

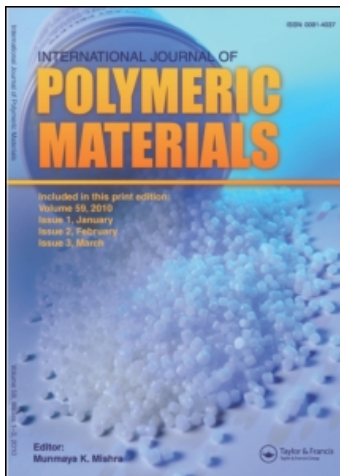
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E.S.R. Investigations of Polypentenamers Degradation

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E.S.R. Investigations of Polypentenamers Degradation

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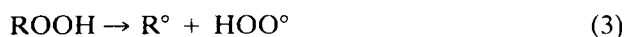
Electron spin resonance investigations of the thermo-oxidative degradation of trans-polypentenamer rubbers, containing various stabilizers, are reported. The dependence of the resonance line parameters on the degradation time and temperature as well as the effect of various stabilizers on the resonance line are studied in detail. The activation energies for the generation of free radicals, the reaction order for the overall generation of free radicals and the associated constant rate, are estimated.

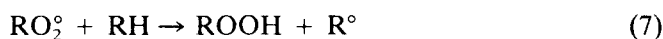
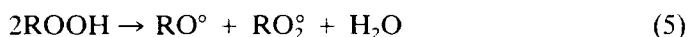
KEY WORDS Polypentenamer, electron spin resonance, thermo-oxidative degradation, free radicals, stabilizers

1. INTRODUCTION

Trans-polypentenamer is a general purpose rubber exhibiting physical properties similar to those of natural rubber. The thermal and thermo-oxidative degradation of trans-polypentenamer as well as the stabilization of this synthetic rubber, has been investigated by few authors.^{1–6} Electron spin resonance (e.s.r.) spectroscopy is a powerful tool in the investigation of polymer degradation processes^{7–9} allowing the identification of free radicals, the estimation of their concentration as well as the study of interactions among these radicals. From the time dependence of free radical generation, the global reaction order as well as the rate constant for the overall free radical production process may be derived. From the temperature dependence of the reaction rate constant, the activation energy may be estimated, supposing that an Arrhenius like dependence is obeyed.

Usually the thermo-oxidative degradation of the polymers is described by the following chemical reactions.¹⁰

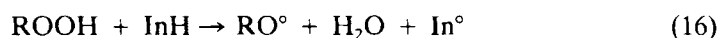
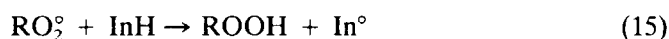
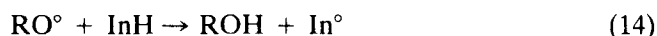




where RH represents the polymer

As the free radicals R° react frequently and rapidly with the oxygen dissolved or diffused within the polymer, the resonance spectra of polymers subjected to thermo-oxidative degradation corresponds to the peroxy (RO_2°) free radicals.

In the case of stabilized polymers, the following supplementary reactions may occur¹⁰;



at high temperatures, even the stabilizers (designated by InH) are thermally degraded, competing with polymer thermo-oxidative degradation. In this case the resonance spectrum may be a convolution of several resonances, due to the free

radicals produced by polymer and stabilizer degradation. This description is frequently complicated by volatilization processes.⁵

Traces of transition metals, usually from catalytic systems may play a significant role in the onset of the thermo-oxidative degradation of polymers and in some cases may be monitored by e.s.r. spectroscopy.⁶

2. EXPERIMENTAL METHODS

Thermal degradation processes in stabilized and unstabilized samples of trans-polyentenamer have been investigated by e.s.r. spectroscopy using a JES-ME-3X spectrometer, operating in the X band (~ 9 GHz). All samples have been degraded in air. Several experiments have been performed:

i) some bulk stabilized and unstabilized samples have been thermally degraded in air, in opened quartz tubes in an oven, in the temperature range 185°C to 350°C during an hour and in the temperature range 250°C to 500°C during 30 minutes. The temperature has been measured with an accuracy of $\pm 1^\circ\text{C}$ and the time stability of the temperature was better than $\pm 2.5^\circ\text{C}/\text{hour}$. The degraded samples have been measured 30 minutes after the degradation has been stopped.

ii) some bulk trans-polyentenamer samples, stabilized with various compounds have been thermally degraded in air, in opened quartz tubes, in the spectrometer's cavity, using a JES-VT-3X variable temperature accessory. The temperature has been measured with an accuracy of $\pm 2.5^\circ\text{C}$ and the time stability of the temperature was better than $1^\circ\text{C}/\text{hour}$.

iii) in order to investigate the contribution of oxygen diffusion through trans-polyentenamer, we have investigated the thermal degradation, in air, of thin films of polymer (0.1 mm thickness) deposited from solution on the internal wall of a quartz tube, opened at both sides. The samples have been thermally degraded in a heated air stream, at about 220°C.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

The resonance spectrum of stabilized and unstabilized trans-polyentenamer, thermally degraded in air in the temperature range 185°C to 350°C and 250°C to 500°C during 60 and 30 minutes, respectively, is a narrow, slightly asymmetric singlet, with no structure, as may be noticed from the spectra represented in Figures 1a-1d. The resonance line position is located at $g = 2.042 \pm 0.008$, close to the free electron g value (~ 2.00237) and is independent of the degradation time, degradation temperature, presence of various stabilizers, as well as on their concentration, within experimental errors. Consequently, we have tentatively ascribed this resonance line to peroxy radicals, probably generated according to the following reaction chain³:



