

Peroxide Modification of Linear Low-Density Polyethylene: A Comparison of Dialkyl Peroxides

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SYNOPSIS

A commercial-grade LLDPE resin was cross-linked using three different dialkyl peroxides, at three different concentrations. The peroxides were ranked in order of their cross-linking efficiency and their effectiveness at increasing the storage modulus of the virgin resin at the cure temperature. The chemical mechanism by which the cross-linking occurs is shown to be closely related to the changes in concentrations of reactive vinyl species on the polyethylene molecules, which follows well with proposed mechanisms of previous publications. Finally, a direct relationship is shown to exist between the rate of peroxide decomposition and the rate of increase in storage modulus of the rubbery modified resin during the curing reaction. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Organic peroxides have become increasingly important as initiators of free-radical degradation mechanisms in polyethylene (PE) in order to modify the polymer structure and properties. One of the more popular peroxides, dicumyl peroxide, has been shown to be effective in the introduction of long-chain branches in otherwise linear polyethylenes,¹ and at low concentrations, it favorably alters molecular weight distributions.²⁻⁴ At higher peroxide concentrations, cross-linked polyethylene is obtained.⁵⁻⁷

Dicumyl peroxide is a popular choice because of its favorable decomposition rate at normal processing temperatures of polyethylene. Other dialkyl peroxides have been studied in PE-modification schemes, but not to the same extent as has dicumyl. The mechanism of action of α,α -bis (tertiary butylperoxy) -*p*-diisopropyl benzene⁸ and 2,5-dimethyl-2,5-di(tertiary butylperoxy)-hexyne-3⁹ in their roles as PE cross-linking agents have been studied, but without particular attention to the chemical mechanisms involved.

The mechanical properties of PEs cross-linked with peroxides other than dicumyl is also of interest, and some literature does exist on this topic. Kunert¹⁰ reported on the results of cross-linking PE using three different peroxides: dicumyl peroxide, 2,5-dimethyl-2,5-di(tertiary butylperoxy)-hexane, and 2,5-dimethyl-2,5-di(tertiary butylperoxy)-hexyne-3. The comparison of the peroxides themselves in this instance is somewhat lacking in detail, as the author claims that "all the peroxides in this study gave similar results," and therefore the results for only one peroxide were given. The different peroxide decomposition rates are perhaps the primary factor in choosing a particular peroxide for an intended application. Dialkyl peroxide decomposition occurs through a two-step process, involving formation of an intermediate alkoxy radical species. The lifetime of this strongly abstracting species will alter the peroxides overall efficiency rating significantly, and therefore the peroxides studied in the above study could be expected to behave somewhat differently in terms of curing rates. It is useful to see the times taken for complete cure, and this phenomenon has been studied here.

The purpose of the present work is to compare the relative efficiencies of three different dialkyl peroxides in their ability to cross-link a PE resin. The peroxides are also ranked according to their

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effectiveness in increasing the modulus of the molten polymer as the cross-linking process proceeds. The mechanism of cross-linking on a molecular level was investigated through infrared spectroscopic methods and determination of reactive vinyl group concentrations. The participation of these reactive species has been shown to be of primary significance in peroxide-initiated mechanisms.^{4,7} Following the changes in concentration of these groups permits an assessment of the relative extent of competitive chain coupling vs. chain-scission reactions that occur simultaneously in the PE melt.

A connection is also made between the rates of peroxide decomposition and the subsequent effects of the peroxide-initiated reactions on the storage modulus of the modified resin. The parallel seen between the rate of peroxide decomposition and the rate of increase in storage modulus with time may reflect the role the peroxide plays in cross-linking, since elementary rubber elasticity theory¹¹ relates the storage modulus to the average cross-link spacing through the relationship

$$M_c = \frac{\rho RT}{G_{\omega=0}} \quad (1)$$

where M_c is the average molecular weight between cross-links; ρ , the polymer density at the experimental temperature (g cm^{-3}); R , the universal gas constant ($8.314 \times 10^7 \text{ ergs mol}^{-1} \text{ K}^{-1}$); T , the reaction temperature (K); and $G_{\omega=0}$, the value of the modulus at an extrapolated frequency (ω) of zero (dyn cm^{-2}).

A second, more empirical observation may also be made in connection with this increase in storage modulus. Peroxide reactions are normally carried out with the assumption that the decomposition rate in a viscous polymer matrix is the same as that in a dilute organic solvent solution, in which the majority of decomposition rates are measured. An im-

portant consideration from a practical and economical standpoint is that the peroxide be fully consumed over the time of the reaction. The assumption of equal decomposition rates in both solvent and polymer media may or may not be valid. However, if we use the attainment of a maximum in the value of the storage modulus as an indicator of a complete reaction, it is reasonable to equate this point in time with the end of the effective contribution of peroxide to increasing the modulus [or increasing cross-link density, according to eq. (1) above]. In this way, the suitability of specifying a reaction time of five half-lives (" $5 \times t_{1/2}$ ") for complete reaction can be tested under particular reactions and shown to be valid.

EXPERIMENTAL

Sample Preparation

The polymer used in this study was a commercial linear low-density polyethylene (LLDPE), with a 1-hexene comonomer ($M_n = 48,800$; $M_w = 201,000$). The resin was provided in granular form and contained a hindered phenolic antioxidant at a level of 200 ppm.

All peroxides used were kindly provided by Atochem Inc., with decomposition rates summarized in Table I. Peroxide addition to the powdered resin was achieved by dissolving appropriate quantities of peroxide in cyclohexane solvent and adding this solution to the resin. The slurry was allowed to tumble blend for 8 h with no loss of solvent, after which time the lids were removed from the blending containers, allowing free evaporation during the continued tumble mixing process. The solvent was allowed to evaporate for a full 48 h period, after which time the containers were placed in a vacuum oven at 50°C at a vacuum at approximately 80 kPa vacuum for an additional 8 h period. This process has

Table I Peroxides Used and Half-Lifetimes in Dilute Hydrocarbon Solvent

Peroxide	Sample Code	Half-Life (s)		
		at 155°C	at 166°C	at 174°C
Dicumyl peroxide	Luperox 500R	538.8	—	—
α,α -Bis(tertiary butylperoxy)- <i>p</i> -diisopropylbenzene	Luperox 802	655.3	—	—
2,5-Dimethyl-2,5-di-(tertiary butylperoxy)-hexyne-3	Luperox 130	2558.4	832.8	381.0

Half-lifetimes are shown only for peroxide/polymer mixtures used in this study.

