that a bicumene process operating at 290 °C offered no measurable advantage over conventional peroxides in terms of HDPE grafting selectivity.

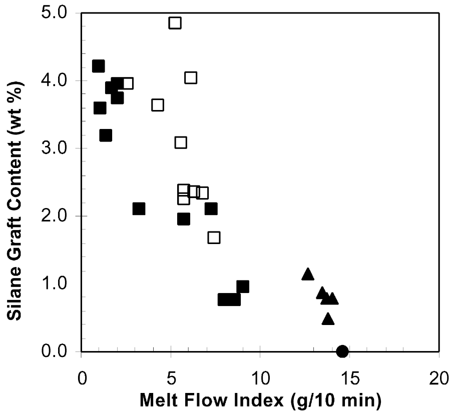


Fig. 4. Selectivity plot for HDPE modification (5 wt% VTEOS) (● unmodified HDPE; ■ L-101 at 180 °C; ▲ no initiator at 290 °C; □ bicumene at 290 °C).

3.3. *Selectivity of bicumene initiated modification of LLDPE*

In contrast to the HDPE grafting results, unique high-temperature behavior was observed in LLDPE grafting experiments (Tables 3 and 4). Fig. 5 is a selectivity plot for LLDPE modification using bicumene at 290 °C, and dicumylperoxide (DCP) at 180 °C. Both processes facilitated VTEOS graft addition, but produced opposite MFI effects. The low-temperature DCP process generated standard polyethylene selectivity wherein the molecular weight was altered predominantly by radical combination (r_7, Scheme 1), resulting in a decline of MFI with increasing silane graft content. The opposite trend was observed in the bicumene process.

Graft modification of LLDPE at 290 °C using bicumene produced silane-modified resins with MFIs much greater than the parent material. This suggests that macroradical fragmentation (r_6, Scheme 1) was promoted by high-temperature processing, leading to a net loss of molecular weight. This behavior is related to controlled polypropylene degradation wherein fragmentation affects MFI to a greater extent than does radical combination [8]. In the present application, LLDPE fragmentation was not dominant at 180 °C where DCP was activated, but it became increasingly important at 290 °C where bicumene was functional. Others have noted [9] that high temperatures favor radical termination by combination over disproportionation (r_8, Scheme 1). Therefore, a shift in radical termination preferences did not contribute to the MFI increases observed at 290 °C.

Tzoganakis et al. have demonstrated a similar effect of temperature on polypropylene degradation using a *t*-butoxy radical initiator system [8]. Their results have confirmed that MFI increased with both initiator concentration and processing temperature, and that a shift in the M_w of polypropylene was the origin of these MFI changes. The LLDPE employed in this work contained only 7.3 mol% octene (31 tertiary carbons per 1000 carbons), and the

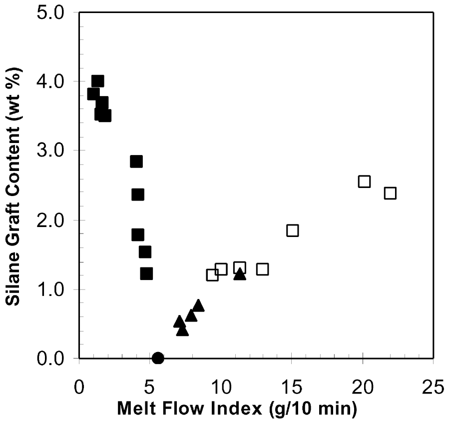


Fig. 5. Selectivity plot for LLDPE modification (5 wt% VTEOS) (● unmodified LLDPE; ■ DCP at 180 °C; ▲ no initiator at 290 °C; □ bicumene at 290 °C).