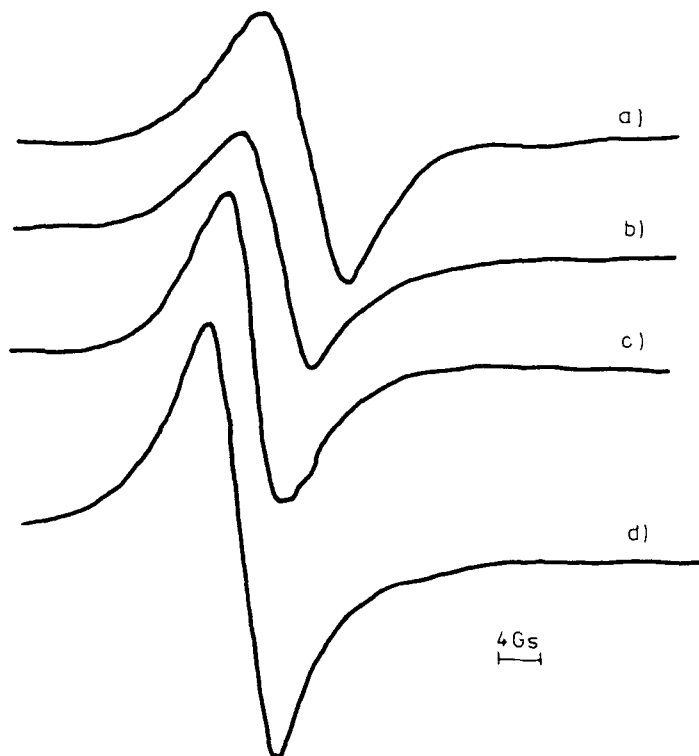
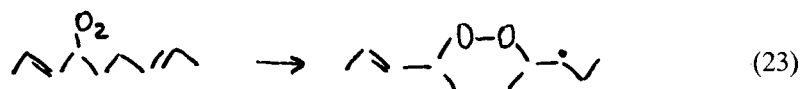
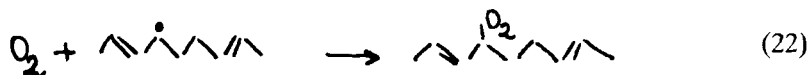
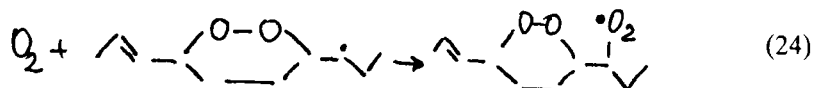


FIGURE 1 The e.s.r. spectra of thermally degraded trans-polybutadiene (sample 99/8), at various temperatures: a) $T = 250^{\circ}\text{C}$; b) $T = 350^{\circ}\text{C}$; c) $T = 300^{\circ}\text{C}$; d) $T = 500^{\circ}\text{C}$.



If oxygen is in excess, a peroxide-peroxy radical may be produced³;



The peak to peak resonance line width, H_{pp} , is sensitive to the above mentioned parameters, ranging from 3.5 Gs to about 10 Gs (1 Gs = 10^{-4}T). For the samples of trans-polybutadiene, thermally degraded in air, during 1 hour, in the temperature range 185°C to 350°C , H_{pp} decreases as the degradation temperature is raised up to 300°C , as may be noticed from Figure 2. This behaviour may be explained by the competition between dipolar and exchange interactions. At a low degradation temperature, the concentration of free radicals is low and the distance

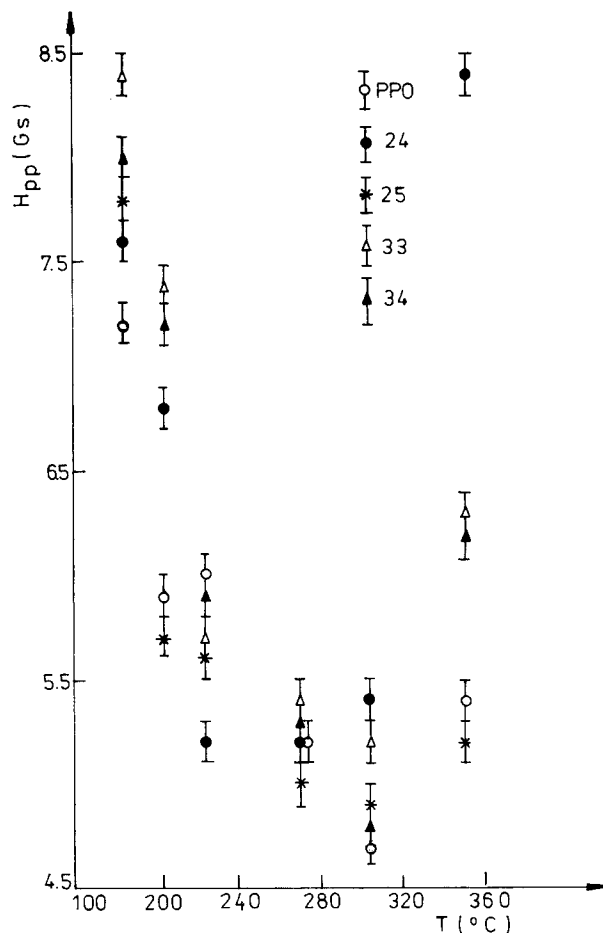


FIGURE 2 The temperature dependence of the peak to peak line width, H_{pp} , for various samples of trans-poly-pentenamer thermally degraded in air, in the temperature range 185°C–350°C.

between free radicals is large; accordingly, dipolar interactions are dominant and the resonance line is broadened.^{11–12} As the degradation temperature is raised, the concentration of free radicals increases and the average distance between them is reduced, leading to the enhancement of exchange interactions, which become dominant over dipolar ones.^{11–12} Consequently the resonance lines are narrowed.