Table II Summary of Peroxide Concentrations

Peroxide	Masterbatch Concentration		Dilution Concentration	
	w/w %	FR/gram ^a	w/w %	FR/gram ^a
500	0.472	3.5×10^{-4}	0.10	7.5×10^{-6}
500	0.472	3.5×10^{-4}	0.15	1.1×10^{-5}
500	0.472	3.5×10^{-4}	0.20	1.5×10^{-5}
802	0.296	3.5×10^{-4}	0.06	7.5×10^{-6}
802	0.296	3.5×10^{-4}	0.09	1.1×10^{-5}
802	0.296	3.5×10^{-4}	0.13	1.5×10^{-5}
130	0.256	3.5×10^{-4}	0.05	7.5×10^{-6}
130	0.256	3.5×10^{-4}	0.08	1.1×10^{-5}
130	0.256	3.5×10^{-4}	0.11	1.5×10^{-5}

^a FR/gram is the abbreviation for moles of free radicals per gram of resin, based upon a 100% peroxide decomposition. This abbreviation is to be used for the remainder of this article.

in the past been determined to be effective in providing uniform peroxide dispersion on the surface of the resin, along with negligible residual solvent concentration.⁴

A masterbatch concept was used in preparing the various concentrations that were needed for the analyses completed in this study. Table II summarizes the peroxide concentrations of all samples studied. It should be noted that the peroxides were added to the resin to provide identical active free radical concentrations per gram of resin, as opposed to the common practice of comparing peroxide efficiency on a weight percent basis. The latter procedure is convenient for practical purposes, but cau-

tion must be exercised in comparing those results to other studies, especially if a different peroxide is used. Figure 1 shows a comparison of weight percent concentration and a measure of moles of free radicals produced per gram of polymer (FR/gram), which will be the concentration units used throughout this report. Note the divergent behavior at higher free-radical concentrations.

Sample Analysis

(i) Dynamic Mechanical Analysis

A Rheometrics Model 605 dynamic mechanical spectrometer was used for all PE curing reactions.

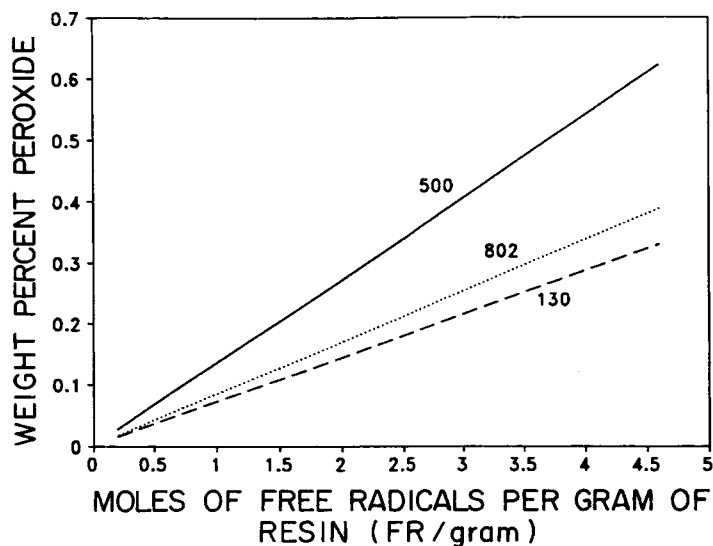


Figure 1 Peroxide weight percent vs. moles of free radicals produced per gram of polymer. The labels on the figure correspond to the peroxide coding as shown in Table I.

The virgin resin was used to determine the instrument parameters that would provide adequate signal response and to ensure that experiments were conducted in a linear viscoelastic region. Samples were analyzed in the shear mode at a constant temperature, imposing a 5% strain at a frequency of 40 rad/s. All samples, at all concentrations, were cured at a temperature of 155°C, with the exception of samples prepared with peroxide 130. All concentrations of this polymer/peroxide blend were run at two additional temperatures of 166 and 174°C.

Once fully cured, a frequency sweep experiment was completed at the same 5% strain value. Oscillatory frequencies over a range of 0.01 to 40 rad/s were used to determine the value of the shear storage modulus, G' , at each frequency. This experiment was conducted to allow an approximation of modulus at zero frequency.

Samples were loaded into the preheated chamber of the spectrometer, which was set at an initial temperature of 130°C. The sample loading time was kept to a minimum to reduce the peroxide decomposition, and accurate records of the loading time and time to reach the desired cure temperature were kept so that the peroxide decomposed during this period could be accounted for in the total analysis. In all cases, less than 5% of the peroxide was decomposed in loading and heat-up stages.

Samples were run for periods of time equal to at least six half-lives of the peroxide being studied. This time was found to be adequate in arriving at a plateau values of the storage modulus, G' . Degradation was minimized over the course of the analysis by heating the environmental chamber with hot nitrogen gas.

(ii) Preparation of Thin Films for Infrared Analysis

All samples used for infrared analysis were prepared using a hydraulic press with thermostatically controlled upper and lower platens. Reaction temperatures and times were chosen to mimic as closely as possible the dynamic mechanical analyses cure times and temperatures. Thin films of approximately 0.3 mm thickness were generated in this manner.

(iii) FTIR Analysis

Analysis for *trans* and terminal unsaturations and carbonyl species was completed using a Nicolet Model 520 FTIR operating at 1 wavenumber resolution. Peaks from the absorbance spectra were assigned to out-of-plane C—H bends associated with terminal vinyls (908 cm^{-1}), pendant vinyls (888

cm^{-1}), and *trans* unsaturations (964 cm^{-1}). *Cis* vinyl unsaturations are unfortunately not quantifiable by this method, since their absorption peak at 735 cm^{-1} is obliterated by the large CH_2 absorption at 720 cm^{-1} . Sample thicknesses were measured with a digital micrometer. Band assignments and quantitation of the vinyl groups present was carried out by utilizing the extinction coefficients reported in the well-accepted method of Haslam et al.¹² In this method, extinction coefficients were obtained by studying model compounds of monomeric hydrocarbons with known levels of unsaturation.

