

# Stabilization of Poly(vinyl chloride) with Preheated Metal Stearates and Costabilizers. II. Use of a Polyol

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Received 21 April 1997; accepted 1 August 1997

**ABSTRACT:** Continuing with the evaluation of costabilizers along with preheated metal stearates to stabilize poly(vinyl chloride) (PVC), pentaerythritol was chosen as a long-term costabilizer. During normal stabilization conditions, the polyol enhances the induction time to degradation but produces large amounts of polyenes. The use of the preheated mixture of metal soaps and preheated ZnSt<sub>2</sub> enhanced even more such times, while preheated CaSt<sub>2</sub> reduced them. The same effect was seen with the  $\beta$ -diketone; and, as in that case, the results seems to be the sum of both separated effects. Evaluations of induction times to degradation, carbonyl formation, visible reflectance, and UV-visible and fluorescence spectroscopic techniques support these findings. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 11–27, 1998

**Key words:** stabilization; PVC; thermal treatment; metal stearates; pentaerythritol

## INTRODUCTION

Pentaerythritol is a compound widely used to considerably delay the degradation time for PVC. It is considered a long-term costabilizer and used mainly for colored materials, since it imparts some initial yellowness to the polymer, in opposition to the common behavior of the  $\beta$ -diketones.

It is known that the function of the polyols relies on complexation with zinc or calcium chloride<sup>1</sup>; although, more recently, other authors<sup>2</sup> have found that chelation of this compounds with the metal stearates itself avoid the ionic dissociation and, consequently, increase the rate of replacement of allylic chlorines. Other people<sup>3,4</sup> have mentioned that these compounds are not sta-

ble at processing temperatures, and it may be that the effects are due to the reaction of the decomposition products rather than to the compounds themselves.

As a continuation of part I of this series, we have evaluated the influence of costabilizers on the action of preheated metal stearates as stabilizers for PVC. In this case, the polyol is studied, and the results will be added to those obtained with the diketone to give a general conclusion.

## EXPERIMENTAL

Samples were prepared using the same type of poly(vinyl chloride) (PVC) as in part I. Metal stearates received the same pretreatment before being added to the polymer; basically, the only difference was the type of costabilizer. Pentaerythritol was chosen for being a long-term costabilizer.

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The performance of the mixtures was evaluated by means of induction times as well, using the same methods of thermogravimetric analysis (TGA) and HCl evolution. In this case, as the times are considerably long, it was decided to increase the degradation temperatures to accelerate the process and have more comparable traces. For TGA experiments, a temperature of 190°C was used; for HCl evolution, 195°C was enough to have convenient shapes of the curves.

The degradation stabilization process was followed by Fourier transform infrared (FTIR) (carbonyl formation) and visible reflectance spectroscopy, as in part I. Apart from that, double bond formation was evaluated by UV spectroscopy. The instrument used was a Phillips UV-visible (UV-VIS) spectrophotometer model PU 8720 in the absorbance mode and the 200–600 nm range. Samples were extracted with peroxide-free tetrahydrofuran (THF) for 60 h, and solutions used for the UV evaluations.

The same solutions were taken for fluorescence evaluations in an attempt to clarify the type of double bonds formed throughout the degradation time. The instrument used was a Perkin–Elmer luminescence spectrometer LS50B. Intensities of fluorescence from the samples were recorded applying four different excitation wavelengths, 245, 280, 330, and 360 nm to each sample. The spectra were recorded in the ranges of 265–470, 300–540, 340–640 and 370–700 nm, respectively, with a slit width of 5.

The aliquots were returned to their respective solutions, where 100 mg of sodium borohydride (NABH<sub>4</sub>) was added for reduction of the carbonyl–polyenes groups. They were flushed with nitrogen and subsequently left for 24 h under continuous magnetic stirring for a complete reduction. After filtration to obtain clear solutions, samples were taken again for UV and fluorescence evaluations. Similar studies have been reported for noncostabilized samples.<sup>5</sup>

## RESULTS AND DISCUSSIONS

### Induction Time Evaluations

It has been mentioned that pentaerythritol considerably delays the degradation of PVC, this being the reason for increasing the degradation temperatures since the longer the time, the lower rate of dehydrochlorination. This would make difficult the intercomparison of results with previous experiments (noncostabilized and with diketones).

Table I shows the induction times to degradation obtained for PVC stabilized with preheated metal soaps and pentaerythritol as a costabilizer.

As in the use of the short-term costabilizer (part I of this series), the results show some characteristic features. First, the values obtained by both methods follow the same following general trends: Large  $T_i$  values with preheated CaSt<sub>2</sub>-ZnSt<sub>2</sub> mixtures and preheated ZnSt<sub>2</sub>, and short  $T_i$  values with preheated CaSt<sub>2</sub>.

HCl evolution results show a very small enhancement on the  $T_i$ s during the evaluation of the complex, independently of the preheating temperature. The latter is due to the fact that HCl is evolved since the beginning, generating the yellowing of the samples. This shows the formation of average size polyenes and a relatively low rate of dehydrochlorination, which helps to reduce the  $T_i$  values since they were determined graphically and low rates implies low pendants in the graphs; hence, low interpolation values (see the method of determining  $T_i$  values in Benavides et al.<sup>6</sup>)

Similar behavior of  $T_i$  values found with the diketone is even more dramatic with the preheated ZnSt<sub>2</sub>. The first value of  $T_i$  is lower than the blank, but the second is considerably enhanced. It has been mentioned that the first value is apparent for the case of costabilizers, and the real one and the expected (according to other experiments) is the second. In this case, the effect of the low rate of dehydrochlorination during the induction time is higher. There also seems to be no important substitution of allylic chlorines with this set of samples since they had a red coloration from the very beginning.

The observed results may be attributed to the normal mechanism known to happen when pentaerythritol is used as secondary stabilizer with the mixture CaSt<sub>2</sub>/ZnSt<sub>2</sub>. The polyol forms complexes with the prodegradant ZnCl<sub>2</sub>, inhibiting its strong catalytic action. When the complex or the new structures of the zinc soap (formed with the heat treatment), the formation of the zinc chloride is even lower, delaying the consumption of the costabilizer and subsequently delaying the blackening of the polymer.

When the CaSt<sub>2</sub> was preheated at 150 and 180°C (melts at 155°C), the  $T_i$  values were reduced, giving improvement in the initial coloration of the polymer. There are two possibilities: the metal soap is not involved in the stabilization mechanism, or it is substituting allylic chlorines. The first possibility would be rationalized in that it is not interacting with ZnSt<sub>2</sub> and subsequently allowing it to substitute more allylic chlorines,

**Table I** Effect of the Costabiliser Pentaerythritol on the Preheated Mixtures

Sample: PVC Solvic 271GC +	Induction Time, $T_i$ (min)	
	TGA (190°C)	HCl Evolution (195°C)
CaSt <sub>2</sub> + ZnSt <sub>2</sub> + Pe	11.1	16.5
CaSt <sub>2</sub> -ZnSt <sub>2</sub> (180°C) + Pe	12.4	17.3
CaSt <sub>2</sub> -ZnSt <sub>2</sub> (150°C) + Pe	12.8	17.2
CaSt <sub>2</sub> -ZnSt <sub>2</sub> (130°C) + Pe	14.9	17
CaSt <sub>2</sub> -ZnSt <sub>2</sub> (100°C) + Pe	11.5	17
ZnSt <sub>2</sub> + Pe	6.8	13.9
ZnSt <sub>2</sub> (180°C) + Pe	7.3	13.3
CaSt <sub>2</sub> (180°C) + ZnSt <sub>2</sub> + Pe	9.1	14.1
CaSt <sub>2</sub> (150°C) + ZnSt <sub>2</sub> + Pe	10	12.8
CaSt <sub>2</sub> (130°C) + ZnSt <sub>2</sub> + Pe	11.2	16.5
CaSt <sub>2</sub> (100°C) + ZnSt <sub>2</sub> + Pe	12	17.1
CaSt <sub>2</sub> + ZnSt <sub>2</sub> (180°C) + Pe <sup>a</sup>	14.8	14.2 (20.1)
CaSt <sub>2</sub> + ZnSt <sub>2</sub> (150°C) + Pe <sup>a</sup>	14	15.2 (21.8)
CaSt <sub>2</sub> + ZnSt <sub>2</sub> (130°C) + Pe <sup>a</sup>	13.4	15.4 (21.2)
CaSt <sub>2</sub> + ZnSt <sub>2</sub> (100°C) + Pe	11.8	17.5

<sup>a</sup> These samples showed a second  $T_i$  on HCl evolution measurements.