Above 350°C, mainly in stabilized samples, an increase of H_{pp} as the degradation temperature is raised, has been remarked. This behaviour may be related to an increase in the weight of the free radicals produced by the thermo-oxidative degradation of the stabilizers, probably associated with a nonhomogeneous exchange coupling between the free radicals generated by polymer and stabilizer degradation. As may be noticed from Figure 2, the resonance line of the unstabilized sample (PPO) is frequently (but not always) narrower than the corresponding resonance line of the stabilized samples suggesting that the stabilizers affect the balance between dipolar and exchange interactions, due to their thermal degradation, even

below 300°C. However, volatilization processes and the preferential volatilization of some components, may be important.

The temperature dependence of the peak to peak line width, for various samples of stabilized and unstabilized trans-polypentamer, degraded in air, during 30 minutes, in the temperature range 250°–300°C is given in Figures 3 and 4. In these cases a continuous decrease of H_{pp} as the degradation temperature is increased, has been observed. This behaviour is due to the enhancement of exchange interactions and associated with the increase in free radical concentration. Accordingly, the above mentioned increase of H_{pp} for the samples degraded at 350°C during 60 minutes may be associated with the onset of stabilizer degradation; in this case the free radicals produced by polymer degradation are coupled by exchange interactions whereas the free radicals produced by stabilizer degradation are coupled by dipolar interactions, as their concentration is low. Anisotropic exchange interactions between the free radicals generated by polymer and stabilizer degradation are pos-

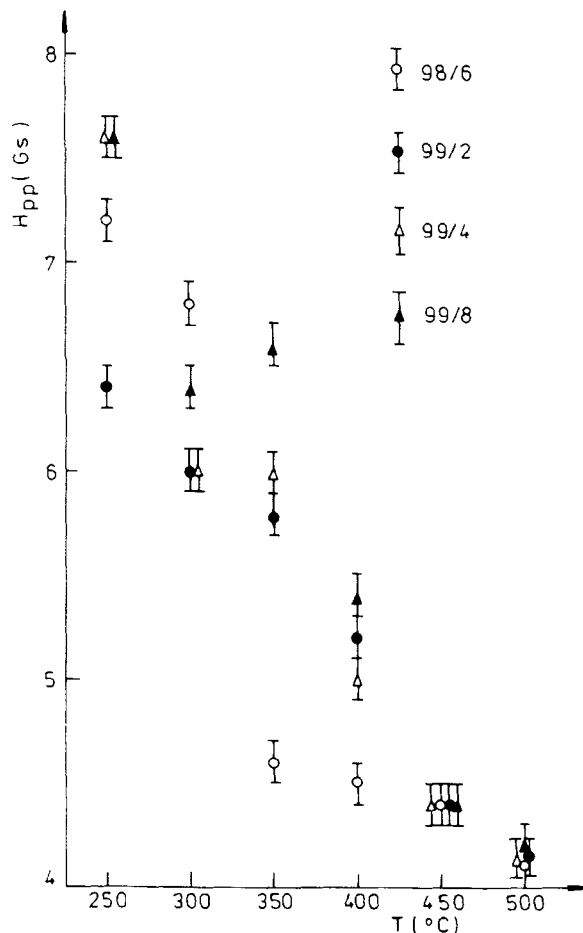


FIGURE 3 The temperature dependence of H_{pp} for samples degraded in air, in the temperature range 250°C–500°C.

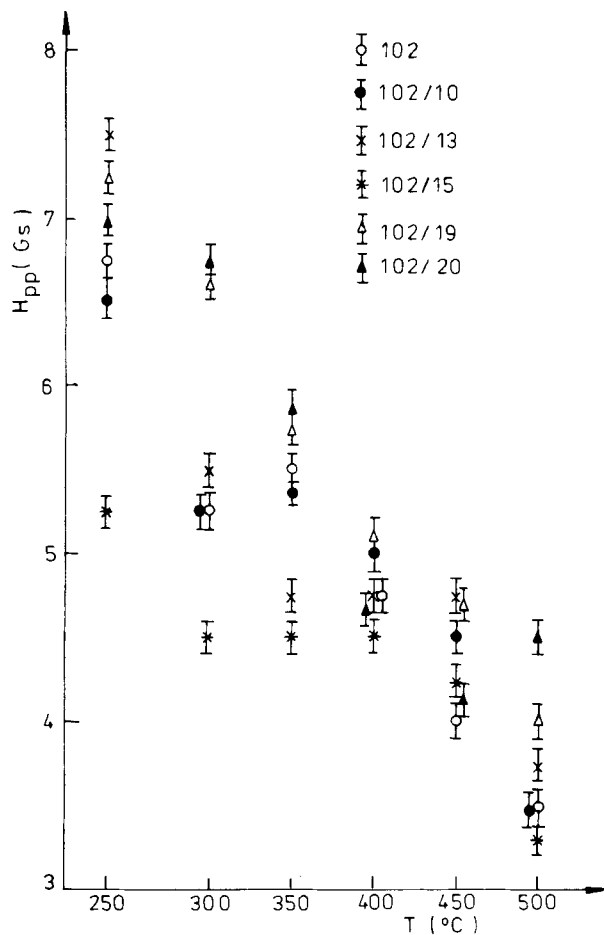


FIGURE 4 The temperature dependence of H_{pp} for sample degraded in air, during 30 minutes, in the temperature range 250°C–500°C.

sible. Increasing the degradation temperature, the exchange interactions become dominant, narrowing the recorded resonance line, which is, in this case, a convolution of at least two resonances.