(iv) Gel Content Analysis

Gel contents were determined by a solvent extraction technique, whereby cross-linked PE samples were placed in preweighed 200 mesh stainless-steel baskets and immersed in refluxing toluene. The samples were allowed to dissolve for 8 h, after which time they were removed from the toluene solvent and immediately placed in a vacuum oven at 70°C under a vacuum of approximately 60 kPa. After a 48 h period, the samples were removed from the oven, allowed to cool, and then weighed. This technique of gel content measurement has been found to give reproducible results, yet is understood to be very dependent upon factors such as solvent type, reflux time, and sample size, as reported by Manley and Qayyum.¹³

RESULTS AND DISCUSSION

The first experiments conducted on the dynamic mechanical spectrometer were completed to determine reproducibility of the curing reactions. Figure 2 shows the results of three separate resin curing reactions with peroxide 802 as the active peroxide, at a concentration of 1.5×10^{-5} FR/g. The value of $\log G'$ at maximum cure is of interest for the purposes of this study and is shown to be quite reproducible for this sample, as it was for all other peroxide/polymer combinations studied.

A comparison of the three peroxides in their role as cross-linkers was made on the basis of each peroxide's ability to provide a maximum value of $\log G'$ according to the relationship shown in eq. (1). Figure 3 shows a set of three cure curves, one for each peroxide studied, with all peroxides at a concentration of 7.5×10^{-6} FR/g. The vertical bars on the figure are drawn in at a time corresponding to five times the peroxide half-lifetime at the experimental temperature of 155°C. A clear ranking order is ob-

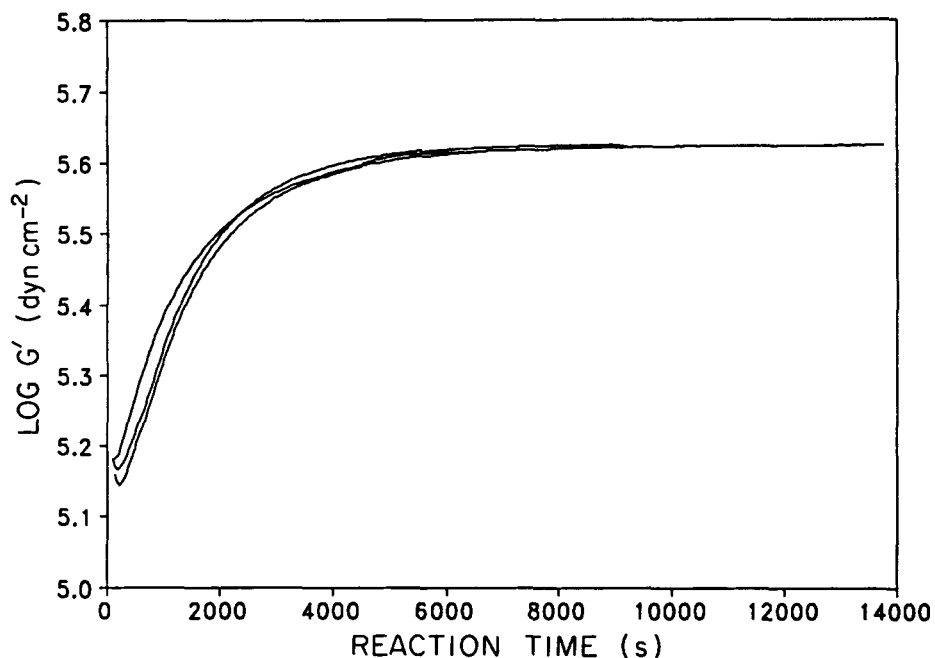


Figure 2 Reaction time vs. $\log G'$ (storage modulus) for peroxide 802 [α,α -bis(tertiary butylperoxy)-*p*-diisopropylbenzene] at 1.5×10^{-5} FR/gram. Three runs were completed at 155°C and show very good reproducibility. An average value for $\log G'$ at a time of $5 \times t_{1/2}$ was found to be 5.624, with a standard deviation of 0.0053.

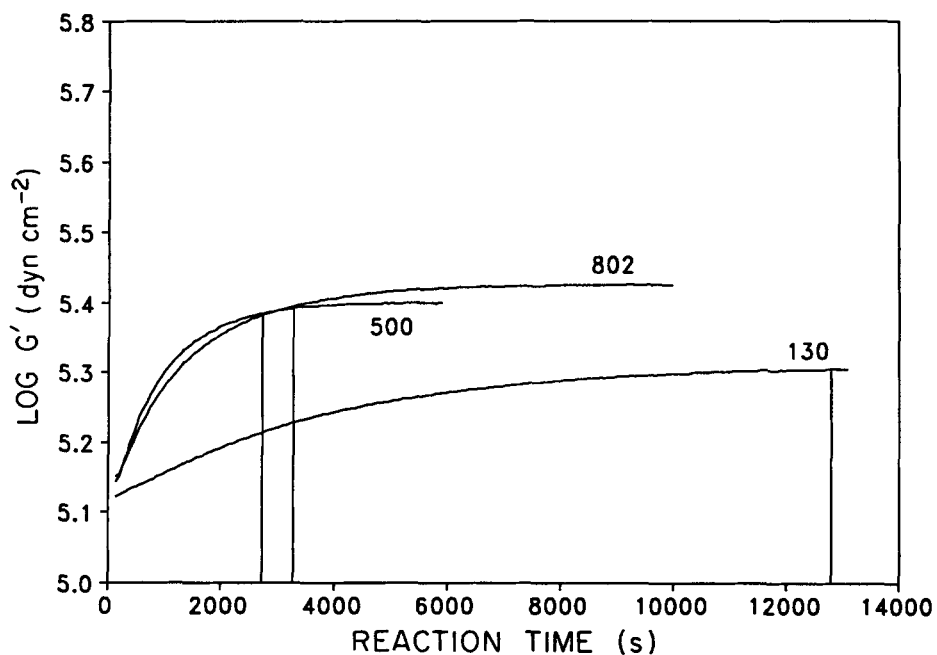


Figure 3 Reaction time vs. $\log G'$ for constant peroxide content of 7.5×10^{-6} mol of free radicals per gram of resin. All samples were cured at 155°C . The number codes above each cure curve refer to the peroxide as coded in Table I. Vertical bars signify a time of $5 \times t_{1/2}$ as measured in dilute solution and correspond to peroxides 500, 802, and 130 from left to right.

tained; 802 > 500 > 130. Peroxide 130, the slowest decomposing peroxide, produces a modulus value well below those of peroxides 802 and 500, which are reasonably close to each other.