Table 1
HDPE modification with bicumene

Flow rate (g/min)	Res. time (min)	Bicumene loading (wt%)	Extruder torque (N m)	Graft content (wt%)	MFI (g/10 min)
$T_1 = 150$ °C; $T_2 = T_3 = 240$ °C					
10.4	8.9	0.00	9.0	0.0	17.4
9.2	8.8	0.05	13.2	0.9	9.4
12.5	6.0	0.05	8.2	0.5	12.1
23.2	4.4	0.05	17.7	0.0	13.9
24.1	3.5	0.05	16.6	0.3	14.3
3.8	17.1	0.10	8.1	2.8	4.4
6.0	12.8	0.10	9.6	1.5	7.6
8.8	8.9	0.10	11.9	1.4	9.3
13.5	6.0	0.10	14.1	1.2	10.9
24.8	3.5	0.10	21.4	0.2	13.1
$T_1 = 150$ °C; $T_2 = T_3 = 290$ °C					
4.9	18.4	0.00	5.5	1.1	12.7
10.7	8.8	0.00	–	0.9	13.5
16.1	5.9	0.00	11.8	0.8	14.1
21.8	4.4	0.00	15.7	0.5	13.8
26.7	3.5	0.00	17.6	0.8	13.7
4.2	18.1	0.05	6.3	4.9	5.3
8.9	8.9	0.05	9.9	2.4	5.7
19.1	4.4	0.05	–	2.3	6.8
25.8	3.5	0.05	19.6	1.7	7.4
3.9	18.4	0.10	7.1	3.1	2.5
4.1	17.1	0.10	7.9	4.0	2.6
6.1	13.4	0.10	8.4	3.3	3.9
8.5	8.9	0.10	11.5	3.6	4.3
9.3	8.9	0.10	11.5	3.6	4.3
13.8	6.0	0.10	14.4	3.1	5.6
18.7	4.4	0.10	16.9	2.3	5.8
24.4	3.6	0.10	19.2	2.4	6.3

[VTEOS] = 5.0 wt%.

susceptibility of this material to chain scission is much less than that of polypropylene (333 tertiary carbons per 1000 carbons). As a result, the MFI of our LLDPE resin was not dominated by fragmentation at 180 °C, but was increasingly influenced by chain scission at 290 °C.

Although we could find no precedent for bicumene-initiated grafting of VTEOS to polyethylene, bicumene has been used to degrade HDPE and LLDPE at temperatures similar to those employed in this work. Rauer and Demel [10] have demonstrated that 0.1 wt% bicumene cross-linked a LLDPE resin when employed at 280 °C, but degraded the material at temperatures exceeding 300 °C. They also disclose experiments in which HDPE was degraded by 0.1 wt% bicumene at 330 °C. This suggests that the selectivity of

Table 2
HDPE modification with Lupersol-101

Flow rate (g/min)	Res. time (min)	L-101 loading (wt%)	Extruder torque (N m)	Graft content (wt%)	MFI (g/10 min)
9.9	8.9	0.011	19.9	2.1	7.3
15.4	5.8	0.011	23.2	0.8	8.0
19.9	4.4	0.011	27.5	1.0	9.0
25.1	3.5	0.011	28.7	0.8	8.6
9.7	8.8	0.025	25.3	4.0	2.0
13.0	5.9	0.025	30.4	3.9	1.7
18.0	4.4	0.025	32.3	2.1	3.2
26.5	3.5	0.025	32.3	2.0	5.8
8.1	8.9	0.035	30.1	4.2	0.9
13.3	5.9	0.035	30.7	3.6	1.1
17.6	4.5	0.035	37.0	3.2	1.4
24.2	3.5	0.035	37.2	3.7	2.0

$T_1 = 150$ °C; $T_2 = T_3 = 180$ °C; [VTEOS] = 5.0 wt%.

Table 3
LLDPE modification with bicumene

Flow rate (g/min)	Res. time (min)	Bicumene loading (wt%)	Extruder torque (N m)	Graft content (wt%)	MFI (g/10 min)
6.1	18.4	0.00	6.2	1.2	11.3
13.4	8.8	0.00	13.2	0.8	8.5
19.0	5.9	0.00	–	0.6	7.9
25.5	4.5	0.00	21.8	0.5	7.1
32.9	3.6	0.00	27.2	0.4	7.3
8.0	18.4	0.02	8.2	1.8	15.1
14.0	8.8	0.02	12.8	1.3	13.0
21.6	5.8	0.02	16.9	1.3	11.3
28.9	4.4	0.02	20.0	1.3	10.0
33.4	3.6	0.02	14.2	1.2	9.4
9.0	17.5	0.05	10.6	2.6	20.1
17.9	8.9	0.05	13.3	2.4	22.0

$T_1 = 150$ °C; $T_2 = T_3 = 290$ °C; [VTEOS] = 5.0 wt%.

