# Effect of Polymerization Initiator on Early Colour of Poly(Vinyl Chloride)

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## SYNOPSIS

The development of early colour and the dehydrochlorination rate were compared for poly(vinyl chloride) samples obtained by suspension polymerization using two different initiators, dicetylperoxydicarbonate and butylperoxyneodecanoate. The degree of discolouration was measured on pressed plates and expressed as yellowness index (YI), the polyene sequence distribution was monitored by UV/Vis-spectroscopy, and the degradation rate was determined by measuring evolved HCl conductometrically. The PVC sample initiated by dicetylperoxydicarbonate exhibited more extensive early colour and a higher dehydrochlorination rate as compared to the sample obtained with butylperoxyneodecanoate as initiator. The UV/Vis-spectra showed that the early colour originates from polyene sequences. After extraction of the PVC resins with heptane : acetone (85 : 15) the early colour turned out to be almost the same for the two samples. From $^{13}$C-NMR measurements it was found that the extract of the sample polymerized with dicetylperoxydicarbonate contains unreacted initiator. We suggest that the radicals formed when the remaining initiator decomposes initiate dehydrochlorination. Our results also indicate that radicals from dicetylperoxydicarbonate may cause long-chain branches during polymerization. The radicals formed from butylperoxyneodecanoate, on the other hand, do not seem to react with the polymer molecules. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The economic importance of poly(vinyl chloride) (PVC) combined with its limited thermal stability has stimulated large efforts in both fundamental research and technical development concerning the degradation and stabilization of PVC. Under processing conditions PVC degrades by dehydrochlorination leading to conjugated polyene sequences causing discolouration. To avoid this degradation, thermal stabilizers must be added. The vast majority of the extensive literature concerned with PVC stability belongs to either of two categories. One area deals with the degradation mechanism and the reasons for the low stability. The most generally accepted view is that low concentrations of defects, such as tertiary and internal allylic chlorine, formed during polymerization are important contributing factors, although random initiation may occur as well.[1-3] The other important area concerns the effect of the addition of thermal stabilizers and the mechanisms behind their function.[4]

The discussion of stabilization is mainly concerned with the issue of how different stabilization systems perform with respect to long-term stability. Thus, the time to "blackening," that is, total loss of stability, is one important measure. This has also become increasingly important as the requirements for PVC in certain applications have increased, for example, wire insulation for low-voltage cables in cars. In other applications, the degree of discolouration obtained directly because of processing (early colour), or as a result of long-term ageing at room temperature (often called "dark yellowing"), is a much more important issue. This is of course most obvious for noncoloured and nonfilled materials, in particular for medical and food applications.

It is easy to obtain a measure of the stability of the virgin PVC powder by measuring the rate of

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dehydrochlorination at high temperatures, typically 190°C, under inert conditions.[5] For the long-term stability of stabilized materials this measure is, however, less relevant. Other factors, such as the type and amount of stabilizer, mixing, and compounding are much more important. Concerning early colour on the other hand, it is known within the PVC industry that the polymer itself may be the most important factor. Using the same stabilizer package and processing conditions, different PVC grades may well give widely different early colours.

It should be pointed out that the level of dehydrochlorination associated with the early colour problems is very low, say less than 0.01% deHCl. Therefore one must be very careful when referring early colour to dehydrochlorination, and question whether additives may contribute, either directly or after oxidation. In a previous study we found that pressing virgin unstabilized PVC powder at 160°C for 1 minute is a sensitive method to develop low levels of discolouration, which is related to early colour in stabilized materials.[6] It was also shown that the discolouration could be related to dehydrochlorination.

Over the years, the PVC industry has found that certain additives may contribute to early colour and these are, if possible, avoided. The empirical knowledge is thus substantial; but only a few relevant papers can be found in the scientific literature. A paper by Hagii et al.[7] discusses the importance of residues of the polymerization initiator. They concluded that such residues contributed to degradation and that easily hydrolysed initiators gave less residues and consequently also showed the best results. No suggestion for the detailed mode of action of the initiator residues during the degradation was given, however.

In this paper we have investigated the effect of two different initiator classes, peroxydicarbonates and peresters. The first was chosen as a reference because this type of initiator is the most common in commercial production of PVC today. Peresters,

on the other hand, are known to give PVC with less discolouration.[8] The pro-degradative effect was studied by standard dehydrochlorination measurements and by colour measurements after mild thermal treatment. To find the reason for the observed differences, we have determined residual initiators and defect structures in the polymer.