Tentatively, we have tested an Arrhenius like dependence of H_{pp} on the degradation temperature T ;

$$H_{pp} = H_{pp}^{\circ} \exp - \frac{E_A^H}{RT} \quad (25)$$

where H_{pp}° is a constant.

R is the perfect gas constant.

E_A^H is the activation energy related to the resonance line narrowing.

The values obtained for E_A^H , using a linear regression program, written in BASIC, are given in Table I. It seems interesting to point out that the correlation coefficients

TABLE I

The activation energies for samples of trans-polypentenamer, thermally degraded in air

Sample code	E_A^S (MJ/Kmol)	E_A^H (MJ/Kmol)	Stabilizer		
			type	concentration (%)	
1	102	50 ± 9	7.5 ± 1.5	none	0
2	102/10	55 ± 13	7.1 ± 1.1	H*	0.4
3	102/13	69 ± 17	9.1 ± 1.2	phenolic**	1.2
4	102/15	66 ± 17	5.1 ± 1.1	Irganox 1076*	3.0
5	102/19	19 ± 2	7.0 ± 1.3	Topanol OC*	0.8
6	102/20	59 ± 12	6.2 ± 1.7	Santoflex IP*	0.2
7	98/6	61 ± 5	9.8 ± 1.4	Irganox 802*	0.5
8	99/8	70 ± 13	8.6 ± 1.4	Irganox 1010*	0.5
9	99/4	66 ± 14	8.9 ± 0.7	Ongrostab 2246*	1.0
10	99/2	58 ± 11	6.6 ± 1.2	Irganox 1076	2.5
11	24	23 ± 2	6.5 ± 1.0	Santoflex IP	0.5
12	25	21 ± 5	3.0 ± 0.5	Santoflex IP	0.8
13	33	25 ± 3	5.0 ± 3.0	Ongrostab 2246	0.5
14	34	41 ± 5	4.5 ± 2.0	Ongrostab 2246	0.2

*Chemical structure given in Dimonie *et al.*⁵

**Bisphenolstyrene.

for this dependence are in the range of 60% to 96%. Large deviations from Equation 25 are noticed in the case of samples 33 and 34 whereas the best correlation coefficients have been obtained for samples 25, 103/13 102/19, 98/6, 99/8 and the unstabilized trans-polypentenamer (over 92%). From the experimental data, we may conclude that amine based stabilizers reduce the value of E_A^H and that the correlation coefficients are lower in the case of samples stabilized with phenolic compounds, suggesting that the best stabilizers for trans-polypentenamer are amine-based systems.

The free radical concentration S , has been estimated according to;

$$S = KIH_{PP}^2 \quad (26)$$

where K is the resonance line shape parameter, estimated according to the slope method.⁸

I is the resonance line amplitude.

For the samples degraded in air, during 1 hour, in the temperature range 185°–350°C, the concentration of free radicals in relative units, increases as the degradation temperature is raised to about 300°C, as may be noticed from Figure 5. This behaviour is in good agreement with the temperature dependence of the peak to peak line width, supporting the enhancement of exchange interactions due to the increase in free radical concentration, in this temperature range.

The temperature dependence of free radical concentration S , in relative units, in stabilized and unstabilized trans-polypentenamer, thermally degraded in air, during 30 minutes, in the temperature range 250°–500°C is represented in Figures 6 and 7. The free radical concentration increases as the degradation temperature is raised to about 450°C, confirming that the temperature dependence of the peak to peak line width is associated with the enhancement of exchange interactions. A maximum value of S is noticed around 450°C, probably as above this temperature,

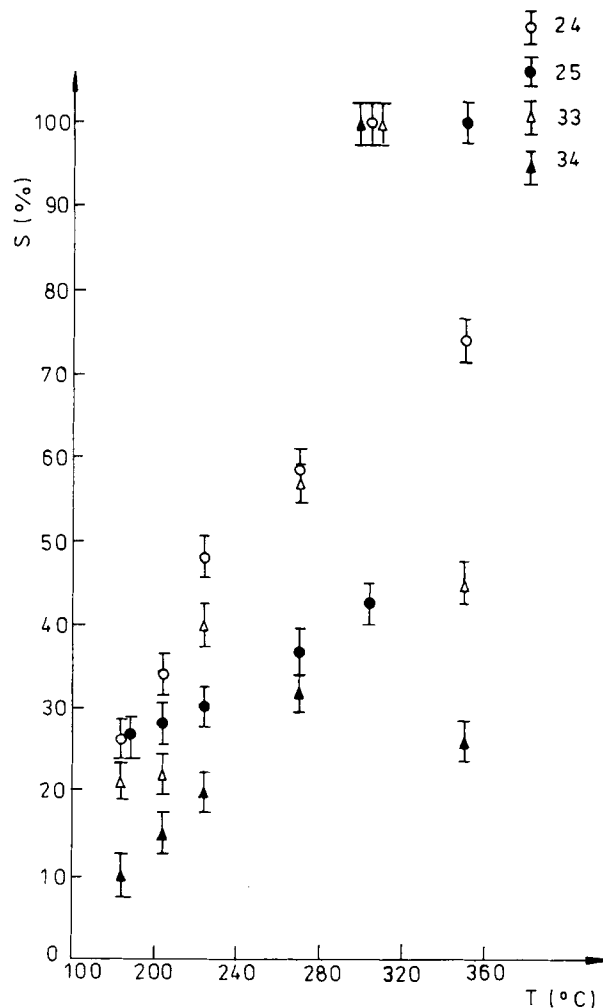


FIGURE 5 The temperature dependence of free radicals concentration S , in relative units, for samples degraded in air, during 1 hour, in the temperature range 185°C–350°C.

polymer and stabilizers volatilization processes are significant. The decrease of this maximum from 450°C for a degradation time of 30 minutes to about 300°C for samples degraded during 1 hour, is expected, suggesting a correlation between the degradation time and the degradation temperature.