VTEOS grafting to high-density polyethylene may be enhanced by operating at temperatures greater than those employed in this work.

We note that the full impact of bicumene-initiated grafting on molecular weight distribution is not reflected in measurements of MFI. It is anticipated that radical fragmentation and combination will broaden the molecular weight distribution [11], thereby affecting the physical properties of the resin. Our objective was to demonstrate the basic principles of bicumene initiated grafting, and a detailed assessment of product structure and physical properties is considered to be beyond the scope of this work.

3.4. Kinetics of bicumene decomposition

The close relationship between peroxide decomposition kinetics and radical-mediated reaction dynamics is such that peroxide homolysis rates receive a great deal of attention. To gain insight into the dynamics of a bicumene-initiated grafting process, we have undertaken a study of bicumene decomposition kinetics at elevated temperature. The results of this work are presented as plots of bicumene conversion versus time (Fig. 6). We observed nearly equal amounts of cumene and α-methylstyrene in all the experiments except those employing benzenethiol, which produced only cumene in measurable quantities.

The unfettered decomposition of bicumene in trichlorobenzene was a first-order process whose rate could be characterized by the constants $k_d^{260\ °C} = 8.37 \times 10^{-3}\ \text{min}^{-1}$ and $k_d^{240\ °C} = 1.40 \times 10^{-3}\ \text{min}^{-1}$, which are in good agreement with values recorded using monochlorobenzene as solvent [12]. These rate constants translate into half-lives of 1.4 and 8.3 h for bicumene decomposition at 260 and 240 °C, respectively. The latter result is particularly interesting, since appreciable extents of HDPE modification were observed at 240 °C within 20 min of extruder residence time (Fig. 2). According to the conventional model of peroxide-initiated grafting, an initiator with a decomposition half-life on the order of hours could not support a viable reactive extrusion process unless the number of graft additions per cumyl radical was extremely high.

The decomposition of bicumene in the absence of an appropriate hydrogen donor provides no alternate reaction pathway to bimolecular cumyl radical termination (Scheme 2). Given that cumyl radical combination is preferred over disproportionation [13], measuring the rate of bicumene homolysis without experiencing complications due to radical recombination requires that a very rapid, irreversible termination reaction pathway be generated. These conditions are

Table 4
LLDPE modification with dicumylperoxide

Flow rate (g/min)	Res. time (min)	DCP loading (wt%)	Extruder torque (N m)	Graft content (wt%)	MFI (g/10 min)
5.4	16.6	0.05	20.8	1.5	4.7
9.9	8.8	0.05	25.9	1.2	4.8
13.1	5.9	0.05	24.6	2.8	4.1
18.4	4.4	0.05	28.3	1.8	4.1
22.3	3.5	0.05	30.5	2.4	4.1
5.0	17.5	0.15	33.2	3.5	1.9
10.2	8.9	0.15	42.6	3.5	1.6
14.9	5.9	0.15	49.3	4.0	1.4
20.0	4.4	0.15	55.4	3.8	1.0
24.4	3.6	0.15	57.0	3.7	1.6

$T_1 = 150$ °C; $T_2 = T_3 = 180$ °C; [VTEOS] = 5.0 wt%.

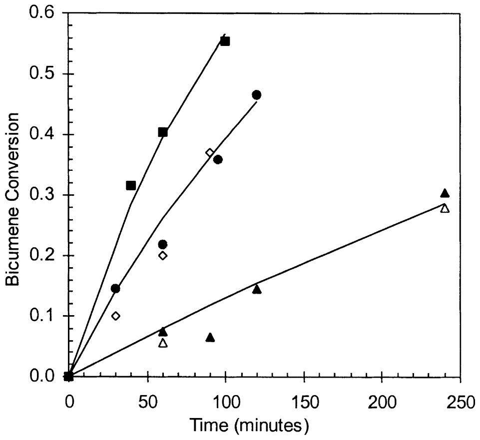
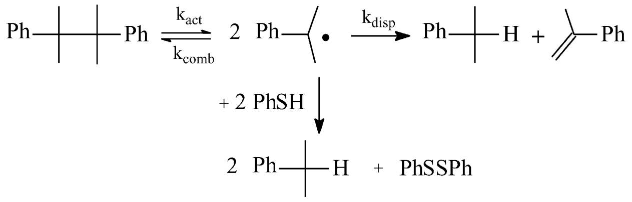