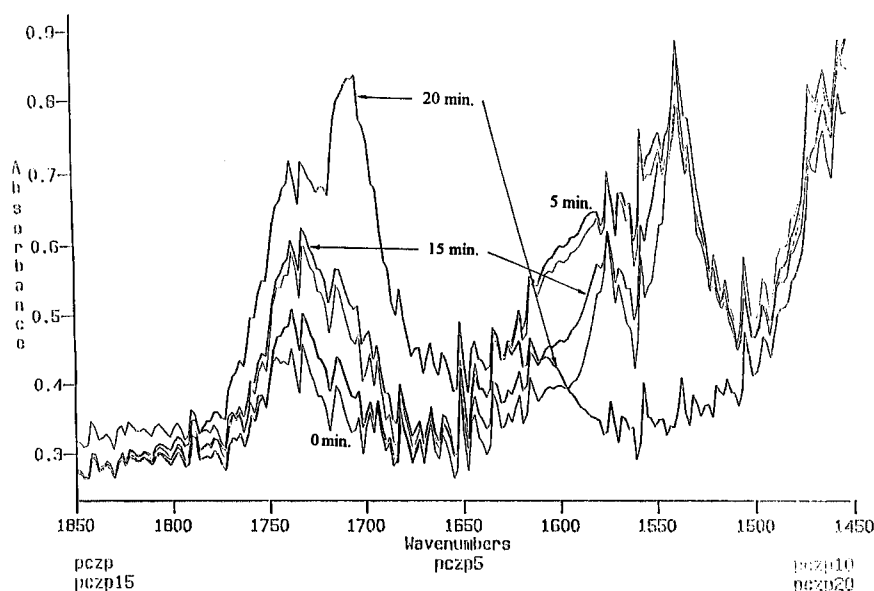
with the benefit of better initial color, but shorter induction times. The second possibility would happen if it becomes active enough to alkylate the polymer by itself, instead of only capturing HCl, subsequently producing more metal chlorides and accelerating the degradation.

#### FTIR Studies

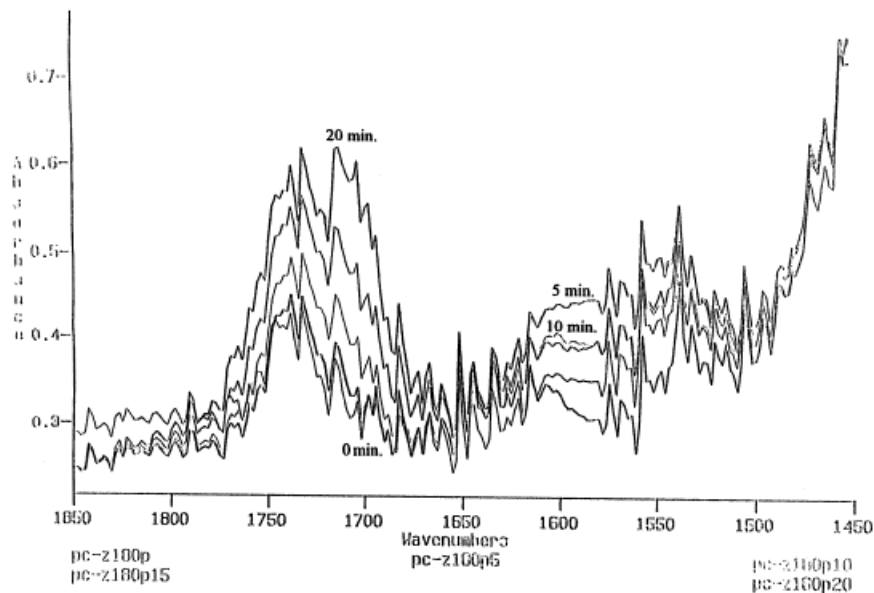
FTIR studies of the polymer costabilized with Pe brought to light some interesting features. Figure 1 shows the trend observed for the control sample

(no preheating of metal soaps). The complex ( $1600\text{ cm}^{-1}$ ) is observed at 5 min of degradation and remains there until 15 min, where it is slightly reduced. It is noticeable that the bands corresponding to the metal stearates ( $1580$  and  $1539\text{ cm}^{-1}$ ) are reduced after the complex band has disappeared. At 20 min, there is no complex at all, nor for the metal soaps.

The  $1735\text{ cm}^{-1}$  bands increased throughout the degradation time, reaching values of almost double those obtained without this costabilizer, while



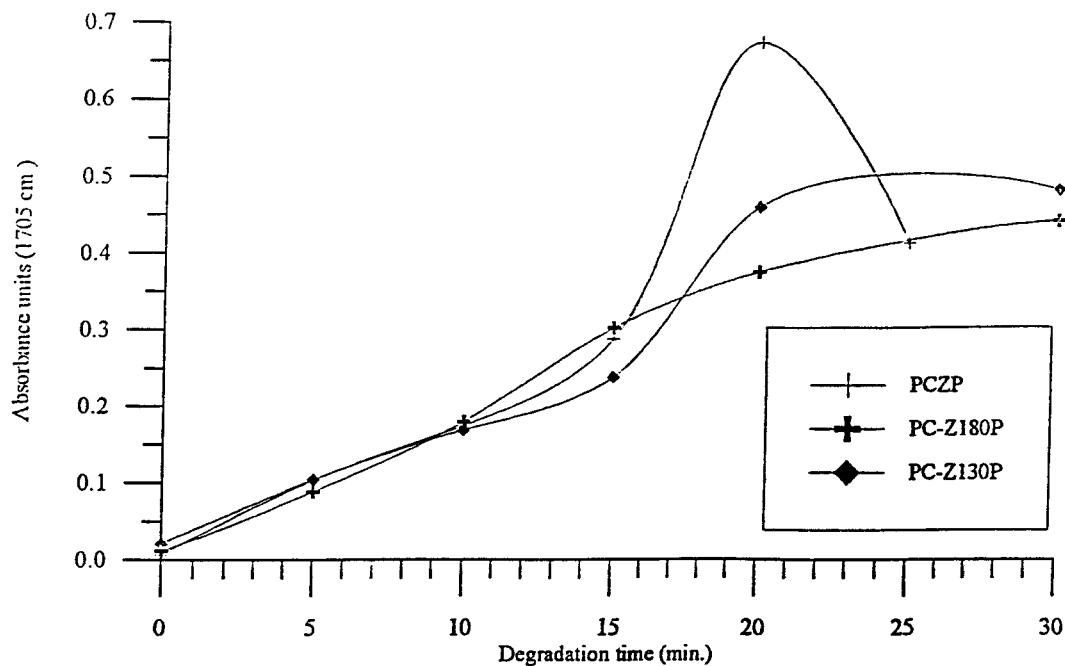
**Figure 1** PVC + CaSt + ZnSt + Pe degraded up to 20 min.



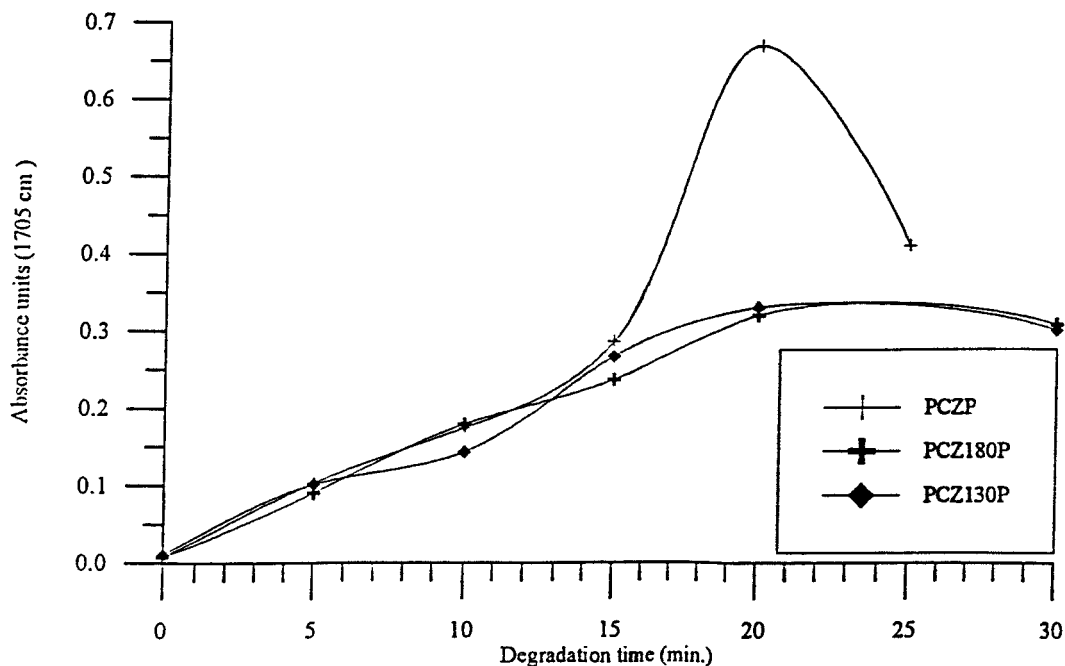
**Figure 2** PVC + CaSt + ZnSt (180) + Pe degraded up to 20 min.

the  $1705\text{ cm}^{-1}$  band increased up to common values. The former bands were used by Frye and Horst<sup>7</sup> to prove the sterification of the metal soaps on the polymer chain; but, as it has been mentioned by other authors,<sup>8</sup> the same region depicts absorptions of the monomeric species of the stearic acid formed during the evolution of HCl. The

promotion of high sterification seems unreasonable since that would lead to little discoloration of the polymer, which has not been observed at all with this costabilizer. If such an increase is due to the latter reason, the addition of pentaerythritol is somehow altering the dimeric–monomeric species ratio of the stearic acid. It may be



**Figure 3** Carbonyl formation in PVC stabilized with the CaSt–ZnSt mixture (preheated at different temperatures) and pentaerythritol and degraded up to almost total dehydrochlorination.