From the temperature dependence of free radical concentration it is possible to extract the activation energy E_A^S for the free radical overall generation process supposing an Arrhenius like dependence of S on the degradation temperature;

$$S = S_0 \exp - \frac{E_A^S}{RT} \quad (27)$$

where S_0 is a constant.

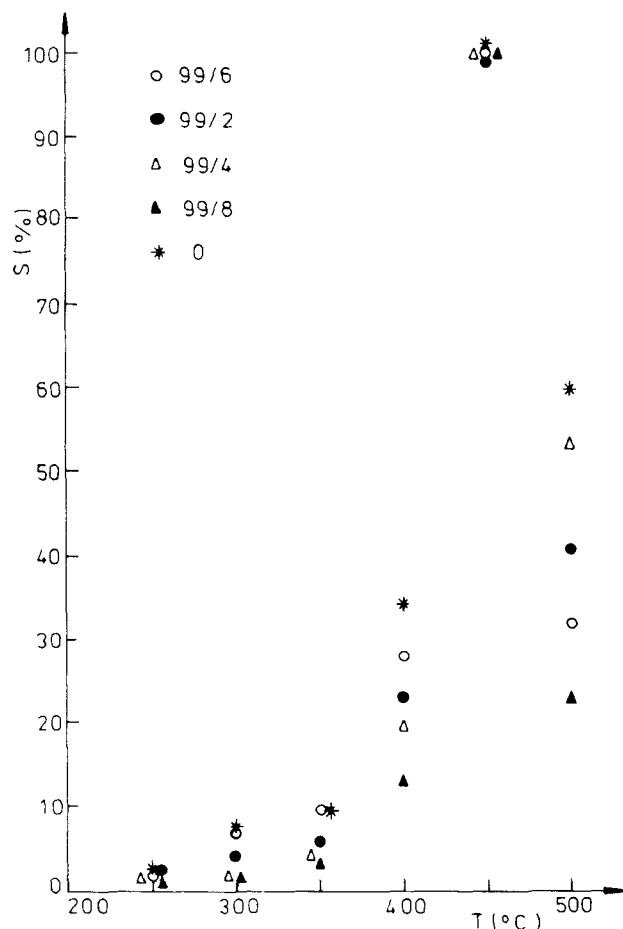


FIGURE 6 The temperature dependence of S , in relative units for samples degraded in the temperature range 250°C–500°C.

The activation energies E_A^S , for various samples of trans-polypentenamers with different stabilizers, estimated using a linear regression program, are collected in Table I. In this case the correlation coefficients range from 90%–99%, supporting an Arrhenius like dependence of the free radical concentration on the degradation temperature. A higher activation energy has been noticed for the sample 98/6. This is the best phenol based stabilizer for trans-polypentenamer.⁴ The activation energies measured by e.s.r. spectroscopy are lower than the activation energies estimated from DSC data.^{3,5} Generally, the same dependence of the activation energy on the nature and concentration of the stabilizer has been noticed by both e.s.r. and D.S.C. data.⁵

The resonance spectrum of various, stabilized and unstabilized bulk samples of trans-polypentenamer, degraded in the electron spin resonance spectrometer's cavity, using a JES-VT-3X variable temperature accessory, is also a narrow, slightly asymmetric singlet, located at $g = 2.044 \pm 0.008$. The time evolution of the peak

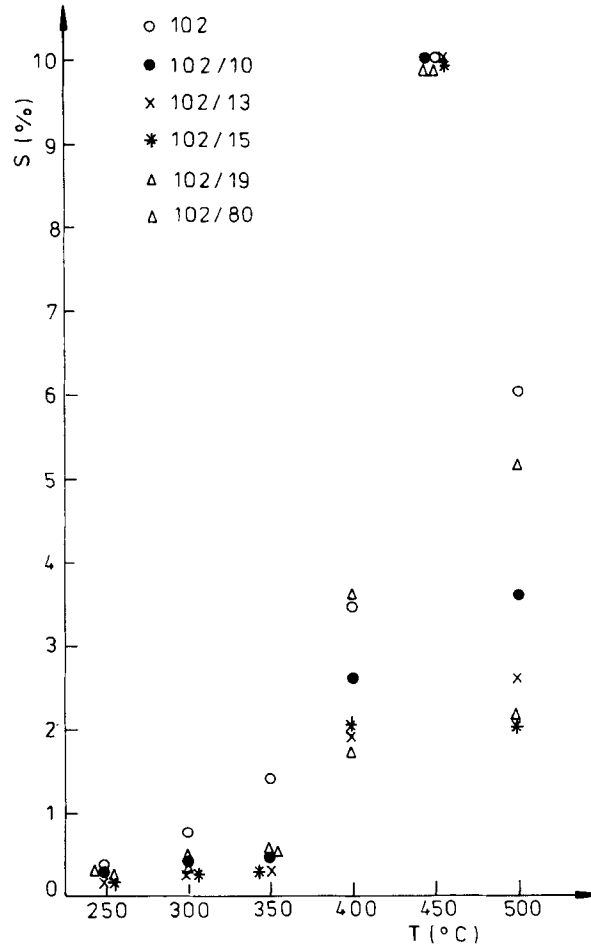


FIGURE 7 The temperature dependence of S , in relative units, for samples of trans-polyentenamer, thermally degraded in air, during 30 minutes, in the temperature range 250°C–500°C.

to peak resonance line width for samples of trans-polyentenamer containing various stabilizers, degraded in air at 220°C, is given in Figure 8. A continuous decrease of H_{pp} as the degradation time is longer is ascribed to the enhancement of exchange interactions due to the increase in free radical concentration, is noticed.