Fig. 6. Bicumene decomposition kinetics in trichlorobenzene (■ 260 °C; ◇ 240 °C, 5 equiv. PhSH; ● 240 °C, 10 equiv. PhSH; ▲ 240 °C; △ 5 equiv. cyclooctane).

difficult to establish given the magnitude of alkyl radical combination constants [9]. Nevertheless, we have attempted to characterize bicumene homolysis using a large excess of benzenethiol to terminate cumyl radicals by hydrogen atom donation, thereby reducing their concentration to such an extent that their bi-radical termination frequency is greatly reduced [13,14].

The addition of 5 mole equiv. of benzenethiol to a solution of bicumene generated cumene as the sole initiator byproduct and accelerated the decomposition process, yielding $k_d^{240\,^{\circ}\mathrm{C}} = 5.04 \times 10^{-3}\ \mathrm{min}^{-1}$ (Fig. 6). Increasing the concentration of benzenethiol to 10 mole equiv. had no incremental effect, suggesting that the chain transfer agent was successful in trapping all cumyl radicals that escaped cage effects. That the decomposition rate and product distribution was unaffected by cyclooctane (Fig. 6) indicates that the hydrocarbon is not an effective hydrogen donor to cumyl radicals. This has implications regarding the initiation mechanism, which is discussed in Section 4.

The involvement of oxygen in the initiation of VTEOS grafting was explored by heating a tetradecane solution of bicumene to reflux (ca. 253 °C) in air. Gas chromatography–mass spectrometry (GC–MS) confirmed the presence of significant amounts of acetophenone and cumyl alcohol. These are the expected oxidation products derived from the trapping of cumyl radicals by oxygen, and their presence implies that an auto-oxidation mechanism may initiate grafting in a high-temperature, bicumene-based process.



Scheme 2.

4. Discussion

There are three conceivable mechanisms through which bicumene may initiate the graft modification of polyethylene: direct hydrogen abstraction from the polymer by cumyl radicals, cumyl radical addition to VTEOS followed by hydrogen abstraction by the monomer-derived radical, and interaction of cumyl radicals with oxygen to support an auto-oxidation pathway. All three mechanisms are influenced by the homolysis of bicumene to generate cumyl radicals. Therefore, bicumene decomposition will be discussed prior to considering the significance of various initiation pathways.

Peroxide homolysis (r_1; Scheme 1) is generally treated as an irreversible process, given that oxygen-centered radicals are proficient in hydrogen atom abstraction from hydrocarbons and they fragment readily to generate alkyl radicals and the corresponding ketone. Recombination of alkoxy radicals outside the radical cage is not, therefore, a dominant reaction pathway, and insight into pseudo steady-state radical concentrations requires information regarding peroxide decomposition (k_d: Scheme 1), and alkyl macroradical termination (k_{tc}, k_{td}: Scheme 1).

Under conditions where no suitable hydrogen atom donor is present and no low-energy fragmentation pathway is available, bimolecular radical termination is expected to dominate the reactivity of the system. In the case of bicumene, radical combination yields the starting compound while disproportionation generates cumene and α-methylstyrene (Scheme 2). Only the latter reaction is irreversible and bicumene decomposition data recorded in the absence of benzenethiol reflect only the kinetics of disproportionation, and not the rate of bicumene homolysis (Fig. 6).