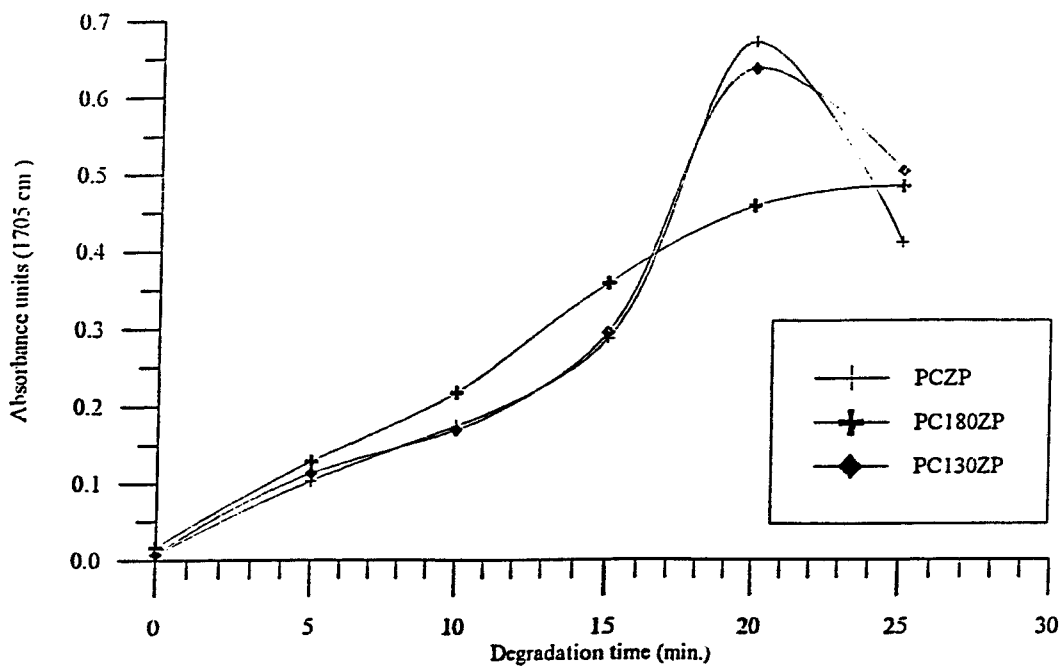


**Figure 4** Carbonyl formation in PVC stabilized with CaSt + ZnSt (preheated at different temperatures) and pentaerythritol and degraded up to almost total dehydrochlorination.

that a new ester type compound, not mentioned before, is forming and enhancing the absorption at that wavelength, or perhaps there is a higher

formation of this compound due to the higher temperature (195°C) used to degrade the samples.

Stabilization of PVC with the preheated mix-



**Figure 5** Carbonyl formation in PVC stabilized with CaSt (preheated at different temperatures) + ZnSt and pentaerythritol and degraded up to almost total dehydrochlorination.

ture of metal soaps and Pe (Fig. 2) resulted in a lower production of carboxylic groups, namely, dimeric stearic acid. However, the  $1735\text{ cm}^{-1}$  band increased almost as high as in Figure 1, suggesting that these bands have no relation with the stearic acid formation, or that the difference found is due to a lower formation of carboxylic groups other than stearic acid, so accounting for the difference in the bands formed at  $1705\text{ cm}^{-1}$ .

As in part I of this series, the formation of carboxylic groups was followed quantitatively for the samples; graphs are shown in Figures 3–5. There is a general trend observed on the three graphs: The rate of formation of carbonyls is almost the same for all the cases, during the first 10–15 min of degradation. Such a rate is smaller when compared with the ones obtained for the diketone, but that does not mean that the polyol gives better performance in the first stages.

Pentaerythritol induces the lengthening of the induction period; once it is consumed, the degradation becomes as it is without the costabilizer. The latter has been seen by the rapid increase of the carbonyl groups at 20 min degradation for the control sample (PCZP) in the graphs. The rapid decay of the curve could be due to the degradation of these groups, which are obviously less stable at the temperature of these experiments ( $195^\circ\text{C}$ ).

Figure 3 (preheated mixture  $\text{CaSt}_2\text{--ZnSt}_2$ ) shows clearly how the preheating temperature ( $T_p$ ) of  $180^\circ\text{C}$  generates a lower amount of carboxylic groups, keeping a similar rate throughout the degradation time; while the  $T_p$  data for  $130^\circ\text{C}$  give a curve closer to the one obtained from the control.

The presence of preheated  $\text{ZnSt}_2$  in the stabilization mixture (Fig. 4) reduces the production of carboxylic species even more, being almost the same for the  $T_p$ s of  $130$  and  $180^\circ\text{C}$  (note that at both temperatures, the zinc soap is melted). This agrees with previous results, where this sample gave the longest induction times. A difference with Figure 3 is that the curves show a decrease in the carbonyl content at longer degradation times, indicating that the maximum is obtained (even though smaller) at 25 min of degradation.

Figure 5 shows the samples doped with preheated  $\text{CaSt}_2$ . It is clearly seen that the  $T_p$  of  $130^\circ\text{C}$  (not enough for melting) has not induced any changes in the curve, compared with the control. At the preheating temperature of  $180^\circ\text{C}$ , a higher rate of formation of carboxylic groups is observed, but without any decrease in absorbance values at longer degradation times. This behavior is characteristic with the use of costabilizers, since it also happened with the Diketone (part I

**Table II Reflectance Values for the Control PVC +  $\text{CaSt}_2$  +  $\text{ZnSt}_2$  + Pe**

Degradation Time (min)	Percentage of Reflectance		
	400 nm	600 nm	800 nm
0	100	100	100
5	89	98	99
10	70	95	96
15	60	90	94
20	3	20	38

of this series). Indeed, this supports the theory of complexation between calcium and zinc soaps. In the normal mechanism, it delays the formation of carboxylic groups (including stearic acid) until the sample becomes dark; when the calcium soap was preheated (no complex formation), its curve had a maximum before the end of the degradation time. With the addition of the costabilizers, the maximum disappears, indicating that this action is supplied by them, evidently by means of complex formation with the metal compounds, as mentioned in the literature.<sup>1,2</sup>

#### Visible Reflectance Studies

Visible reflectance studies were carried out to correlate the coloration of the samples. For this case, samples of the control, degraded at  $180$ ,  $190$ , and  $195^\circ\text{C}$ , were analyzed in order to observe the differences induced by the change in temperature. No changes in the shape of the traces were found, indicating that there was no extra effect from the higher temperature, apart from the fast blackening or the shorter induction times.

The control for this set of samples, when Pe was added as costabilizer, gave the results shown in Table II. The main characteristic for these samples is that the formation rate of double bonds (400 nm value) is high from the beginning of the degradation, compared with the rate of formation of black species (800 nm value). This suggests that the secondary reactions that form the black species (multiaromatic compounds supposedly) have a low rate comparing with the double bond formation rate. The specific absorptions, observed in previous experiments, are clearly seen for the 5, 10, and 15 min degradation, but not for 20 min, indicating that there is little formation of carboxylic groups that shift the absorptions before the fast blackening of the sample.

It is convenient to mention that the residues left from these samples, after the degradation,

**Table III Reflectance Values for PVC + CaSt<sub>2</sub>-ZnSt<sub>2</sub>(T<sub>p</sub>) + Pe**

Degradation Time (min)	Percentage of Reflectance					
	T <sub>p</sub> = 180°C			T <sub>p</sub> = 130°C		
	400 nm	600 nm	800 nm	400 nm	600 nm	800 nm
0	100	100	100	100	100	100
5	85	98	99	83	97	99
10	66	95	97	62	94	97
15	51	90	95	48	89	94
20	25	71	83	23	70	83

have different physical properties, compared with the residues when the diketone was used or when no costabilizer was added. They are more rubber-like and can be powdered only with difficulty after their degradation. This might be due to the cross-linked nature of the samples, which, in turn, could be an explanation for the lack of multiaromaticity in them. That is, the polyenes are showing intermolecular reactions that lead to crosslinking, instead of intramolecular cyclization needed for the formation of aromatics, according to what some authors have mentioned.<sup>9</sup>

Using the mixture CaSt<sub>2</sub>-ZnSt<sub>2</sub>, along with Pe to stabilize PVC, the results shown in Table III were obtained. The shape of the curves (not seen here) are, in general, very similar to the control. However, the values at 400 nm are higher for this sample and slightly smaller at 800 nm (for 5–15 min), indicating a higher production of polyenes, with the beneficial low production of dark material. This is very clear at 20 min degradation, where the 400 nm value is slightly lower than the control, and the 800 nm is largely reduced for this sample. In other words, the difference between absorbance values at 400 and 800 nm is very noticeable.

This effect has been already observed in the samples without costabilizer (see Benavides et al.,<sup>10</sup>) and it is considerably enhanced by the addition of pentaerythritol. This suggests that ZnCl<sub>2</sub> acts as a catalyst for the intramolecular cyclization reaction and that the lack of it, when the complex is used, stop such reactions, subsequently allowing more crosslinking reactions in the polymer.

There are no important differences found between the T<sub>p</sub>s of 180 and 130°C, as happened with the diketone, supporting previous findings findings where the latter temperature is enough to form the complex CaSt[ZnSt<sub>3</sub>].