Table III is a summary of the values of $\log G'_{\max}$, which is the maximum value attained before the onset of obvious thermal degradation, and the value of $\log G'$ at five times the $t_{1/2}$ value for the peroxide in dilute solution. The right-hand column expresses the value of $\log G'$ at $5 \times t_{1/2}$ as a percentage of $\log G'$ at maximum cure. As the peroxide concentrations are increased, the value of $\log G'_{\max}$ for all samples increases, as expected, but the difference between the maximum values for peroxides 500 and 802 diminishes such that at the highest peroxide concentration (1.5×10^{-5} FR/g), the values of $\log G'_{\max}$ are essentially identical. Another important fact to note, which will be discussed further in this article, is that the polymer has achieved essentially full cure by the time five peroxide half-lives have elapsed, as indicated in the rightmost column of Table III.

The differences in the values of $\log G'_{\max}$ produced by each of the peroxides reflects the differences in overall peroxide activity, even though each has been blended to obtain the same number of free radicals upon full decomposition. For each of the peroxides, the chemistry of decomposition is a two-step process: Step 1 involves cleavage of the oxygen-oxygen bond, producing alkoxy radicals, and the second step produces a single methyl radical from each alkoxy rad-

ical fragment by a beta-scission process. (The peroxide decomposition reactions are sketched in the Appendix.) The intermediate alkoxy radical species is a strong hydrogen atom abstracting species, and the lifetime of this radical in the melt prior to the beta-scission reaction can be expected to have a significant impact on the outcome of the cross-linking process. The formation of methyl radicals by beta scission is expected to be slow,¹³ with the abstracting power of the methyl radical being approximately 1 kcal mol⁻¹ lower than the butoxy radical, based upon measurements of bond dissociation energies.¹³

The results presented are expected, where higher peroxide concentrations lead to increased melt viscosity and elasticity^{14,15} and higher cross-link densities.^{2,5,16} A typical plot of gel content as a function of peroxide concentration has a shape not unlike the cure curves shown in Figures 2 and 3, where gel content is plotted on the y-axis. What this means is that at a peroxide concentration just above that required for the onset of gel very large increases in gel content are seen with very small increases in peroxide (a steep initial slope). As the gel content approaches its maximum value, increasing the peroxide level has little or no effect on the amount of cross-linked material (i.e., a shallow or zero slope).

With this simplified description in mind, the diminishing separation between $\log G'_{\max}$ for peroxides 802 and 500 with increasing peroxide level may be explained as follows: Peroxide 802 is evidently more efficient than is 500 at increasing the PE modulus

Table III Comparison of Modulus at Full Cure and at Time = Five Half-Lives

Peroxide	Concentration (FR/gram)	Reaction Temp (°C)	$\log G'$ (max)	$\log G'$ at $5 \times t_{1/2}$	Percent of Full Cure at $5 \times t_{1/2}$
Virgin	0.0	155	5.122	—	—
500	7.5×10^{-6}	155	5.399	5.384	99.7
802	7.5×10^{-6}	155	5.425	5.394	99.4
130	7.5×10^{-6}	155	5.304	5.304	100.0
500	1.1×10^{-5}	155	5.484	5.465	99.7
802	1.1×10^{-5}	155	5.497	5.448	99.1
130	1.1×10^{-5}	155	5.382	5.381	100.0
500	1.5×10^{-5}	155	5.605	5.596	99.8
802	1.5×10^{-5}	155	5.602	5.546	99.0
130	1.5×10^{-5}	155	5.427	5.427	100.0
130	7.5×10^{-6}	166	5.359	5.338	99.6
130	1.1×10^{-5}	166	5.399	5.381	99.7
130	1.5×10^{-5}	166	5.545	5.510	99.4
130	7.5×10^{-6}	174	5.334	5.333	100.0
130	1.1×10^{-5}	174	5.378	5.377	100.0
130	1.5×10^{-5}	174	5.493	5.493	100.0

at equal concentrations. The diminishing separation between the two maximum moduli may indicate that peroxide 802 has reached close to its maximum useful contribution to cross-linking and that additional increases in the concentration of this peroxide has little effect on increasing gel. Peroxide 500, on the other hand, still shows considerable gains in $\log G'_{\max}$ with increasing peroxide concentration and, therefore, may be thought to still be in the regime of a "steep initial slope," as discussed in the preceding paragraph.

This is a very important factor to consider, in that two peroxides with approximately equal decomposition rates, ultimately producing the same active radical species, behave quite differently in terms of their efficiencies as cross-linkers. To emphasize this even more, consider the results of a study incorporating the same three peroxides studied here and their relative efficiencies in grafting of maleic anhydride onto polypropylene.¹⁴ In this study, peroxide concentrations from 250 to 500 ppm (0.025–0.05% w/w) were blended into the polypropylene melt in the presence of maleic anhydride in order to graft this reactive monomer onto the polypropylene chains. The authors ranked the peroxides in order of their relative efficiencies in the grafting process, using the same concentration considerations as in this study, and derived a different order from that found here. Although this reaction system is considerably different from the one we studied, it effectively illustrates the complexity associated with peroxide activity in polymer systems and emphasizes the necessity for careful selection of a peroxide to perform a specific task.

Peroxide 130 consistently gave the lowest values for $\log G'_{\max}$ when compared to peroxides 802 and 500, as shown in Table III. An additional series of experiments was conducted using peroxide 130 as the cross-linker at the two higher temperatures of 166 and 174°C. The time required for loading the sample and temperature equilibration in the dynamic mechanical spectrometer made these higher temperature experiments inaccessible to the two faster reacting peroxides. Examination of the data in Table III shows that curing at a temperature of 166°C gives the highest value of $\log G'_{\max}$ at all three concentrations studied.

These results serve well to support the proposed mechanisms of peroxide-initiated cross-linking in PE that have been published previously,^{4,7,17,18} where the general consensus may be summarized as follows: In a free radical-initiated degradation scheme, two simultaneously competing submechanisms exist: chain-scission reactions (e.g., beta-scission at

branch points and interchain scission) and chain growth reactions (e.g., long-chain branch formation, termination by radical coupling). The degree to which one or the other of these submechanisms dominates the overall reaction is strongly affected by the reaction temperature, where higher reaction temperatures favor chain scission and nongrowth disproportionation reactions. Low temperatures tend to favor successful chain growth reactions, as evidenced through significant increases in molecular weights, and formation of new long-chain branches. On a molecular level, it has been found that monitoring the presence of terminal and *trans*-vinyl unsaturations on the polymer chains is an excellent way to follow the progress of one or the other of these submechanisms.⁴ The formation of new *trans* unsaturations is a direct result of chain-coupling reactions occurring at a terminal allylic radical site.