## EXPERIMENTAL

### Polymerization

Suspension polymerizations were performed at 54°C in a 14 L reactor. The polymerizations were stopped at 1.5 bar pressure drop. The following recipe was used: water (170 phr); vinyl chloride (100 phr); polyvinylalcohols (0.3 phr, degree of hydrolysis: 40–80%). Samples A and C were obtained with dicetylperoxydicarbonate (CC) as initiator, while butylperoxyneodecanoate (BN) was used for sample B (Table I). Except for the initiator, all additives were the same. The resins were dried at room temperature.

### Preparation of PVC Plates and Colour Measurement

PVC resins, 2 g, were pressed at 160°C for 1 min between high-gloss steel plates protected by Mylar films (Melinex, untreated polyester film). Transparent plates (0.5 mm) were obtained. The colour was measured according to CIE with a Colourimeter Tricolour LFM 3, Dr. Lange. The result is reported as yellowness index (DIN 6167 and ASTM D 1925).

### Extraction

PVC samples, 150 g, were extracted by stirring 1.5 L heptane:acetone (85 : 15) at 20°C over a period of 20 h. After filtration, the extract was evaporated and vacuum dried at room temperature.

**Table I Data on Investigated Polymers**

| Sample | Initiator | $M_n \cdot 10^{-3}$ | $M_w \cdot 10^{-3}$ | $\lambda \cdot 10^6$ | Soluble Fraction[a] (%) |
|---|---|---|---|---|---|
| A | 0.105 phr CC | 47.5 | 117 | 14 | 0.12 |
| B | 0.075 phr BN | 44.5 | 105 | 2 | 0.062 |
| C | 0.0525 phr CC | | | | |

$\lambda$ is the number of long-chain branches per molecular weight unit.

[a] Extraction with heptane : acetone (85 : 15).

## Polyene Sequence Distribution

The polyene sequence distributions were determined qualitatively by UV-visible spectroscopy. The absorbance spectra were obtained from the pressed plates with a Perkin–Elmer 554 Spectrophotometer.

## Thermal Degradation

The degradation experiments were performed in a specially designed apparatus.[5] Samples (100 mg) were heated at 190°C in nitrogen atmosphere (5 ppm of $O_2$). The dehydrochlorination was followed conductometrically and after about 0.1% HCl loss, the plots were linear and the slope was taken as a measure of the stability. The rate is expressed as evolved HCl in percent of the theoretical amount per minute (% deHCl/min).

## NMR Measurement

Proton decoupled $^{13}$C-NMR spectra were obtained with a Varian VXR-300. Samples were studied in $CDCl_3$ at room temperature. The tip angle was 50° and the delay time 10 s. The number of scans accumulated was 1000.

## Degradation Products of Butylperoxyneodecanoate

The reaction products of butylperoxyneodecanoate, decomposed as pure substance at 160°C, were investigated by GC-M/S. The products were separated on a capillary column DB-5. The temperature program included 30°C isothermally for 2 min, then 10°C/min temperature rise up to 250°C. Mass spectrometer VG 30-250 and gas chromatograph HP 5890 were used.

## Molecular Weight Distribution and Long-Chain Branching

Size exclusion chromatography (SEC) and viscosimetry were used for the determination of molecular weight distribution (MWD) and degree of long-chain branching (LCB). A Waters Associates GPC Model 200 operating at 25°C with tetrahydrofuran as solvent was used. The column combination consisted of five Styragel columns with permeabilities from $10^3$ to $10^7$ Å. Intrinsic viscosity was determined at 25°C with an Ubbelohde viscometer. Details of the analysis and the dissolution procedure have been given earlier.[9] To calculate MWD, molecular weight averages, and LCB the computer program devised

by Drott and Mendelson[10] was used, assuming trifunctional branch points.

## RESULTS AND DISCUSSION

The main purpose of this work is to illustrate the effect of different initiators on early colour and to try to find a molecular explanation for the observed differences. Two different classes of initiators of commercial interest were chosen. To obtain sample A, the polymerization was initiated by CC, $C_{16}H_{33}OC(O)OOC(O)OC_{16}H_{33}$, while BN, $RR_1R_2$-$CC(O)OOC(CH_3)_3$, was used for sample B. The amount of initiator (Table I) was chosen such that the same polymerization time and the same conversion was reached in the two polymerizations. Apart from the initiator, all additives were the same.