When the ZnSt<sub>2</sub> was preheated, mixed with

CaSt<sub>2</sub>, and added along with pentaerythritol to PVC, the reflectance values are shown in Table IV. The shape of the traces are very similar to the previous ones (Table III), but the values show some interesting features. First of all, the percentages of reflectance are noticeably higher at the 400 nm wavelength and slightly lower at 800 nm; this increased gap between the values indicates more polyenes, less blackness, and perhaps more crosslinking.

It is noteworthy to mention that the values at 400 nm for the 10–20 min of degradation show a steady increment, while the first 5 min show a marked change that was not seen with the control or the previous sample. This suggests that the dominant degradation reaction, namely, polyene formation, is happening from the beginning, with basically zero formation of dark material (cyclization). This could be the effect of the costabilizer, which is complexing the new structures of ZnSt<sub>2</sub>, and the low amount of ZnCl<sub>2</sub> formed from the lower availability of the soap, not allowing the cyclization to occur. Once some ZnCl<sub>2</sub> is in the media, the formation of aromatics start to rise, as seen in the 20-min degradation values.

The main difference between T<sub>p</sub>s of 180 and 130°C is that for the latter, the values at 20 min degradation show a low increment for the 400 nm value but a considerable increment at the 800 nm value. This indicates that the effect of preheating was not as effective as at 180°C and that the new structures of the soap, generated by the thermal treatment, are consumed earlier.

For the preheated CaSt<sub>2</sub> mixed with ZnSt<sub>2</sub> and added along with the costabilizer to the PVC, the results are shown in Table V. The latter indicates that the quantities of polyenes produced are even less than the ones produced in the control (Table II), at early degradation times. However, at 15 and 20 min, when fast dehydrochlorination starts, the values are considerably higher. The big differ-

**Table IV Reflectance Values for PVC + CaSt<sub>2</sub> + ZnSt<sub>2</sub>(T<sub>p</sub>) + Pe**

Degradation Time (min)	Percentage of Reflectance					
	T <sub>p</sub> = 180°C			T <sub>p</sub> = 130°C		
	400 nm	600 nm	800 nm	400 nm	600 nm	800 nm
0	100	100	100	100	100	100
5	80	95	99	78	95	98
10	51	87	98	56	90	97
15	37	82	97	36	82	92
20	21	70	87	31	78	89

ence when comparing this sample with the previous one is that the gaps between the 400 and 800 nm values are not as high. The fact that it is not showing higher gaps than the control could mean that the calcium soap has been removed from the mechanism (induced by the preheating) and that the formation of double bonds and dark material is controlled by the zinc soap and the costabilizer. This would then occur at an accelerated rate due to the lack of synergism with the calcium. Hence, it seems that the calcium soap has not become active for the carboxylation, as was mentioned as a possibility in the FTIR studies.

The effect has been simply reduced with the preheating temperature (T<sub>p</sub>) of 130°C, where the same trend is observed, with the values of the first 10 min being similar to the control and the differences thereafter appearing for the longer degradation times.

#### UV-Visible Analyses

It has been mentioned that the coloration of PVC during degradation is due to the formation of polyenes, being the longer ones responsible for the darkness of the plastic. In a previous report,<sup>5</sup> we have proposed that not only long double bond sequences

have to do with coloration but multiaromatic compounds produced during the secondary reactions (cyclization specifically) as well. In such a report, we showed polyene formation by UV spectroscopy in the uncostabilized samples. Three different values of absorbance were reported, at 273 nm, at 360 nm, and the sum of both, which correspond to three conjugated double bonds, to five to seven double bonds, and to the total polyenes, respectively (according to Braun and Sonderhof<sup>11</sup> and Daniels and Rees<sup>12</sup>). Now, the same evaluations were carried out for the samples costabilized with pentaerythritol; for the diketone experiments (part I), it was not possible due to the strong absorptions of the compound in the same UV region.

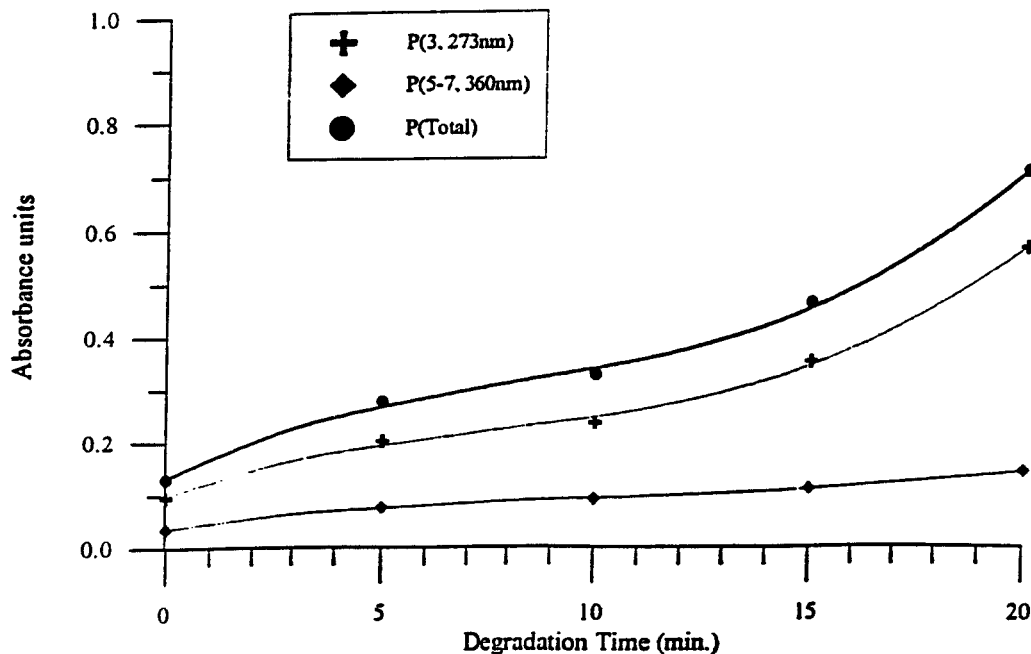
Figures 6 and 7 show the polyene formation trends observed for the blank (no preheating) before and after reduction of carbonyl groups with NaBH<sub>4</sub>. There is not much difference after the reduction treatment, only a slight enhancement in the 0 and 20 min degradation values. This effect was observed as well in the noncostabilized samples (not shown here) and can be attributed to the shifting on wavelength caused by carbonylic groups, which once reduced by the treatment enhance the absorbance values.

Figure 8 shows the resulting graph when PVC

**Table V Reflectance Values for PVC + CaSt<sub>2</sub>(T<sub>p</sub>) + ZnSt<sub>2</sub> + Pe**

Degradation Time (min)	Percentage of Reflectance					
	T <sub>p</sub> = 180°C			T <sub>p</sub> = 130°C		
	400 nm	600 nm	800 nm	400 nm	600 nm	800 nm
0	100	100	100	100	100	100
5	89	97	97	88	97	97
10	76	95	96	71	95	96
15	32	51	65	45	69	78
20	0	0	13	0	5	19

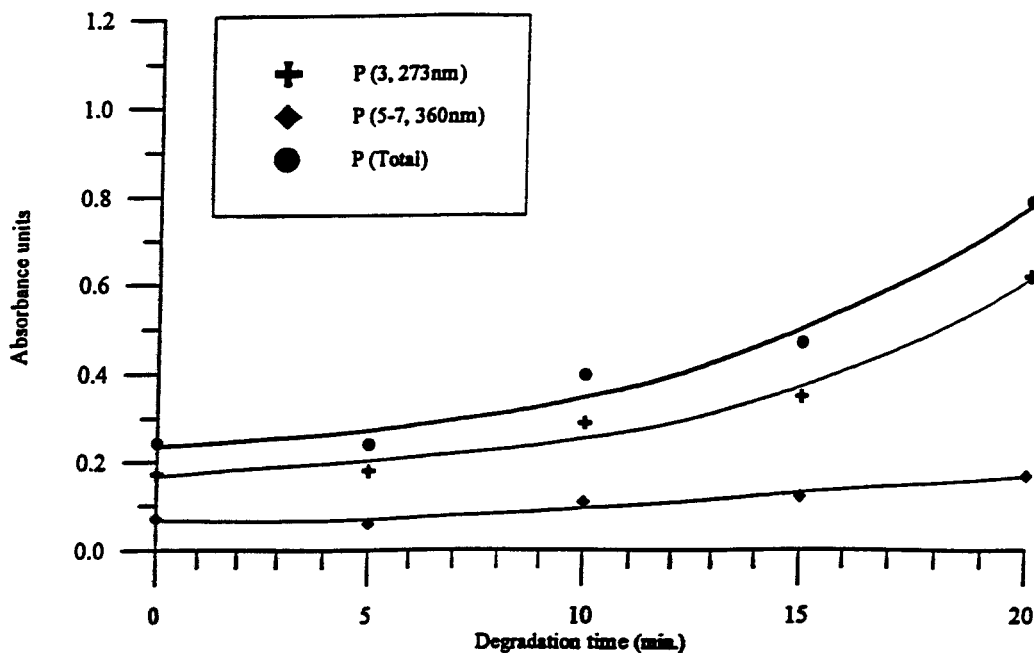




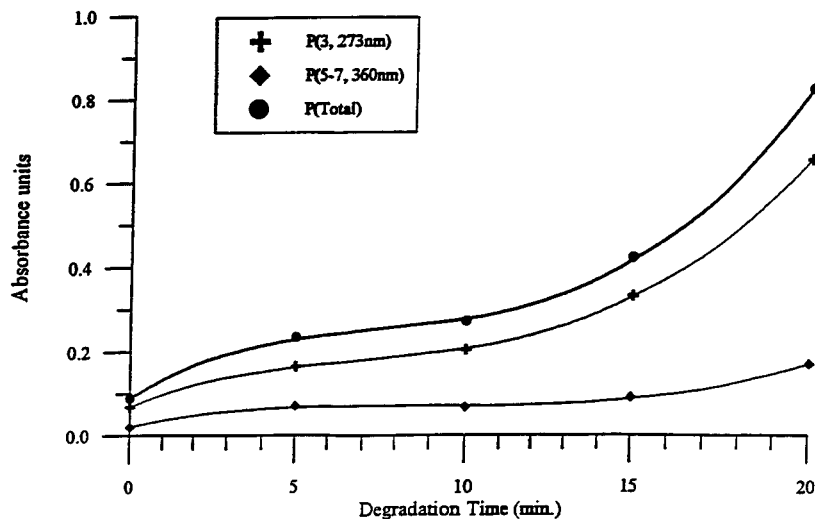
**Figure 6** Total polyenes formed in PVC stabilized with CaSt + ZnSt and pentaerythritol and degraded up to 20 min at 195°C.