In a previous article,⁴ it was shown that at the lowest reaction temperature studied (180°C) the greatest molecular weight increases were seen when reacting low levels of dicumyl peroxide with a commercial-grade HDPE resin. In the current study, a temperature of 166°C is seen to be the best reaction temperature for obtaining a high rubbery phase modulus (i.e., highest degree of cross-linking, from a predominance of chain-coupling reactions over chain-scission reactions) at all concentrations studied. At the higher temperature of 174°C, this equilibrium between the two competing submechanisms has shifted to provide more scission events, and, therefore, the efficiency of peroxide as a cross-linker has decreased.

Further support for this mechanistic proposal is seen through the results of infrared analysis on thin PE films. Figures 4 and 5 show the changes in *trans* and terminal unsaturation as a function of peroxide concentration in resins cured at 155°C.

The terminal unsaturation content in the virgin resin is seen to be high, and the *trans* unsaturation content, quite low. Upon reaction with peroxide, the *trans* unsaturation content increases significantly, and a corresponding decrease in the level of terminal vinyls is also seen as this type of functionality is converted to *trans*-vinyl groups through chain-coupling events. The greatest increase in *trans* unsaturation occurs for peroxide 802, which is consistent with this peroxide producing the greatest increase in modulus of the modified resin. A corresponding largest decrease in terminal unsaturations for this peroxide lends to the idea that consumption of terminal vinyls occurs chiefly through chain-coupling reactions and the formation of new *trans*-vinyl species.

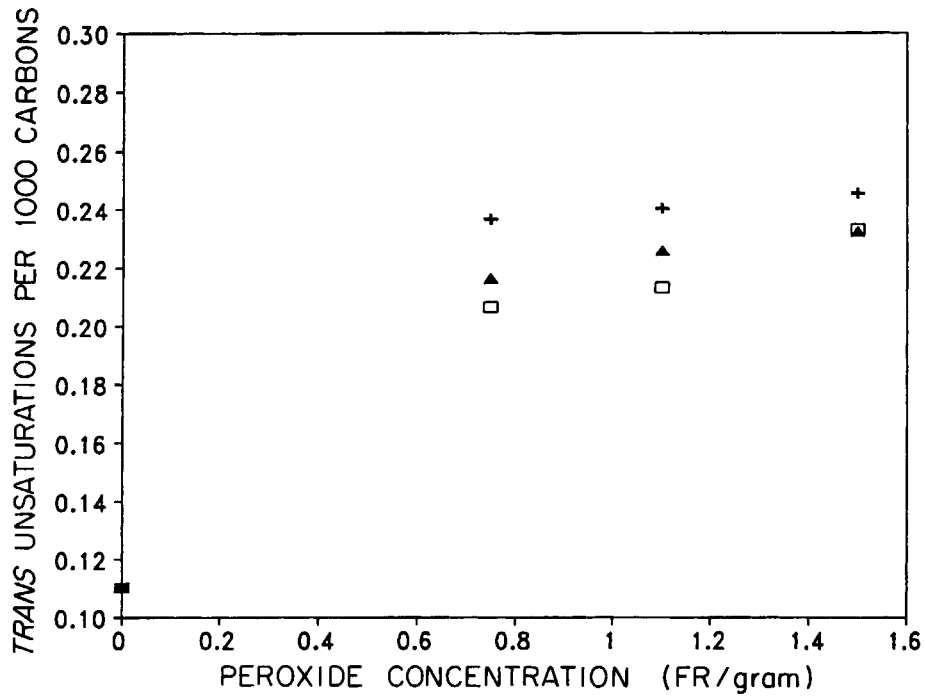


Figure 4 Peroxide concentration vs. *trans* unsaturation content of peroxide modified resin reacted at 155°C: (■) virgin resin; (□) peroxide 500; (+) peroxide 802; (▲) peroxide 130.

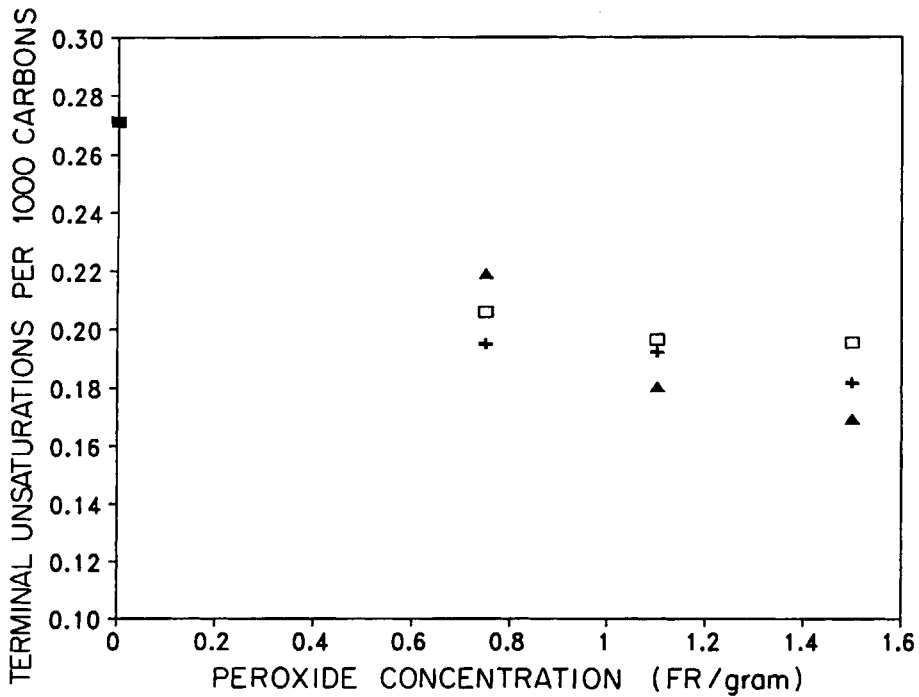


Figure 5 Peroxide concentration vs. terminal unsaturation content of peroxide modified resin reacted at 155°C: (■) virgin resin; (□) peroxide 500; (+) peroxide 802; (▲) peroxide 130.