The rate of bicumene decomposition in the absence of a radical trap can be derived from the mechanism illustrated in Scheme 2. Applying the steady-state hypothesis to the cumyl radical population $[\mathrm{PhMe_2C^\bullet}]$ yields

$$[\mathrm{PhMe_2C^\bullet}] = \sqrt{\frac{k_{act}[\mathrm{bicumene}]}{k_{comb} + k_{disp}}}.$$

The rate of bicumene loss (which is equal to the cumyl radical disproportionation rate) follows directly:

$$-\frac{\mathrm{d[bicumene]}}{\mathrm{d}t} = \frac{k_{act}k_{disp}}{k_{comb} + k_{disp}}[\mathrm{bicumene}].$$

It is clear that measurements of bicumene consumption reflect the dynamics of not only bicumene homolysis (k_{act}), but cumyl radical combination (k_{comb}) and disproportionation (k_{disp}). Studies of cumyl radical termination by Nelsen and Bartlett over a wide temperature range have shown that k_{comb} is several times greater than k_{disp} [13]. The importance of recombination outside the radical cage is such that bicumene activation must be treated as a reversible process, unlike the peroxide systems where homolysis may be considered irreversible without introducing significant error to the analysis. Furthermore, the response of an overall rate constant [$k_d = k_{act}k_{disp}/(k_{comb} + k_{disp})$] to temperature will depend upon the activation energies of all three processes.

The rate of bicumene homolysis (k_{act}) can be measured directly by establishing conditions where a hydrogen atom donor suppresses the cumyl radical concentration to the point where bi-radical termination is insignificant. Cyclooctane proved to be ineffective in this capacity, as it did not alter the rate of bicumene decomposition or the resulting product distribution. However, benzenethiol has been shown to act as an effective hydrogen donor to cumyl radicals that escape cage effects [13,14]. In the presence of excess benzenethiol, the first-order rate constant for bicumene decomposition in trichlorobenzene was $k_d^{240\,°C} = 5.04 \times 10^{-3}\ \mathrm{min}^{-1}$. Should this value represent the homolysis rate constant (k_{act}), it would define the upper limit for the rate of cumyl radical generation from bicumene at 240 °C.

Based upon the generally accepted belief that cumyl radicals are relatively poor hydrogen atom abstractors, it is difficult to attribute the high levels of VTEOS addition to polyethylene to an initiation mechanism involving direct hydrogen atom abstraction from the polymer by cumyl radicals. Although steric and polar factors can be influential [15], Ingold has noted that the activation energy for hydrogen abstraction cannot be less than the heat of reaction, and exothermic hydrogen abstraction reactions, therefore, tend to be more rapid than endothermic analogues [16]. A comparison of bond dissociation energies (Table 5, [17]) indicates that hydrogen atom abstraction from a methylene group by a cumyl radical is energetically unfavorable, unlike a similar abstraction by a *t*-butoxy radical. Further evidence of the limited role of abstraction by cumyl radicals is shown in Fig. 6, in which cyclooctane proved to be incapable of influencing bicumene decomposition by acting as a hydrogen atom donor.

Further doubts concerning the significance of a direct cumyl radical initiation mechanism arise when the silane grafting rate is compared with that of bicumene homolysis. The upper limit of cumyl radical generation, estimated from the benzenethiol-promoted bicumene decomposition experiments, is very slow in comparison to the rate of VTEOS addition and MFI reductions observed during reactive extrusion. Unless the kinetic chain length (defined as the number of silane grafts per polymer macroradical initiated) is much greater at 240 °C than is observed at conventional grafting temperatures, bicumene homolysis would not be fast enough to support the radical activity observed in the melt grafting experiments.

Table 5
Homolytic bond dissociation energies

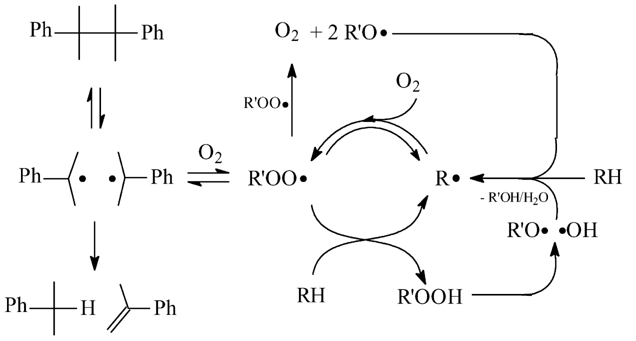
	ΔH (kJ/mol)
$PhCH(CH_3)_2 \rightarrow PhC^{\cdot}(CH_3)_2 + H^{\cdot}$	353.1
$t\text{-}BuOH \rightarrow t\text{-}BuO^{\cdot} + H^{\cdot}$	439.7
$c\text{-}C_6H_{12} \rightarrow C_6H^{\cdot}_{11} + H^{\cdot}$	399.6
$C_3H_8 \rightarrow C_3H^{\cdot}_7 + H^{\cdot}$	420.0

25 °C; from Ref. [17].