was stabilized with the preheated mixture of soaps and Pe. The graph obtained after reduction of carbonyls is not included since it is very similar to this one. The differences before and after the  $\text{NaBH}_4$  treatment are also rather small, and the most noticeable difference is at the middle of the

degradation, where the absorptions for the reduced samples are higher than the nonreduced ones. The low formation of carbonylic groups attached to the polyenes have been observed in the visible reflectance studies of these samples, where the specific absorptions due to the polyenes



**Figure 7** Total polyenes formed in PVC stabilized with CaSt and ZnSt and pentaerythritol and degraded up to 20 min at 195°C, after reduction of carbonyls.

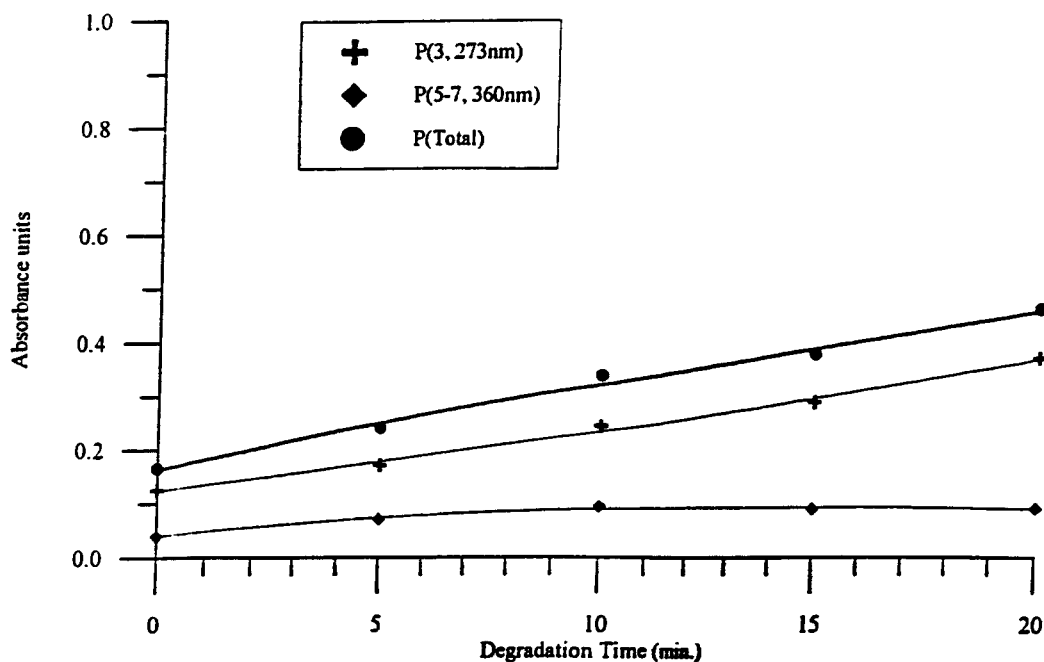


**Figure 8** Total polyenes formed in PVC stabilized with CaSt–ZnSt (preheated at 180°C) + pentaerythritol and degraded up to 20 min at 195°C.

were clearly observed. This effect seems to be due to the lack of the catalyst  $ZnCl_2$ , which is effectively complexed by the polyol, allowing a “clean” production of polyenes throughout the degradation time. The formation of polyenes is not as steady as for the control, suggesting that the complex is actually influencing their formation.

The use of  $ZnSt_2$  along with  $CaSt_2$  and Pe to stabilize PVC gives the results shown in Figure 9. The results from the reduced samples are very

similar as well and are not shown here; the main differences are actually in the enhanced absorbance values after the reduction treatment. This indicates that the polyenes had carbonylic groups attached to them that shifted the specific measured absorptions. There was an effect observed in the visible–reflectance studies of these samples, not seen with this method, that indicated an important production of polyenes in the first 5 min of degradation. This seems to be due



**Figure 9** Total polyenes formed in PVC stabilized with CaSt + ZnSt (preheated at 180°C) + pentaerythritol and degraded up to 20 min at 195°C.

to the fact that the evaluation is actually for polyenes of medium size ( $n = 5-7$ ), with respect to that observed with the other technique (more than  $n = 14$ ). However, the relatively high and stable amount of polyenes that are present in the samples from 5 up to 20 min agrees with those findings, indicating that the degradation process is still at the induction period, as seen by the quite low values after 20 min.

The set of samples when preheated  $\text{CaSt}_2$  was used gives a clear indication of the effect caused by the carbonylic compounds to the polyenes (Figs. 10 and 11). The amount of long polyenes obtained at the 20 min degradation are basically zero for the sample without reduction and very low for the short ones. After the treatment, the same samples show the opposite effect: a high amount of polyenes and the "real" trend, followed by the polyene formation throughout the degradation time. The values are always higher after the reduction, especially at the beginning and the end, indicating a high formation of carbonylic polyenes induced by the addition of this preheated soap. The effect could be due to the lack of calcium stearate in the mixture, as has been found in the previous experiments, which effectively accelerate the degradation process.

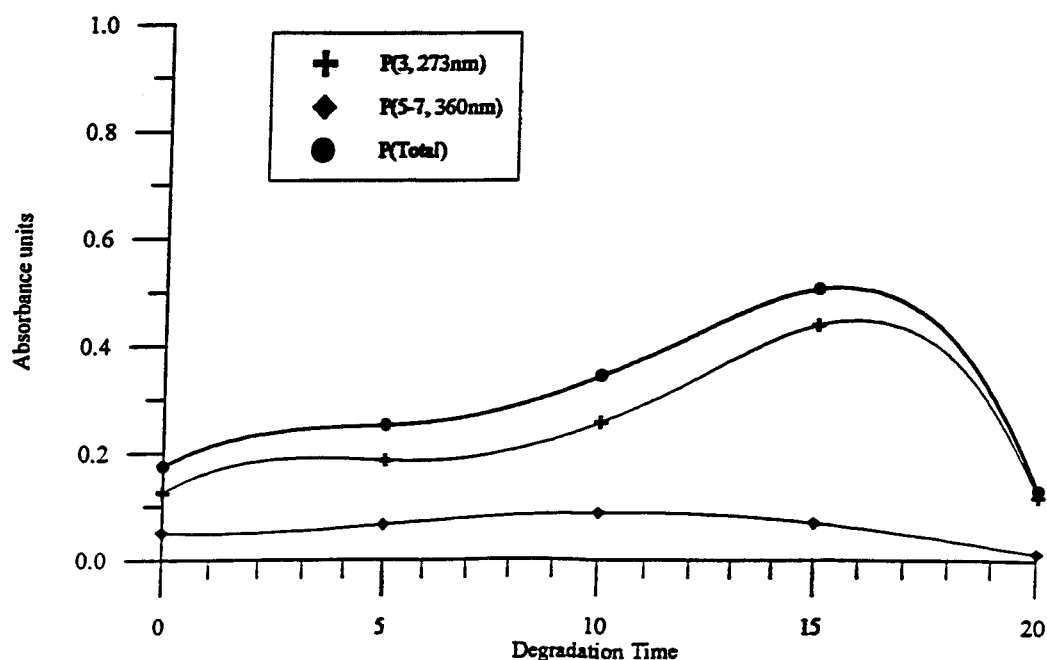
Another way of looking at the polyene formation is through the short : long polyene ratio obtained with the degradation time (see Fig. 12). It

is shown clearly that pentaerythritol is keeping the ratio very stable throughout the degradation since the value is always between 2 and 3, indicating that the mechanism is controlled mainly by this additive. The latter was not seen for the non-costabilized samples (see Benavides et al.<sup>10</sup>). The exception is found for the preheated  $\text{CaSt}_2$  trace, which is showing an enhancement of the ratio at 15 min of degradation. The reason for the latter could be due to the fact that at this time, fast dehydrochlorination is happening, and the formation of short polyenes is more effective since the long ones undergo secondary reactions (sample is already black at 15 min), consuming them and reducing their concentration.