Because initiator residues will decompose to radicals during processing, they should also be regarded as potential initiators for degradation. To obtain a measure of the influence of possible residues, we extracted samples with a mixture of heptane : acetone (85 : 15). Acetone is necessary to give some swelling of the PVC matrix, although it causes the lowest molecular weight fraction to be extracted as well. As shown in Table I, the extracted fraction is larger for sample A than for sample B. The composition of the extracts will be discussed later.

The results of the colour measurements expressed as yellowness index (YI) are given in Table II, and the rates of dehydrochlorination at 190°C in Table III. The initial colour of the virgin resins are the same for both samples, but the sample initiated with dicetylperoxydicarbonate has about 30% higher deHCl/dt value. An even larger difference is observed in YI of the pressed plates, that is, after heat treatment at 160°C for 1 min. In fact, there is a difference between the two samples visible to the eye: sample A has a blue tint, the plates of sample B show almost no discolouration. The extraction

**Table II   Yellowness Index (YI) of Plates**

| Sample | YI |
| --- | --- |
| A | 22 |
| B | 12 |
| C | 6.2 |
| After extraction | |
| A | 6.7 |
| B | 5.5 |
| B + 0.105 phr CC | 26 |
| B + 0.075 phr BN | 5.5 |

influences stability markedly. The rate of dehydrochlorination decreases for both samples, but this is more pronounced for sample A, which decreases the difference between the samples to about 15%. The effect on YI is even greater, in particular for sample A. The extracted samples give in fact similar values and in this case it is not possible to observe any difference by visual inspection.

The discolouration could originate from additives as well as from the polymer. It might be possible to explain the improvement observed after extraction by the removal of species that become discoloured during the short-heat treatment. The UV spectra of the plates obtained by pressing are shown in Figure 1. The sample obtained with dicetylperoxydicarbonate as initiator (sample A) shows the strongest absorption in the visible range consistent with the higher YI value. The maximum is quite broad, and, apart from a relatively high wavelength, that is, long polyene sequences,[11] the general appearance is very similar to that observed for the polyenes obtained

in ordinary thermal degradation of PVC.[12] In Figure 2 a comparison is made between the UV spectra of sample A recorded on the pressed plate and a powder sample degraded to 0.1% deHCl at 160°C, respectively. It must be pointed out that the spectra of the plates were recorded directly on the 0.5-mm thick solid PVC samples, while our ordinary technique was used to record the spectrum of the sample degraded to 0.1%, a dilute solution (4 g/L) and 10-mm cell length. Thus it is obvious that the degree of dehydrochlorination of the pressed plate of sample A is very low, on the order of 0.005%. Assuming a mean sequence length of 13–15 and 800 as the number average degree of polymerization, this would mean that one polyene sequence can be found for every 300–400 polymer molecules.[13] If the reaction occurs homogeneously this implies that the polyenes should be isolated. Because it is thought that the length of the sequences is restricted to a large extent by Diels–Alder reactions between sequences,[14] one would thus expect longer sequences than normally observed for higher levels of dehydrochlorination. This is consistent with the relatively high wavelength of the maximum in the spectrum of the plate of sample A (500 nm) compared to that of the 0.1% degraded sample (440 nm). Hence it is clear that the discolouration of the plate originates from polyene sequences. For the other samples the typical UV spectrum of polyene sequences is not observed, and it can therefore be assumed that the extraction of sample A removes chemical species that initiate dehydrochlorination.
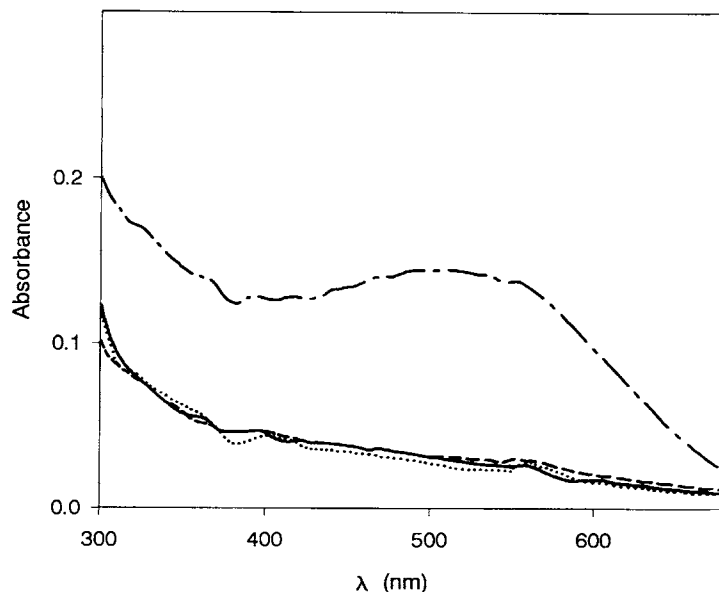