Tentatively, we have tested an exponential dependence of the peak to peak line width, H_{pp} on the degradation time, t_d :

$$H_{pp} = H_{pp}^{\circ} \exp - Kt_d \quad (28)$$

where H_{pp}° is a constant.

K is a constant reflecting the rate with which H_{pp} decreases with the degradation time.

The values of K have been estimated using a linear regression program and

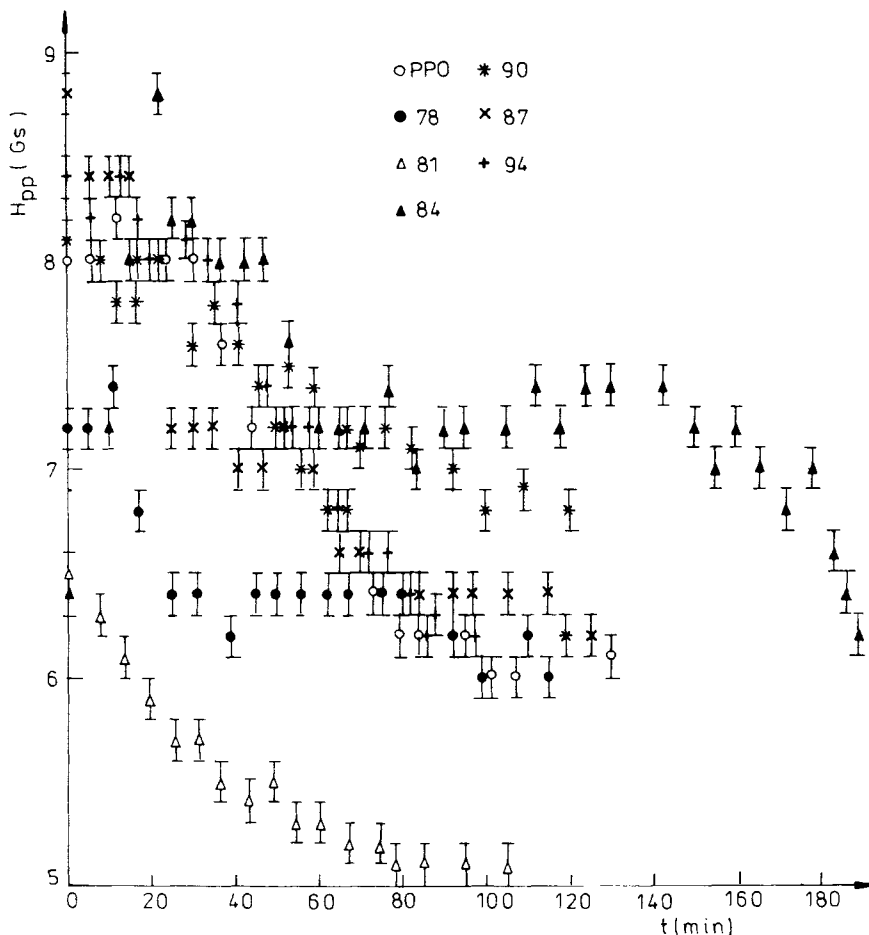


FIGURE 8 The dependence of the peak to peak line width on the degradation time, for bulk samples degraded in the spectrometer's cavity.

collected in Table II. As the correlation coefficient is higher than 99% we suppose that this dependence is obeyed with an acceptable accuracy.

The time dependence of free radical concentration S , on the degradation time, for bulk samples, thermally degraded in air, *in situ*, at 220°C is represented in Figure 9. A continuous increase in free radical concentration with degradation time, is noticed. Using a program, written within the least square approximation, we have found that the overall reaction order for free radicals generation process is around unity and consequently, the reaction rate constant K_p for free radical generation has been estimated using the expression:

$$S = S_0 \exp - K_p t_d \quad (29)$$

where S_0 is a constant.

The values of K_p , estimated using a linear regression program are listed in Table

TABLE II

The rate constants for various samples of trans-polypentenamer, thermally degraded in air, at 220°C

	Sample code	$K \cdot 10^{-5}$ (S^{-1})	$K_p \cdot 10^{-5}$ (S^{-1})	Stabilizer	
				type	Concentration (%)
1	84	1.8 ± 0.2	9.8 ± 0.9	phenolic*	0.25
2	81	3.9 ± 0.4	10.0 ± 0.8	H	0.30
3	87	4.0 ± 0.5	5.0 ± 0.5	Irganoy 1010	0.30
4	0	4.8 ± 0.3	10.1 ± 0.2	none	0
5	90	3.0 ± 0.3	7.0 ± 0.7	DPPD	0.30
6	84	6.0 ± 0.4	11.3 ± 0.4	Irganox 1076	0.50
7	78	2.5 ± 0.4	12.3 ± 0.2	Vixid	0.3
8	70**	—	5.6 ± 0.4	Santoflex IP	0.3
9	75**	—	2.1 ± 0.3	DNDPhA	0.3

*See Table I.