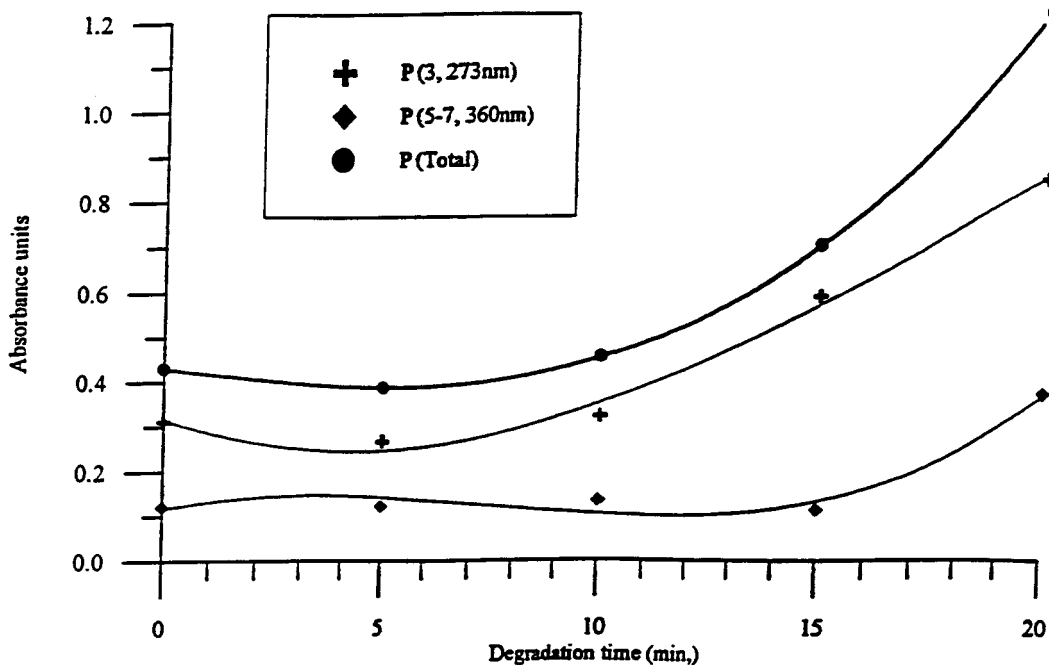
### Fluorescence Analyses

With the aim of elucidating in more detail the type of polyenes formed in the PVC, fluorescence analyses were carried out for the same samples used for the UV-vis analyses. That is, immediately after reading the THF solution in the UV instrument, the same cell was taken to the luminescence instrument for the fluorescence emission readings.

Figures 13-16 show the emission bands obtained from the blank (no preheated soaps) for the four excitation wavelengths used. The trends observed throughout the degradation time are



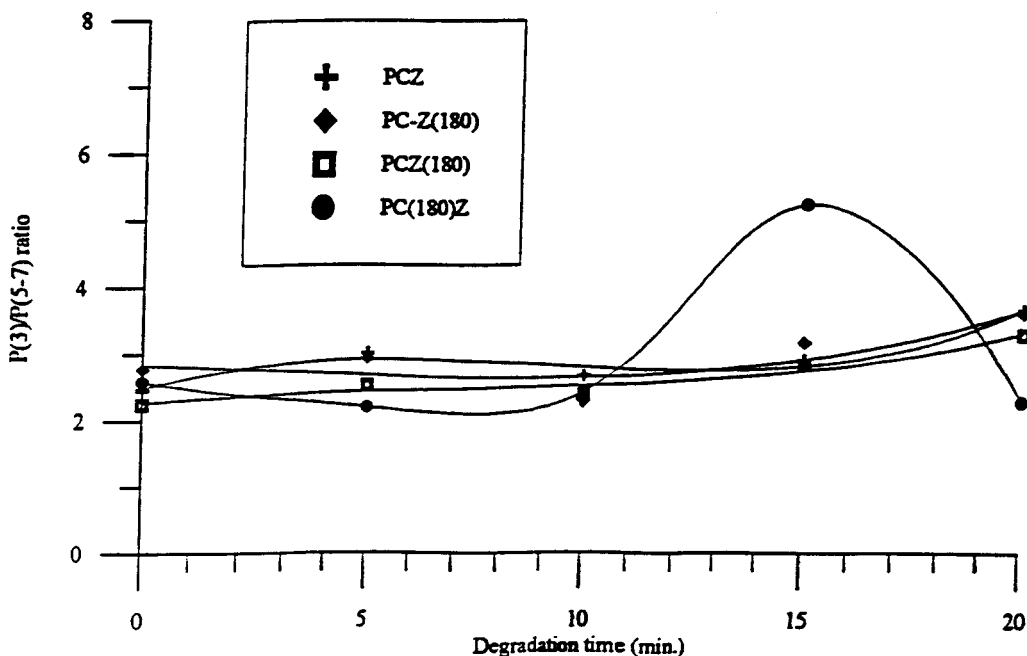
**Figure 10** Total polyenes formed in PVC stabilized with  $\text{CaSt}$  (preheated at  $180^\circ\text{C}$ ) +  $\text{ZnSt}$  and pentaerythritol and degraded up to 20 min at  $195^\circ\text{C}$ .



**Figure 11** Total polyenes formed in PVC stabilized with CaSt (preheated at 180°C) and ZnSt and pentaerythritol and degraded up to 20 min at 195°C, after reduction of carbonyls.

similar for the two short wavelengths (245 and 280 nm) and show the disappearance of the initial band at 316 nm, while a broad red shifted band appears with time. The high excitation wave-

lengths (Ex 330 and 360 nm) show no important bands before any degradation, but a broad blue shifted band appears with the degradation time. Similar bands were seen in the noncostabilized



**Figure 12** Short : long polyene ratios found in PVC stabilized with the preheated metal soaps and pentaerythritol and degraded up to 20 min, after reduction of carbonyls.

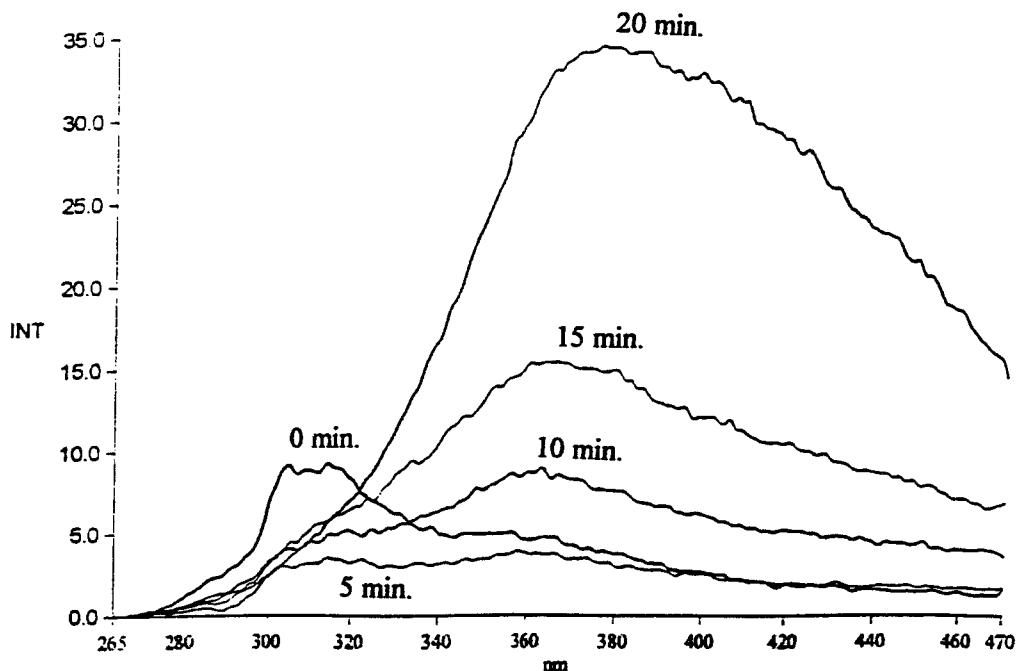


Figure 13 PVC + CaSt + ZnSt + Pe (Ex 245 nm) degraded up to 20 min.

samples,<sup>6</sup> indicating that the use of pentaerythritol is not changing the type of chromophoric groups formed during the degradation of PVC. Figures 17 and 18 show the trends observed for the noncostabilized sample, in the low and high wavelengths, respectively. Basically, the differ-

ence between both sets of samples consists in the maximum intensity obtained at 20 min degradation, which is again an indication that the costabilizer has effectively slowed down the degradation of the PVC (even though the degradation temperature was increased for the latter to 195°C).