As the peroxide level is increased, all peroxides show increases in *trans* unsaturations and decreases in terminal unsaturations. This supports the proposed mechanism as well, such that a higher concentration of initiating radicals is more likely to react with a greater number of terminal unsaturations, increasing the number of chain-coupling reactions, thus increasing the gel content (and modulus). The uneven trends for terminal unsaturation content have been seen before⁴ and are expected since both the production (through beta-chain scission) and consumption (through coupling reactions) of terminal unsaturations are occurring simultaneously. *Trans* unsaturations, on the other hand, are not readily consumed in a peroxide modification of this type, and, therefore, the increasing trend has a smooth shape. This mechanism is consistent with the predominant effect of vinyl chain ends in the radiation cross-linking of low-density polyethylene.¹⁹

Measurement of gel content by the solvent-extraction technique on the lightly cross-linked polymers would be expected to provide a correlation with the values of the storage modulus at maximum cure ($\log G'_{\max}$). Further, if a measure of the cross-linking efficiency of each of the peroxides was measured, the efficiencies would be expected to rank in the same order as the values of $\log G'_{\max}$ from lowest to highest. Cross-linking efficiency was calculated according to the method of Narkis and Miltz,²⁰ which is based on Barton's²¹ modification of the original method of Charlesby and Pinner²²:

$$S + S^{1/2} = \frac{p_0}{q_0} + \frac{1}{(2mEDPn[i])} \quad (2)$$

where S is the soluble fraction of partially cross-linked polymer; p_0/q_0 , the ratio of probability of degradation to cross-link formation per monomer per unit initiator; m , the molecular weight of the monomer repeat unit; E , the number of cross-links per decomposed peroxide molecule; DPn , the number-average degree of polymerization; and $[i]$, the peroxide concentration in moles of free radicals per gram of resin.

Plotting $S + S^{1/2}$ vs. $1/(2 \times m \times DPn \times [i])$ gives a linear relationship with a slope equal to $1/E$, where E is the peroxide efficiency. The intercept on the y -axis gives a measure of the ratio of chain-scission events to chain-extension events.

The results of this calculation are shown in Table IV, and, as expected, the ranking order of the peroxide efficiencies is the same as the order of values of $\log G'_{\max}$. The small difference seen in the efficiencies of peroxides 500 and 130 is believed to arise from the inaccuracy of gel content measurement by the solvent-extraction technique. Also included in this table are values of M_c , which is an estimation of the average molecular weight between cross-links calculated from the relation shown by eq. (1).

The ranking orders seen for the peroxides in cross-linking efficiency and attainment of maximum modulus suggests that there may be some more precise evaluation of the relationship between the rate of peroxide degradation and the rate of increase in modulus during the curing reaction. This is especially true if we remember that essentially all of the increase in the storage modulus is attained by the time five peroxide half-lives have elapsed, representing 99.6% peroxide decomposition.

Table IV Peroxide Cross-Linking Efficiency and M_c^* Values

Sample	Peroxide Concentration (FR/gram)	$\log G'_{\max}$	M_c^a	Percent Gel	Cross-Linking Efficiency ^b
500	7.5×10^{-6}	5.399	110,000	15.5	
500	1.1×10^{-5}	5.484	91,000	23.5	
500	1.5×10^{-5}	5.605	69,000	34.3	2.39
802	7.5×10^{-6}	5.425	104,000	17.6	
802	1.1×10^{-5}	5.497	88,000	24.1	
802	1.5×10^{-5}	5.602	69,000	45.0	3.90
130	7.5×10^{-6}	5.304	137,000	12.6	
130	1.1×10^{-5}	5.382	115,000	19.2	
130	1.5×10^{-5}	5.427	103,000	24.0	2.24

^a Polymer density for calculation of M_c from eq. (1) is from Ref. 23.

^b Cross-linking efficiency is in units of cross-links formed per decomposed organic peroxide molecule.

If we define S to be the relative increase in the modulus from the virgin resin base line,

$$S \equiv \log G_t - \log G_0 \quad (3)$$

where $\log G_t$ is the value of $\log G'$ at time t ; and $\log G_0$, the value of $\log G'$ at time zero, it follows that the rate of growth in modulus could be taken to be dS/dt . The decomposition of the peroxide as a function of time at one given temperature is described by

$$C = C_0 \exp^{-k_d t} \quad (4)$$

where C is the peroxide concentration at time t ; C_0 , the initial peroxide concentration; k_d , the peroxide decomposition rate constant (s^{-1}); and t , the reaction time (s).

The initial postulate relies on the assumption that the rate of increase in the storage modulus is stoichiometrically related to the rate of decrease of unreacted peroxide through some proportionality constant K , written as

$$\frac{dS}{dt} = K \left(-\frac{dC}{dt} \right) \quad (5)$$

From eq. (4),

$$\frac{dC}{dt} = -k_d C_0 \exp^{-k_d t} \quad (6)$$

resulting in the relationship,

$$\frac{dS}{dt} = K k_d C_0 \exp^{-k_d t} \quad (7)$$

We must now make the assumption that the parameter K is, in fact, a constant whose value does not vary with the changes in concentration of unreacted peroxide or with the tightness of the cross-link network. In this case, the gel contents of the cross-linked polymers are low (see Table III) and no equivalent of the gel effect as encountered in polymerizing systems is expected in cross-linking. Integration between time zero and some time t yields

$$\int dS = \int K k_d C_0 \exp^{-k_d t} \quad (8)$$

If we define a term S_{\max} as the maximum attainable value of S_t at some infinite time (neglecting radical and thermal degradative effects for the moment), we may write