**Figure 1** UV-visible spectra for the pressed plates: A (-·-·-); extracted A (—); B (— — —); and extracted B (---).
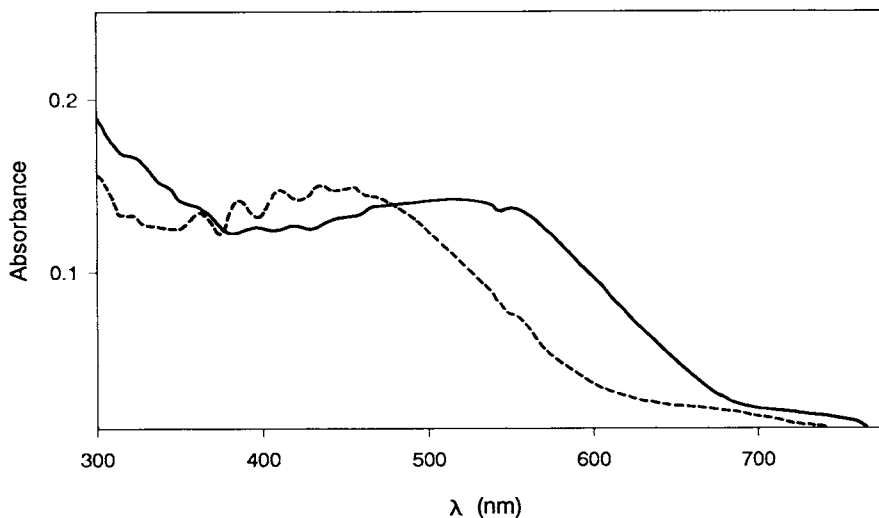
**Figure 2**   UV-visible spectra for sample A, pressed plate (—) and solution of powder degraded to 0.1% deHCl (- - -).

The ^{13}C-NMR spectrum of the extract from sample A is given in Figure 3 together with the spectrum of dicetylperoxydicarbonate. It is obvious that the extract contains unreacted initiator. The other major peaks in Figure 3 can be assigned to PVC (the low molecular weight fraction) and cetylalcohol. The latter is the expected major decomposition product of the initiator:

R—O—C(O)—O—O—C(O)—O—R →

R—O—C(O)—O· → RO· → ROH.
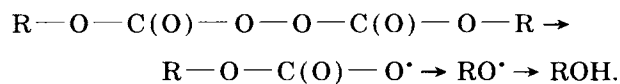
The presence of an initiator is, of course, a potential source of the early colour observed for sample A. A polymerization with a lower concentration of dicetylperoxydicarbonate, 0.0525 phr compared to 0.105 phr for sample A, was made in order to study
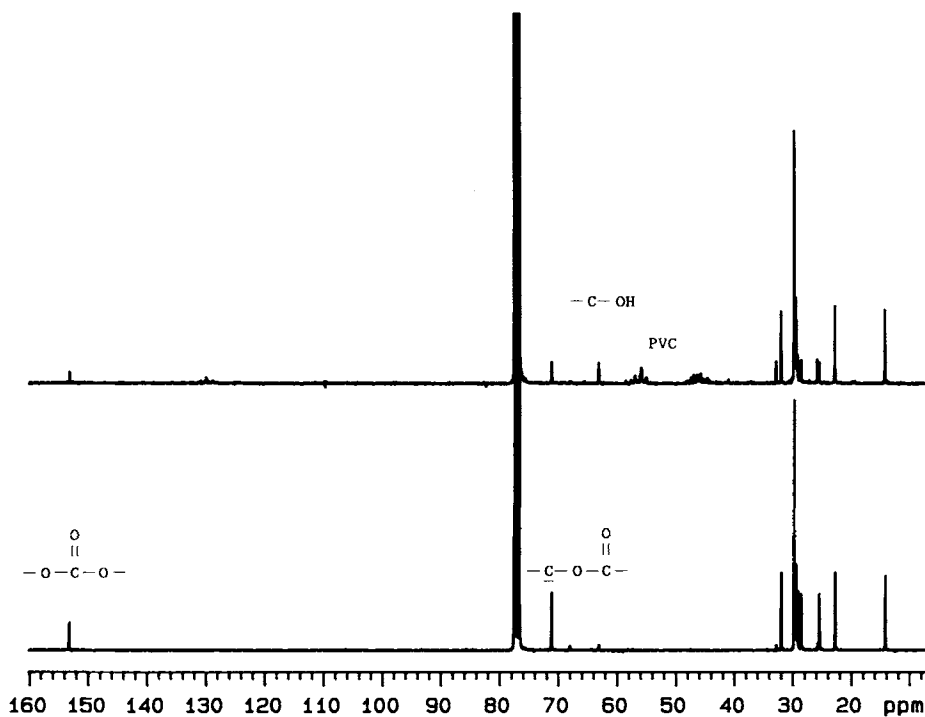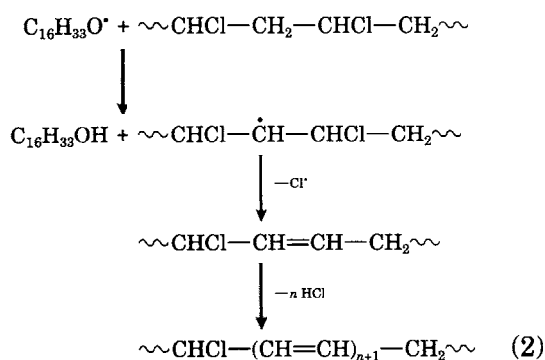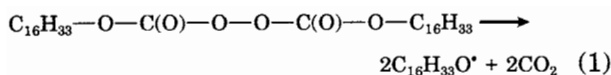