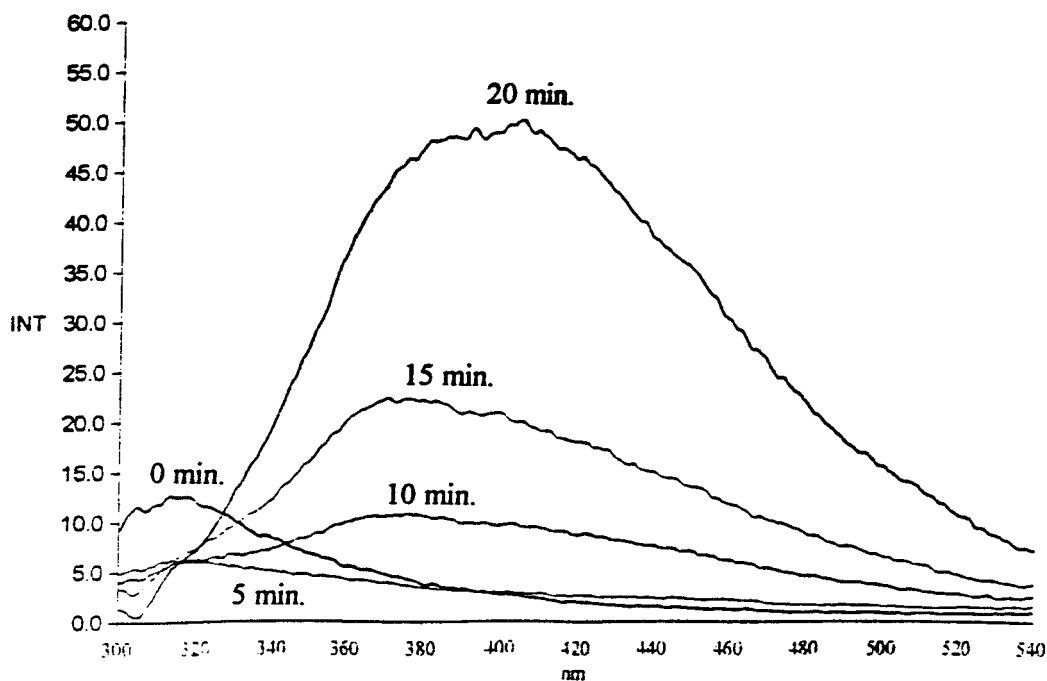


Figure 14 PVC + CaSt-ZnSt + Pe (Ex 280 nm) degraded up to 20 min.

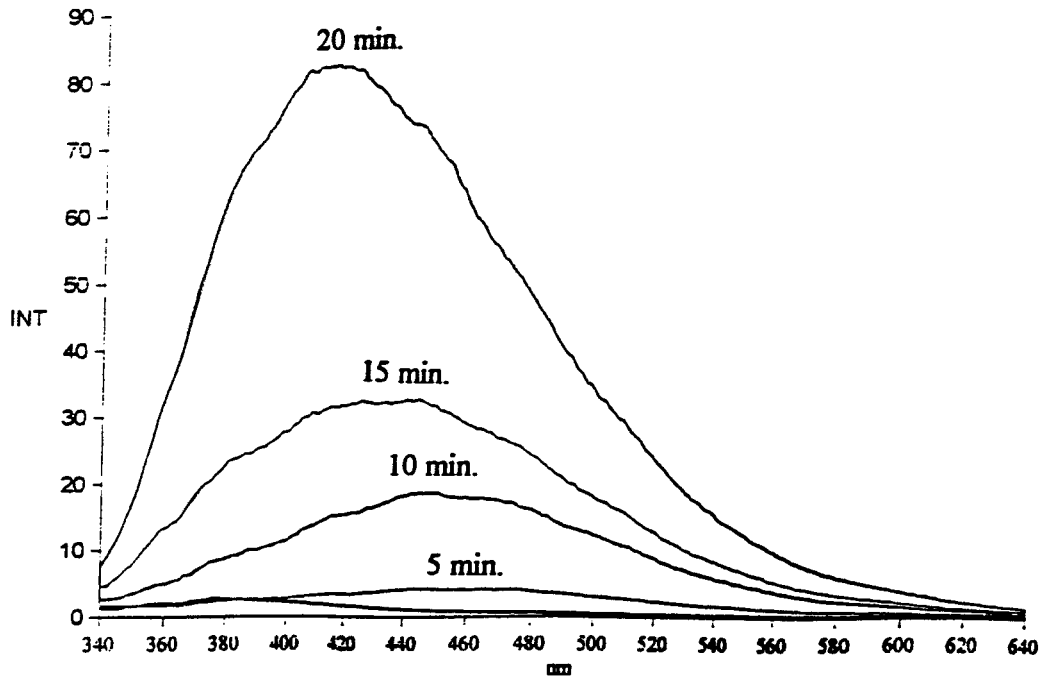


Figure 15 PVC + CaSt + ZnSt + Pe (Ex 330 nm) degraded up to 20 min.

In our previous studies,<sup>5</sup> the 316 nm band was attributed to short double bond sequences ( $n = 2-3$ ) attached to a more rigid (aromatic) structure or a carbonyl group permanently attached to the polymer, since it has been observed that this band does not disappear with solvent extraction.<sup>13</sup>

This band is reduced with degradation time, and the broad band appearing with the degradation, centered at 380 nm, was suggested to be due to the formation of polyenes of different lengths. On the other side, the long excitation wavelengths show the appearance of a broad band at 420–440

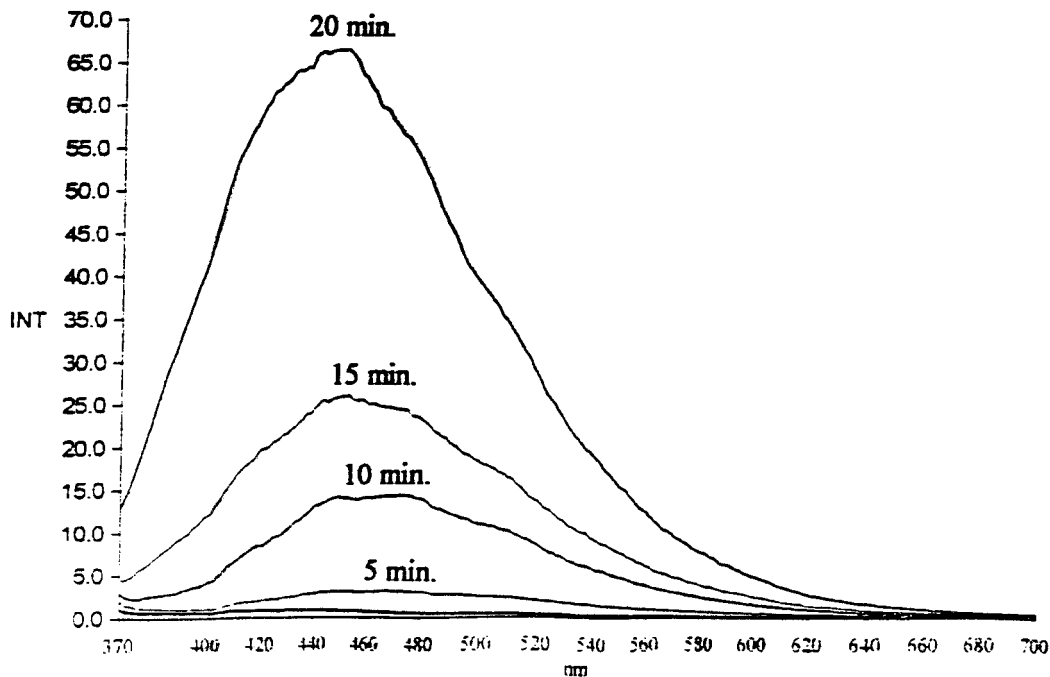


Figure 16 PVC + CaSt-ZnSt + Pe (Ex 360 nm) degraded up to 20 min.

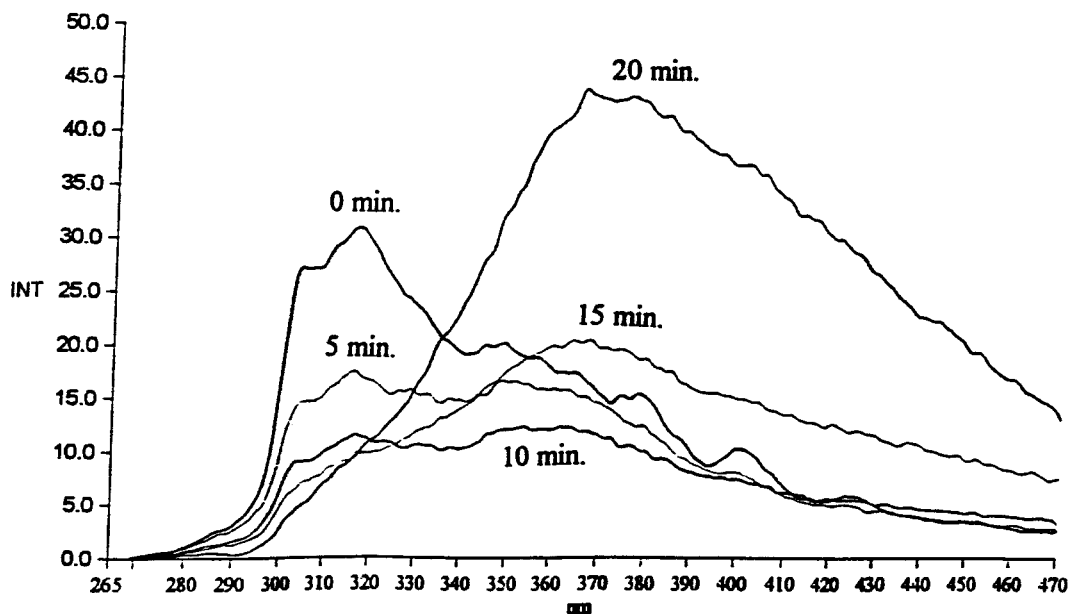


Figure 17 PVC + CaSt + ZnSt (Ex 245 nm) degraded up to 20 min.

nm, tending to shift to lower values. Combining short and long wavelength bands, it has been said that the degraded polymer has emission bands between 380 and 405 nm that correspond to the emissions of short polyene sequences, as mentioned by some authors,<sup>14,15</sup> since the long ones show a gradual decrease of intensity (quantum yield) when increasing the conjugation. They deducted that the shift in emission maxima is due

to multiple emitting states of the polyenic chromophores rather than to multiple energy transitions of an individual polyene of long conjugation.