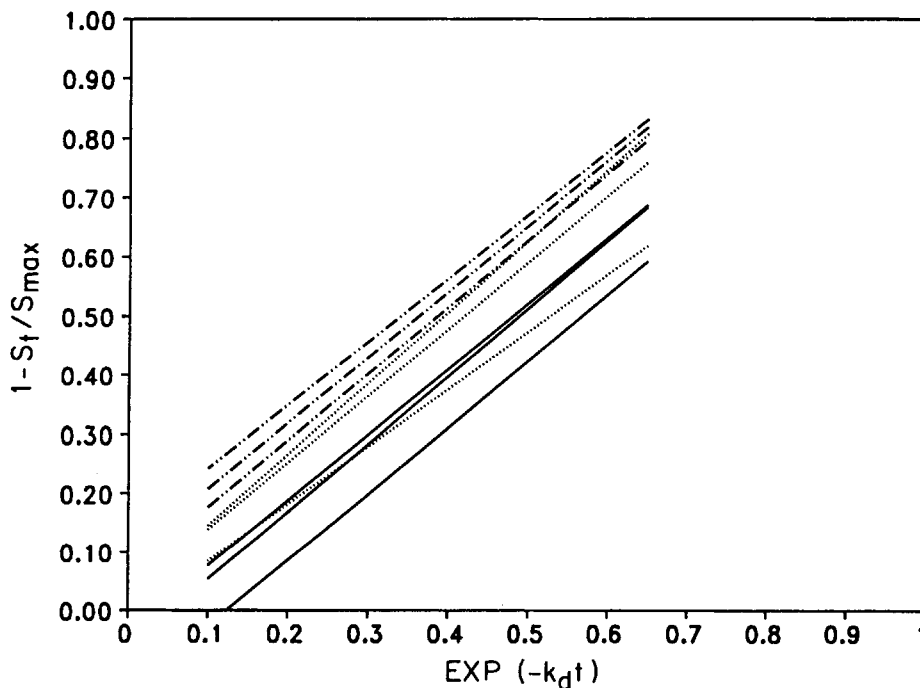


Figure 6 Linear best fits to eq. (12), $1 - S_t/S_{\max} = \exp(-k_d \times t)$, for all peroxides cured at 155°C: (---) peroxide 802; (....) peroxide 500; (—) peroxide 130. For each peroxide, increasing peroxide concentration is in order from top to bottom.

$$S_t = -KC_0(\exp^{-k_d t} - 1) \quad (9)$$

$$S_{\max} = S_{t\infty} = KC_0 \quad (10)$$

$$\frac{S_t}{S_{\max}} = -(\exp^{-k_d t} - 1) \quad (11)$$

or

$$1 - \frac{S_t}{S_{\max}} = \exp^{-k_d t} \quad (12)$$

The above function relates the rate of increase in the storage modulus (relative to an initial base-line modulus defined by the virgin resin) to the rate of decrease of peroxide concentration in the PE matrix during the reaction. If the left side of the equation is plotted against the right-hand side, a linear relationship is, in fact, found for all peroxides studied here. Figure 6 shows the results of best-fit linear relationships as defined by eq. (12) above. The slopes of each of the lines unfortunately does not exactly equal 1, as the derived equation implies, but the agreement of each peroxide to the same overall relationship between extent of cure and unreacted

peroxide is very good, as illustrated by the predominantly parallel lines.

Table V shows the results of linear regression fits for all samples studied, and a generally good agreement is seen for all samples reacted at 155°C. In addition, the results of peroxide 130 reacted at two higher temperatures of 166 and 174°C are shown and depicted graphically in Figure 7. The calculated standard deviations included in the table footnote are taken from the triplicate run of resin modified with peroxide 802 at 155°C at a concentration of 1.5×10^{-5} FR/g. The results of this table indicate that our initial assumption of a direct correlation [i.e., a slope of 1 and an intercept of 0 in the linear interpretation of eq. (12)] was not exact, but was very close to the calculated results shown here. Using the average value of the slope from Table V, we may now rewrite eq. (12) as

$$1 - \frac{S_t}{S_{\max}} = 1.11 \times \exp^{-k_d t} + 0.011 \quad (13)$$

For all peroxides studied at 155°C, the above relationship holds well, but as the reaction temperature is increased, the slope of the line also increases, as can be seen in Figure 7 and Table V. At a temper-

Table V Results of Linear Regression Analysis on Results Calculated Using Eq. (13)

Sample		Slope	Intercept	Value of R^2 in Regression Analysis
Peroxide	Concentration (FR/gram)			
500	7.5×10^{-6}	1.20	0.0258	0.999
500	1.1×10^{-5}	1.13	0.0267	0.998
500	1.5×10^{-5}	0.97	-0.0118	0.994
802	7.5×10^{-6}	1.11	0.0957	0.997
802	1.1×10^{-5}	1.07	0.134	0.996
802	1.5×10^{-5}	1.12	0.0640	1.000
130	7.5×10^{-6}	1.11	-0.0338	1.000
130	1.1×10^{-5}	1.15	-0.0617	1.000
130	1.5×10^{-5}	1.12	-0.139	0.995
Average		1.11	0.0111	
Standard deviation		0.063	0.0837	
130'	7.5×10^{-6}	1.32	0.0896	0.995
130'	1.1×10^{-5}	1.35	0.0480	0.999
130'	1.5×10^{-5}	1.11	0.0792	0.998
130''	7.5×10^{-6}	2.36	0.0296	0.995
130''	1.1×10^{-5}	1.84	0.0048	0.999
130''	1.5×10^{-5}	2.05	0.0226	0.995

The prime superscript on peroxide 130 indicates a reaction temperature of 166°C, and the double prime indicates a reaction temperature of 174°C. Three consecutive identical analyses using peroxide 802 gave an average slope of 1.15 with a standard deviation of 0.0266. The average intercept was 0.120, with standard deviation of 0.049.