**Figure 3**   Proton decoupled ^{13}C-NMR spectra of dicetylperoxydicarbonate (bottom) and extract from sample A (top).

further the influence of initiator residues on the early colour. As can be seen from the absence of the carbonyl resonance in the $^{13}$C-NMR spectrum of the extract, this polymer does not contain any detectable amounts of initiator. Moreover, the early colour is improved markedly (Table II). These observations support the idea that the remaining initiator is an important factor for the discolouration of sample A after the short-heat treatment used to press the plates.
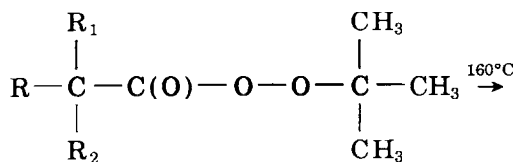
A quantitative evaluation based on the extracted amount and integration of the $^{13}$C NMR spectrum in Figure 3 reveals that about 30% of the initiator added in the polymerization should remain in sample A. It must be pointed out, however, that the calculation is approximate because of Nuclear Overhauser Enhancement (NOE) and long relaxation times. To show directly the effect of the initiator, 0.1 phr dicetylperoxydicarbonate was added to an extracted portion of sample B. This resulted in a substantial increase in the YI of pressed plates, and the discolouration had the same blue tint as observed in sample A (Table II). A control experiment in which cetylalcohol was added instead did not lead to an increase in YI compared to that of the extracted sample B. The most probable explanation for the discolouration, formation of polyenes, observed for sample A as well as sample B with added dicetylperoxydicarbonate, is that the alkoxy radical formed by the decomposition of the initiator abstracts a hydrogen from a polymer molecule, most probably from a methylene unit.[15] The radical formed will then expel a chlorine atom and an internal double bond with allylic chlorine is formed. The chlorine may subsequently abstract another hydrogen. The increased amount of allylic chlorine will initiate a propagation reaction through the normal rapid zipper process leading to a polyene sequence:
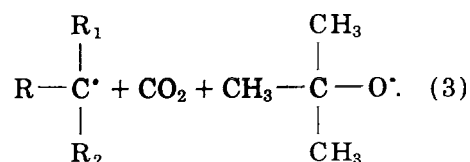
$$C_{16}H_{33}-O-C(O)-O-O-C(O)-O-C_{16}H_{33} \longrightarrow$$
$$2C_{16}H_{33}O^{\cdot} + 2CO_2 \quad (1)$$

$$C_{16}H_{33}O^{\cdot} + \sim\!\!\sim\!CHCl-CH_2-CHCl-CH_2\!\sim\!\!\sim$$

$$\downarrow$$

$$C_{16}H_{33}OH + \sim\!\!\sim\!CHCl-\overset{\cdot}{C}H-CHCl-CH_2\!\sim\!\!\sim$$