The luminescence centers in polymers were originally attributed to carbonylic groups attached to molecular chains<sup>16,17</sup>; and specific emissions in the regions found in this work have been seen for free anthracene, a phenanthrene derivative, and a naphthalene derivative in polyethylene studies.<sup>18</sup>

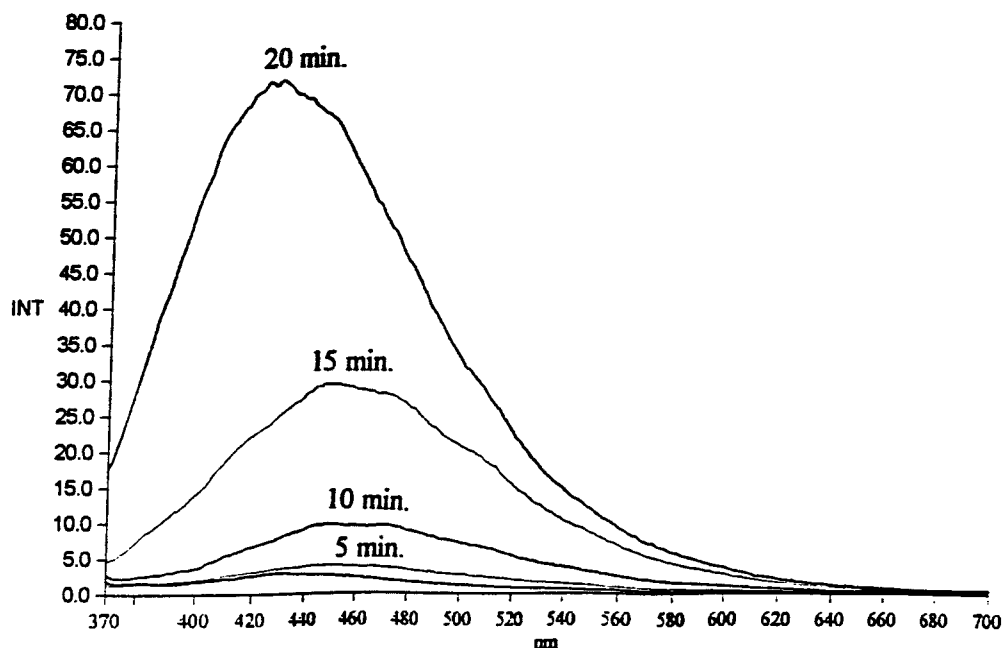


Figure 18 PVC + CaSt + ZnSt (Ex 360 nm) degraded up to 20 min.

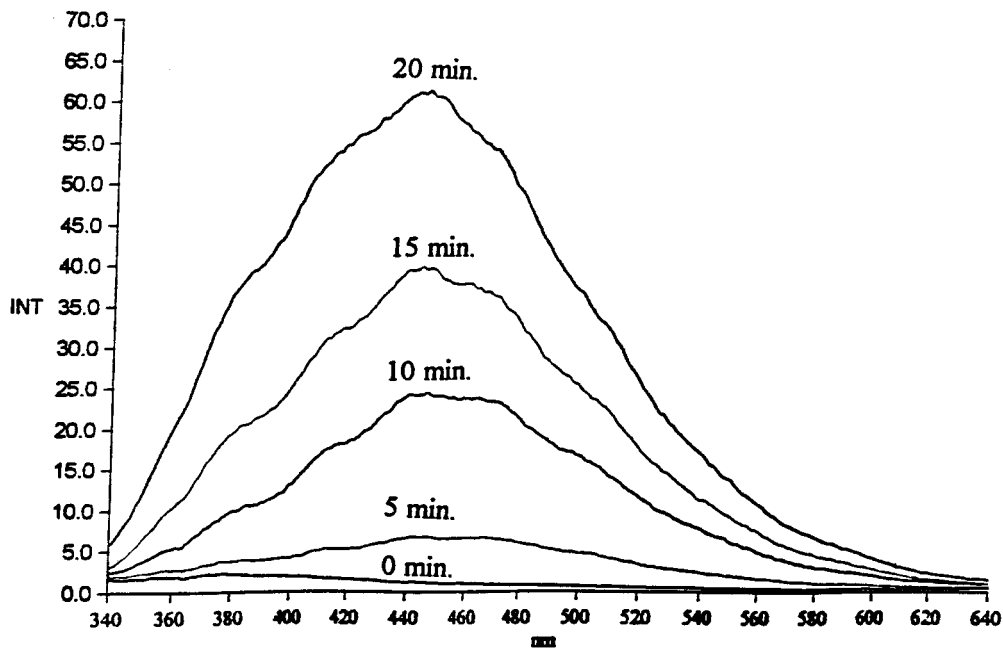


Figure 19 PVC + CaSt + ZnSt (180) + Pe (Ex 330 nm) degraded up to 20 min.

There were no differences found when the samples were  $\text{NaBH}_4$  reduced (not shown here), suggesting that those bands are mainly due to the buildup of short polyenes and to the presence of multiaromatic compounds formed as a result of the secondary reactions of the long double bond conjugations. However, the only difference with

the nonreduced samples consists in the enhancement of the intensity after the reduction treatment. This effect has been attributed to the effective presence of keto groups, which have low fluorescence quantum yields and are lost during the  $\text{NaBH}_4$  treatment.<sup>5</sup> This effect has been seen for all our samples, with and without costabilizer.

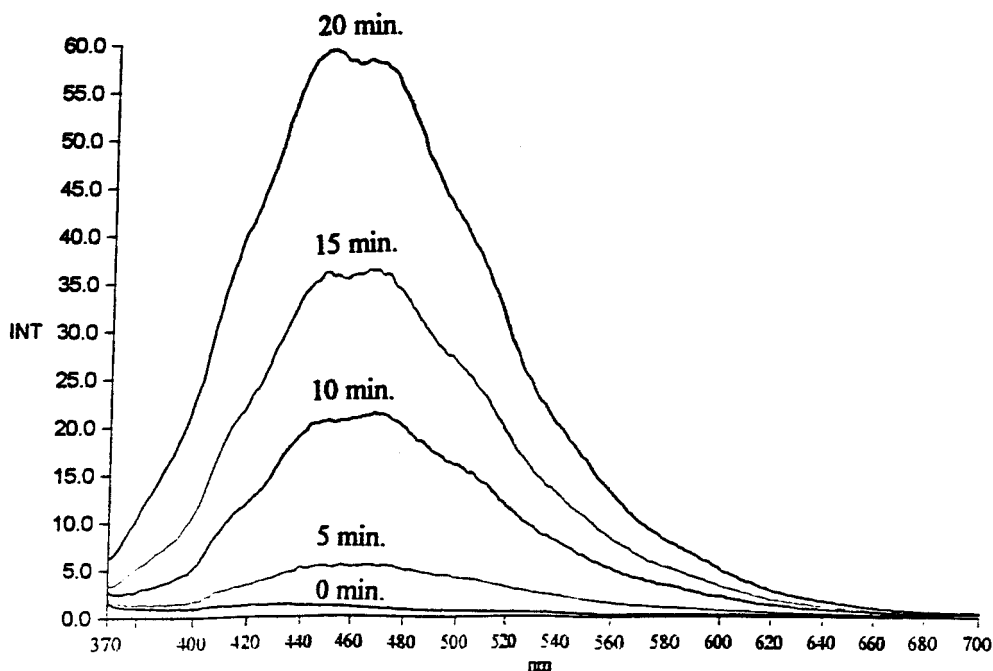


Figure 20 PVC + CaSt + ZnSt (180) + Pe (Ex 360 nm) degraded up to 20 min.



The analyses of samples containing the preheated metal soaps showed the same emission bands and tendencies observed in the samples without costabilizer (see Benavides et al.<sup>5</sup>), even after the reduction of carbonyls, so they are not presented here. The only interesting results are the ones obtained with the preheated ZnSt<sub>2</sub> (Figs. 19 and 20), where the bands increasing throughout the degradation time show specific absorptions, especially at 15 and 20 min of degradation. This supports the findings obtained by visible reflectance studies, where the same specific absorptions were found and ascribed to the high formation of polyene sequences, compared with the low formation of products from secondary reactions. Such an effect is clear for these samples because pentaerythritol and preheated ZnSt<sub>2</sub> induce the formation of long polyenes and less secondary reactions that lead to the polymer blackening.

## CONCLUSIONS

The addition of pentaerythritol along with calcium and zinc stearates to stabilize PVC considerably increases the induction time to degradation, with the disadvantage of generating large amounts of polyenes, and, subsequently, giving rise to discoloration. This is the reason for being known as a long-term costabilizer. When the metal soaps are preheated, the resulting effect seems to be the sum of two mechanisms: the one known for the costabilizer; and that already observed, in previous reports, for the thermally treated metal soaps. The same result was drawn for the diketone studies in part I of this series, where a separated consumption of compounds was observed during the stabilization mechanism.

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