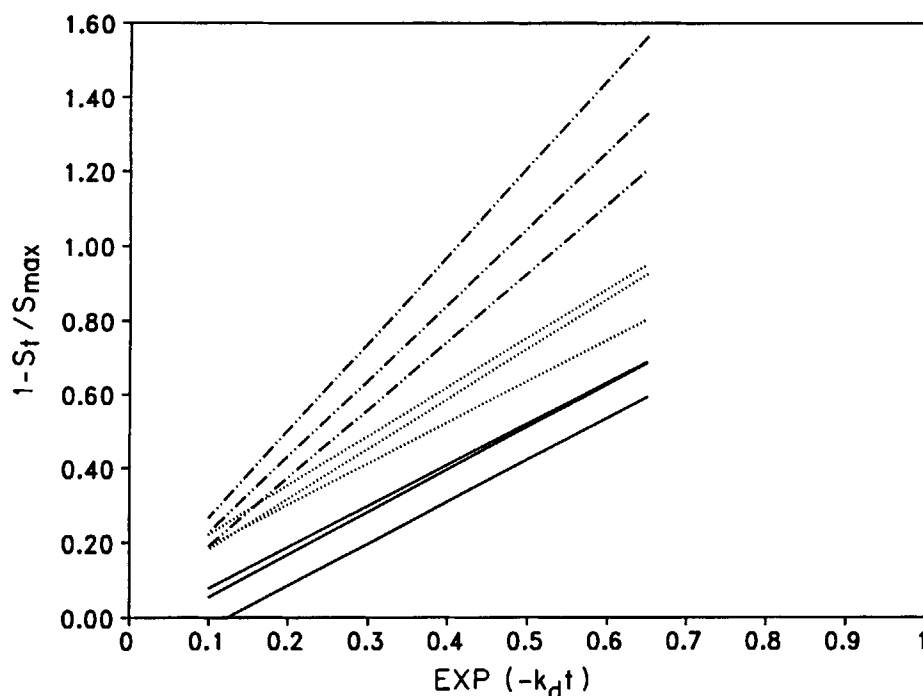


Figure 7 Linear best fits to eq. (12), $1 - S_t/S_{\max} = \exp(-k_d \times t)$, for peroxide 130 cured at three different temperatures: (- · - ·) 174°C; (· · · ·) 166°C; (—) 155°C. At reaction temperatures of 155 and 166°C, the top line in each set corresponds to the lowest peroxide concentration (7.5 E-6 FR/g) and the bottom line corresponds to the highest peroxide concentration (1.5 E-5 FR/g). For samples reacted at 174°C, the order is changed, in that the top line corresponds to the lowest peroxide concentration, but the bottom line corresponds to an intermediate concentration of 1.1 E-5 FR/g.

ature of 166°C, the average slope is 1.26, a slight increase over that seen at 155°C. At a reaction temperature of 174°C, there is a large scatter in the slopes of the three lines, with a calculated average of 2.08. Since the value of the slope is just a proportionality, we can say that this increase in the slope indicates a decrease in the relative rate of growth of the storage modulus. The storage modulus is, in turn, proportional to the cross-link density, with cross-link formation the desired end result of peroxide activity. A steeper slope can therefore be associated with a less efficient utilization of peroxide as cross-linker. This effect of temperature may be explained by considering the increase in nongrowth disproportionation reactions associated with elevated temperatures in peroxide modifications of this type, as reported by several authors.^{4,17,18} At lower temperatures, chain extension and cross-linking reactions predominate, with chain scission reactions being of low priority. Increasing temperatures increase the contribution of chain scission reactions to the overall mechanism, and this manifests itself in a decreased rate of modulus increase.

CONCLUSIONS

Three dialkyl peroxides were compared on the basis of their ability to increase the modulus of a virgin polyethylene resin through a cross-linking mechanism. All peroxides behaved similarly in terms of their initiation of a controlled degradation mechanism consisting of two simultaneously competing submechanisms, these being termed chain-coupling mechanisms and chain-scission mechanisms. As previously discussed by these authors and others,^{2,4,18,19} low reaction temperatures were found to favor chain-coupling reactions (i.e., cross-linking), and increasing reaction temperatures tended to introduce a larger contribution from chain scission and nongrowth disproportionation mechanisms. Increasing the peroxide level in all cases had the expected effect of increasing the gel content, hence, the modulus. The ranking of gel content, cross-linking efficiency, and maximum modulus all follow the same order.

The most useful finding of this comparison was that peroxides with very similar half-lifetimes and

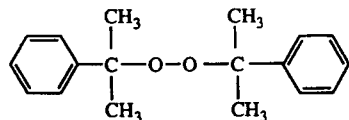
the same ultimate active free-radical species can exhibit very different behavior in the same polymer system. The choice of the best peroxide to fulfill the needs of a desired application should not be made entirely on the basis of the peroxide degradation rate at a specified temperature. The necessity of understanding the behavior of the peroxide in the particular system of interest has been shown through examples to be of primary concern in designing a satisfactory reaction scheme. For example, the order of relative efficiency of the three peroxides studied in a polyolefin grafting process is not that found in cross-linking PE in this study.¹⁴

Finally, it has been shown that a stoichiometric relationship does exist between the rate of increase in storage modulus and the rate of decrease in unreacted peroxide concentration. For the peroxides studied here, reacted at a constant temperature of 155°C, the relationship of eq. (13) was found.

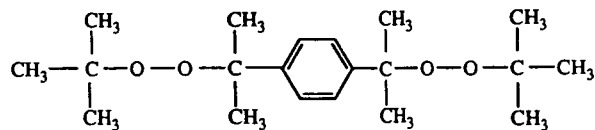
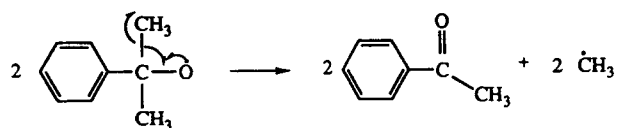
The proportionality constant (or slope) of 1.11 was arrived at by linear regression analysis of a series of experiments. The original derivation arrived at a value of unity for this constant, but it is believed that the positive deviation from this value may reflect the departure from 100% cross-linking efficiency by the peroxide. It was found that as the curing temperature was increased the value of the slope also increased, reflecting a slower relative growth in modulus. This increased reaction temperature has associated with it a higher fraction of nongrowth and chain-scission reactions, and therefore in the ideal case (as was derived), the slope would be of unit value. The fact that it is not unity even at low cure temperatures reveals the nonideality of the reacting system and the existence of some amount of chain-scission-type reactions.

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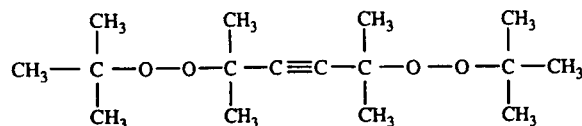
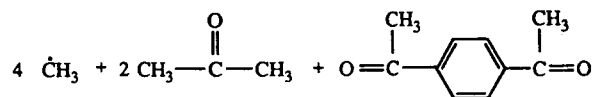
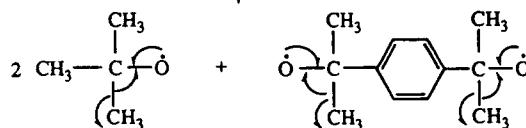
APPENDIX: PEROXIDE DECOMPOSITION REACTIONS



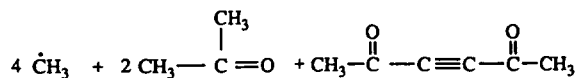
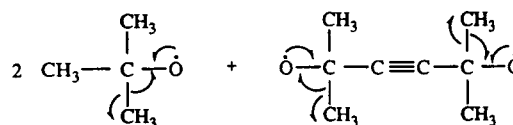
Dicumyl peroxide (Peroxide 500)



a, a'-bis(t-butylperoxy) diisopropylbenzene (Peroxide 802)



2,5-dimethyl-2,5-di(t-butylperoxy)-hexyne-3
(Peroxide 130)



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