**Thin films deposited on the internal wall of the quartz tube.

II. The largest values of K_p have been noticed in unstabilized trans-polypentenamer as well as in the samples containing amine based stabilizers. The correlation coefficients range from 90% to 98% supporting the exponential dependence of free radical concentration on the degradation time, at a constant degradation temperature (actually 200°C).

Thin films of trans-polypentenamer, containing various stabilizers, deposited on the internal wall of a quartz tube, have been thermally degraded in a heated air stream, at 220°C, using a JES-VT-3X variable temperature accessory, at 220°C, in the spectrometer's cavity. The resonance spectra of the unstabilized trans-polypentenamer as well as the resonance spectra of the samples which contain phenol based stabilizers have the same feature (shape, g factor, line width . . .) as the above mentioned spectra. However, in the case of trans-polypentenamer stabilized with amine based compounds, the resonance spectra (Figures 10a + 10d) are a convolution of two resonances, the first weak, with no structure, tentatively ascribed to polymer degradation (peroxy radicals) and the second representing the degradation of stabilizers. We have been able to distinguish among these species as the second resonance consists of three, almost equidistant lines, ascribed to nitroxyl radicals. In this case the structure of this resonance spectrum is due to the delocalization of the uncoupled electronic spin ($S = \frac{1}{2}$) over the nitrogen nucleus ($I = 1$), theoretically described by the following spin Hamiltonian^{8,11-12}

$$\kappa = g_e \beta_e \hat{H} \hat{S} + g_i \beta_i \hat{H} \hat{I} + \hat{S} \hat{A} \hat{I} \quad (30)$$

where the first term represents the electronic Zeemann contribution, the second term, usually neglected, is associated with the nuclear Zeemann contribution and the last term expresses the hyperfine interaction.

The isotropic hyperfine splitting constant is about ^{34}Gs and is almost independent on the degradation time. The dependence of the nitroxyl radical's average resonance line amplitude, in relative units, on the degradation time is given in Figure 11. A continuous increase of this line in the first 100 minutes of degradation is noticed.

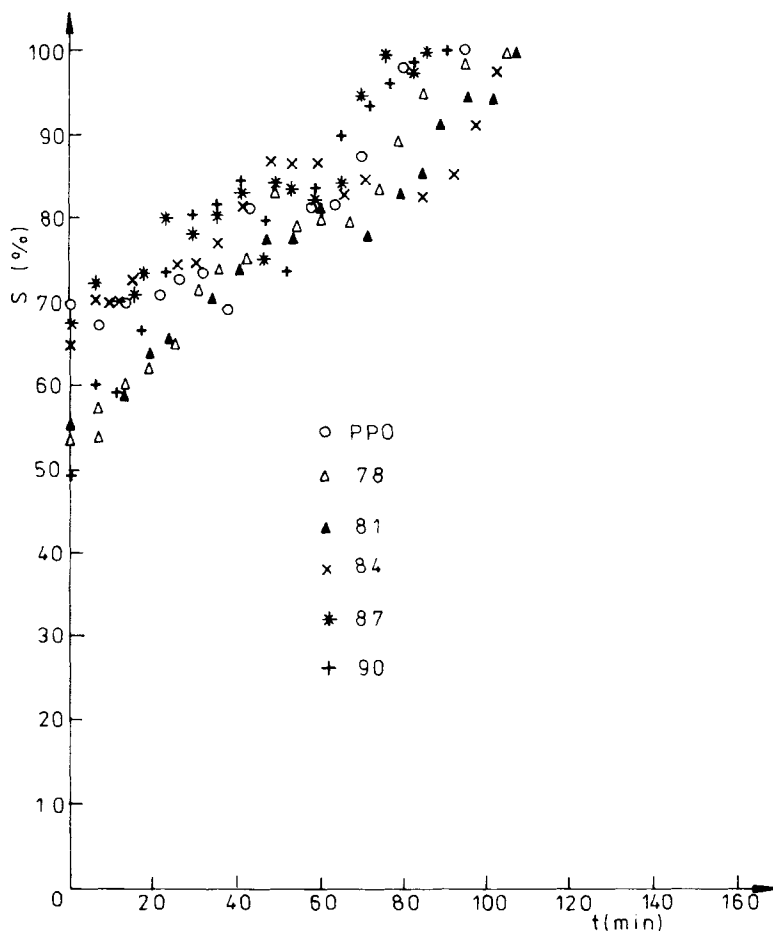
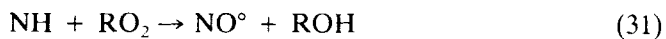


FIGURE 9 The dependence of free radical concentration, in relative units, on the degradation time, for bulk samples degraded in the spectrometer's cavity.

Supposing an exponential dependence of the average resonance amplitude on the degradation time, the reaction rate constant K_p has been estimated and given in Table II. The correlation coefficients, are high supporting this dependence.