$$\downarrow {\scriptstyle -Cl^{\cdot}}$$

$$\sim\!\!\sim\!CHCl-CH=CH-CH_2\!\sim\!\!\sim$$

$$\downarrow {\scriptstyle -n\,HCl}$$

$$\sim\!\!\sim\!CHCl-(CH=CH)_{n+1}-CH_2\!\sim\!\!\sim \quad (2)$$

For sample B, the $^{13}$C NMR spectrum of the ex-

tract did not show any peaks that can be assigned to the starting perester, (Fig. 4). It is therefore not likely that sample B contains any remaining initiator, which can be explained by the higher decomposition rate for butylperoxyneodecanoate compared to dicetylperoxydicarbonate, whose half-life time at 54°C is 2.5 h and 3.3 h, respectively.[16] Furthermore, the perester is more susceptible to hydrolysis[7] that will also give lower residue levels. Thus, the favourable results obtained with sample B in the test for early colour can be ascribed to a low amount of initiator residues.

It cannot, however, be ruled out that perester may be present in the polymer. To discover whether any remaining initiator would have a negative influence, we deliberately added 0.075 phr butylperoxyneodecanoate to sample B and pressed plates. Surprisingly, this did not affect the early discolouring (Table II). To identify possible radicals formed during the decomposition, we heated pure butylperoxyneodecanoate at the conditions used while pressing the plates to 160°C, and performed a GC-MS experiment on the products formed. As seen from the GC-MS chromatogram in Figure 5, the major decomposition products were methane, carbon dioxide, acetone, $t$-butanol, and branched nonenes. The formation of carbon dioxide and $t$-butanol shows that the decomposition starts as could be expected:
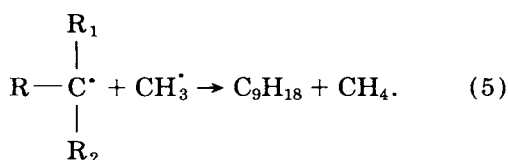
$$\begin{array}{ccc} R_1 & & CH_3 \\ | & & | \\ R-C-C(O)-O-O-C-CH_3 & \overset{160°C}{\rightarrow} \\ | & & | \\ R_2 & & CH_3 \end{array}$$

$(R+R_1+R_2=9C)$

$$\begin{array}{ccc} R_1 & & CH_3 \\ | & & | \\ R-C^{\cdot} + CO_2 + CH_3-C-O^{\cdot}. & \quad (3) \\ | & & | \\ R_2 & & CH_3 \end{array}$$

The alcohol is then formed by hydrogen abstraction in a cage reaction with the tertiary alkyl radical that also yields nonenes. However, about 40% of the $t$-butoxy radicals undergo scission at 160°C explaining the formation of acetone:

$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-O^{\cdot} \rightarrow \\ | \\ CH_3 \end{array}$$

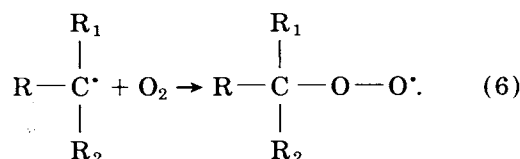$$CH_3-C(O)-CH_3 + CH_3^{\cdot}. \quad (4)$$
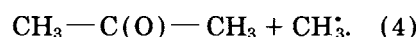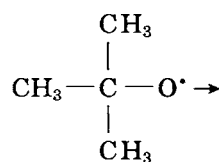
The reactive methyl radical obviously abstracts hydrogen and forms methane. It is probable that the reaction is a cage reaction that also yields nonenes:

$$R \overset{\underset{\textstyle |}{\textstyle R_1}}{\underset{\underset{\textstyle R_2}{\textstyle |}}{-}} C\bullet + CH_3^\bullet \rightarrow C_9H_{18} + CH_4. \qquad (5)$$

$$(R+R_1+R_2=9C)$$

Considering the effect of these radicals on PVC, in comparison to that of the $n$-alkoxy radical formed by the peroxydicarbonate, it can first be noted that the reactivity toward hydrogen atoms should be lower for the $t$-butoxy radical[17] formed in eq. (3). In the presence of oxygen, which cannot be excluded during the short-heat treatment pressing the plates, the $t$-alkyl radical formed in eq. (3) will form a peroxy radical:

$$R \overset{\underset{\textstyle |}{\textstyle R_1}}{\underset{\underset{\textstyle R_2}{\textstyle |}}{-}} C\bullet + O_2 \rightarrow R \overset{\underset{\textstyle |}{\textstyle R_1}}{\underset{\underset{\textstyle R_2}{\textstyle |}}{-}} C -O-O\bullet. \qquad (6)$$

This radical has a lower reactivity than the $n$-alkoxy radical.[18] However, the reactivity of the methyl radical formed in eq. (4) is high, and this radical should be able to abstract hydrogen from PVC chains, and thus initiate formation of polyenes. The fact that the addition of perester does not lead to discolouration is therefore a strong indication that the methyl radical formed is not kinetically free to abstract hydrogen from PVC. It is possible that the cage reaction in eq. (5) is sufficiently efficient in the PVC matrix as well.