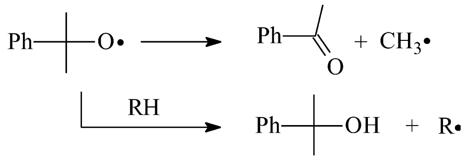
An alternate mechanism through which bicumene may initiate grafting proceeds by the addition of vinylsilane to a cumyl radical (r_3, Scheme 1) [18], followed by hydrogen atom abstraction from the polymer by the resulting silane-derived radical (r_4, Scheme 1). However, graft initiation by this pathway would depend directly on the bicumene homolysis rate, as discussed above. Furthermore, the same MFI reduction of HDPE was generated by bicumene whether or not VTEOS was present (Figs. 2 and 3). Therefore, the data acquired to date suggests that a VTEOS addition–hydrogen abstraction process does not contribute significantly to initiation.

Air oxidation of cumyl and polymeric alkyl radicals is the basis of a third initiation mechanism. It is generally accepted that trapping of carbon-centered radicals by oxygen is a rapid process that accelerates the degradation of polyolefins during high-temperature processing [19,20]. In the present application, the rapid, reversible combination of a cumyl radical with oxygen [21,22] to generate a cumylperoxy species ($PhMe_2COO^{\bullet}$) would improve its hydrogen abstraction proficiency. Scheme 3 illustrates a subset of the subsequent reactions that may support vinylsilane grafting [23]. Hydrogen atom abstraction by cumylperoxy radicals leads to hydroperoxide formation, while the interaction of two such radicals generates the same cumyloxy species yielded by dicumylperoxide (DCP). In support of cumyl radical oxidation is our detection of acetophenone and cumyl alcohol from the decomposition of bicumene in tetradecane under an air atmosphere (Scheme 4). We note that, while hydroperoxides are relatively stable species, their decomposition is expected to be rapid at the temperatures of interest, especially given the metals and other impurities within a polyethylene resin [24,25].

Alkyl macroradicals generated by hydrogen abstraction from the polymer may engage not only in VTEOS addition, but in continued oxidation to support an auto-accelerating initiation process. As indicated in Scheme 3, the combination of alkyl radicals ($R^{\bullet}$) with oxygen is expected to continue the auto-initiation process beyond the point of



Scheme 3.



Scheme 4.

cumyl radical involvement. According to this mechanism, a single cumyl radical may be capable of yielding several polyethylene macroradicals. Excessively high kinetic chain lengths are not required under these conditions, and the level of grafting activity observed at 240 °C is more easily rationalized.

We note that the oxidation of paraffins at temperatures exceeding 300 °C generates olefins and hydrogen peroxide in high yields through disproportionation between secondary alkyl radicals and oxygen [22,26]. Therefore, at the highest temperatures employed in this work, the potential for cumyl and polymeric radicals to engage with oxygen in this manner may be significant [27]. More details concerning the involvement of this reaction and those illustrated in Scheme 3 in bicumene initiation chemistry will be the subject of a forthcoming publication.

5. Conclusions

Bicumene is an efficient radical initiator for the melt grafting of VTEOS to polyethylene at temperatures exceeding 225 °C. Studies of grafting and cross-linking dynamics as well as the kinetics of bicumene decomposition are consistent with an air oxidation initiation mechanism in which polymer macroradicals are generated by oxygen-centered radical intermediates. Improvements on the selectivity of conventional peroxide-initiated processes may be obtained by inducing radical fragmentation at high temperature in order to offset the influence of macroradical combination on MFI.

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