The generation of nitroxyl radicals has been ascribed to the reaction of the stabilizer with peroxy radicals although stabilizer oxidation processes may also occur;



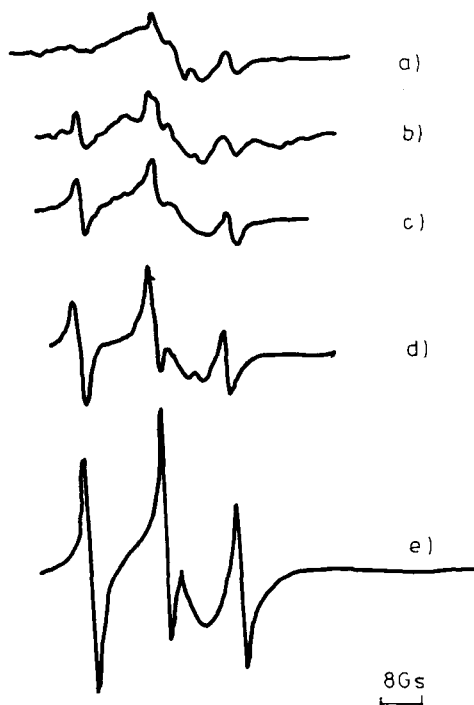


FIGURE 10 The resonance line of trans-polyentenamer stabilized with amine based antioxidants, thermally degraded in air, at 220°C, as a function of degradation time t_d : a) $t_d = 20$ minutes; b) $t_d = 30$ minutes; c) $t_d = 40$ minutes; d) $t_d = 50$ minutes; e) $t_d = 100$ minutes.



The concentration of nitroxyl radicals is enhanced with degradation time in the first stages of polymer degradation. After 200 minutes of degradation at 220°C the stabilizer is exhausted and the triplet resonance line disappears slowly. At large degradation times a single resonance line, with the above mentioned features, is noticed.

The absence of nitroxyl radical resonance lines in bulk samples may be an effect of the nonhomogeneous thermo-oxidative degradation of trans-polyentenamer; the surface of the samples is subjected to a thermal degradation in excess oxygen whereas the core is mainly degraded thermally. Under these circumstances one of the most important source of peroxy radicals is the thermal decomposition of hydroperoxides, which obeys an Arrhenius like dependence on temperature. The experimental data on bulk on samples subjected to thermal degradation in air support this description as the correlation coefficients for the Arrhenius like dependence of free radical concentration on temperature are high and the values of the activation energies E_A^S (given in Table I) are close to the values estimated for hydroperoxide thermally activated decomposition in similar polymers. The pres-

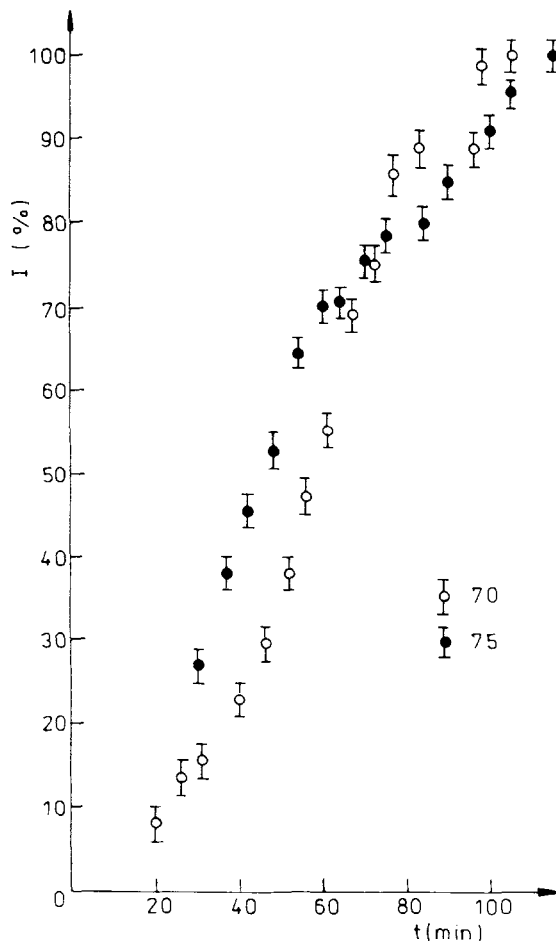


FIGURE 11 The dependence of the average resonance line amplitude for nitroxyl radicals, on the degradation time.

ence of hydroperoxides in thermally degraded stabilized and unstabilized trans-polybutadiene has been confirmed by IR spectroscopy.

4. CONCLUSIONS

E.s.r. investigations of the thermal degradation in air, in stabilized and unstabilized samples of trans-polybutadiene, are reported. The activation energy E_A^H estimated supposing an Arrhenius like dependence of the peak to peak line depends on the stabilizer type and concentration. The lowest values of E_A^H have been observed in the case of samples stabilized with the antioxidants 2246 and Santoflex IP, which contribute satisfactorily to maintaining the physico/chemical characteristics of trans-polybutadiene rubbers.

From the temperature dependence of free radical concentration, the activation

energy E_A^S for overall free radical production. has been estimated. Usually E_A^S has been found to correspond to the activation energy of the thermal decomposition of hydroperoxides, suggesting that this is the main source of peroxy radicals. However, the very low value noticed in the case of the sample stabilized with Topanol may be related to stabilizer volatilization, in agreement with the data reported by M. Dimonie *et al.*⁵ Once again, lower values of the activation energy E_A^S has been noticed for the best antioxidants and depends on the antioxidant concentration.

The time evolution of the peak to peak line width, may be described by an exponential equation characterized by the rate constant K , which is higher for the most efficient stabilizers. From the time dependence of free radical concentration, the reaction order was found to be close to unity and the reaction rate constant has been estimated. In the case of thin films of trans-polyentenamer, stabilized with amine based antioxidants, the presence of nitroxyl radicals has been noticed.

These data reflect the high sensitivity of e.s.r. spectroscopy in the investigation of degradation processes in stabilized and unstabilized polymers.

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