The different reactivities of the radicals from the two initiators may influence the stability of the polymer in different ways. For the virgin materials the most obvious difference is the different levels of discolouration after the short heat treatment used to press the plates (Table II). The stability was also measured in the usual way by recording the dehydrochlorination rate at 190°C in nitrogen. As shown in Table III, sample A shows a higher rate than sample B, which could be expected because of the presence of initiator in the former sample. The results in Table III also show that the extraction, which removes the remaining initiator, leads to a decreased difference, although the degradation rate of extracted A is still about 15% higher than that of extracted B. One possible explanation for this

behaviour is that the higher reactivity of the radicals formed by the dicetylperoxydicarbonate may already cause formation of labile defects during polymerization.

In our previous work we found a definite relation between the dehydrochlorination rate and the amount of tertiary and internal allylic chlorine.[15] These anomalous structures are formed by inter- and intramolecular transfer reactions and the content increases with increasing polymerization temperature and increasing conversion. It should be noted, however, that the polymerization conditions and the conversion were the same for the two polymers studied in this work. One possible reason for the difference in the content of these defects might be the different reactivity of the radicals formed. Butyl branches, which are the most common labile defect, and ethyl branches are formed by intramolecular transfer reactions.[19,20] Therefore, it is not likely that the amount of these structures is influenced by the initiator radicals. Internal allylic chlorine and long-chain branches with tertiary chlorine, on the other hand, are the results of intermolecular chain transfer to polymer:[19,21]



$$(7)$$
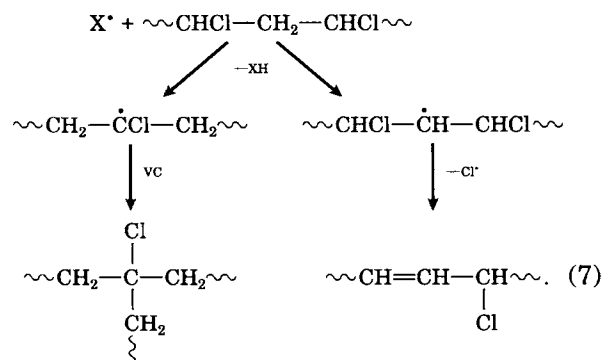
For the polymerization of vinyl chloride it has been reported that the growing macroradical as well as chlorine atoms, which are formed in the mechanism for chain transfer to monomer, may act as chain transfer agents.[19-21] Of course, initiator radicals must also be considered as possible active species in this reaction. Radicals with high enough reactivity will thus lead to long-chain branches and/ or internal double bonds, that is, decrease the thermal stability. It must be remembered that the amount of these structures is very low in ordinary PVC, which makes a quantitative comparison difficult. However, the values of the branching index $\lambda$, obtained by a comparison between the molecular weight calculated from the linear calibration and $[\eta]$ of the whole sample, indicate that sample A contains a higher amount of long-chain branches compared to sample B. Such a difference is also expected
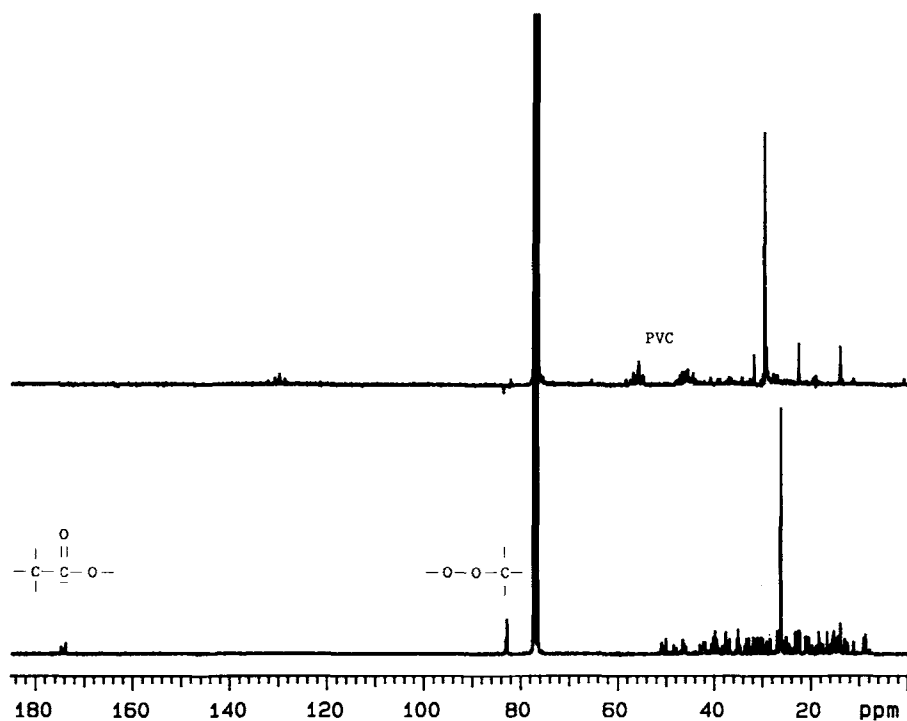
**Figure 4** Proton decoupled $^{13}$C-NMR spectra of butylperoxyneodecanoate (bottom) and extract from sample B (top).

from the differences in radical activity discussed above. The reactivity difference between the radical fragments might furthermore lead to the increased

dehydrochlorination rate for sample A as compared to sample B even after initiator has been removed by extraction.
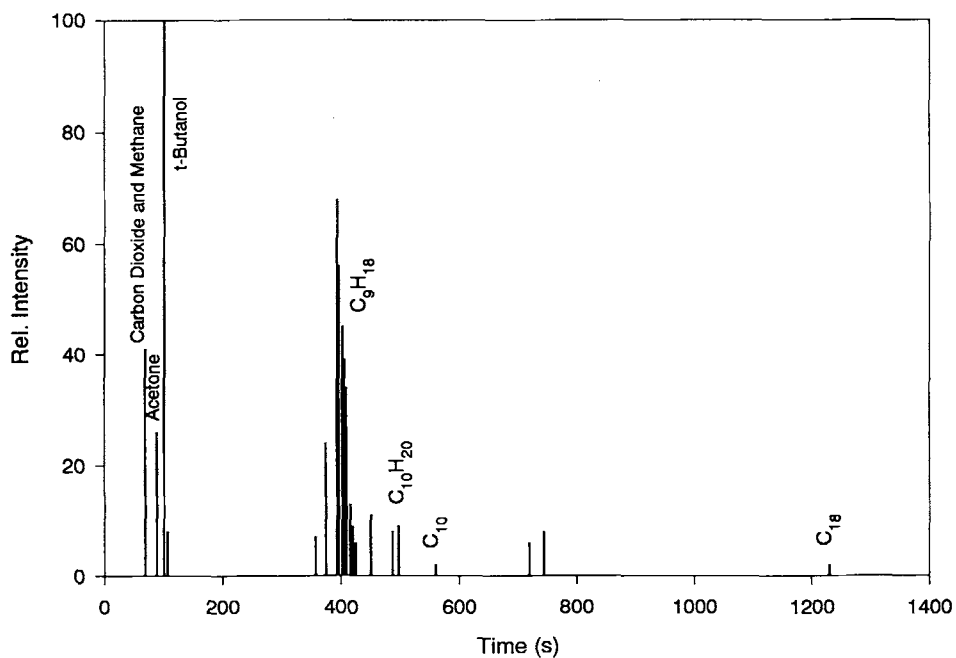


**Figure 5** Diagrammatic representation of the GC-MS chromatogram for the degradation products of butylperoxyneodecanoate at 160°C. $n$-decane ($C_{10}$) and $n$-octadecane ($C_{18}$) were added as markers.

In conclusion, the favourable low degree of early colour of sample B as compared to sample A can mainly be attributed to a much lower content of unreacted initiator. Furthermore, the radicals formed from butylperoxydecanate (sample B) do not seem to be capable of reacting with PVC in contrast to those formed from dicetylperoxydicarbonate (sample A). The results also indicate that sample A has a higher content of long-chain branches that may be a consequence of the higher reactivity of the initiator radicals. The small but significant difference in the amount of labile structures may lead to the observed difference in thermal stability after the removal of the remaining initiator.

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