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Inhibiting Action of Polymeric Hindered Amines on the Oxidation of 1,4-Polybutadiene by Singlet Oxygen*

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ABSTRACT

The oxidation of polybutadiene (PB) by singlet oxygen ($^1O_2$) in the presence of polymeric hindered amine light stabilizers was studied by the determination of viscosity, ESR, IR and GPC. The results show that polymeric hindered amine light stabilizers (HALS) can inhibit the oxidation of PB by $^1O_2$ and the effectiveness is in the order Chimasorb 944 > PDS > Tinuvin 770 > Tinuvin 622. The quenching rate constants of $^1O_2$ by HALS were determined by Monroe's method.[17] *They are 944($3{\cdot}2 \times 10^6$), PDS($8{\cdot}2 \times 10^5$), 622 and 770 $\times 10^5$ $M^{-1}s^{-1}$.*

ESR shows that 944 and PDS can produce stable nitroxy free radicals under the experimental conditions while 622 does not. This is associated with the steric effect of 622. GPC also shows that PDS possesses a grafting–crosslinking effect on PB. A mechanism of grafting–crosslinking has been suggested.

INTRODUCTION

It is well known that singlet oxygen ($^1O_2$) is an active form of oxygen in a higher energy state. It can react with many organic compounds and polymers.[1–3] $^1O_2$ can be prepared by microwave discharge, chemical reaction and energy transfer from excited molecules to oxygen molecules.[1–3] The mechanism of oxidation by $^1O_2$ involves attack at double bonds with the formation of allylic hydroperoxide groups with a shift of the

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double bond.[1-8] It is known that $^1O_2$ can be produced in solution by energy transfer from an excited molecule of an organic dye such as methylene blue, rose bengal, eosin or rhodamine to a molecule of oxygen, the polymer being oxidized by this $^1O_2$ in solution.[1-8]

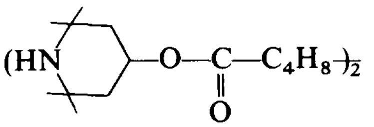
Hindered amines are among the most effective inhibitors of the photo-oxidation of polymers and some of them are effective quenchers of $^1O_2$.[9-13] Therefore, a study of the inhibition of $^1O_2$ oxidation by HALS is very important both practically and theoretically. It has been reported that low molecular weight hindered amines can inhibit the $^1O_2$ oxidation of PB,[8] but it has not yet been reported for polymeric HALS. This paper is devoted to a report of a study of the $^1O_2$ oxidation of PB in the presence of three commercial polymeric HALS.

EXPERIMENTAL

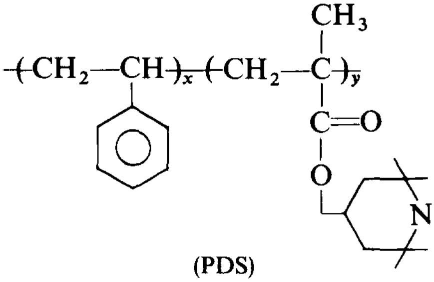
Materials and reagents

1,4-polybutadiene was produced by Shenli rubber factory (Peking, China): gel content, 0·1%; molecular weight, 110 000. Rhodamine, benzene, methanol and chloroform were produced by Beijing chemical factory and AR. Rubrene by the Aldrich chemical company.

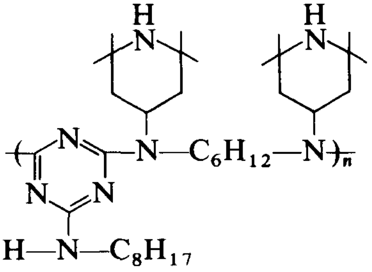
The structures of the hindered amines are as follows:



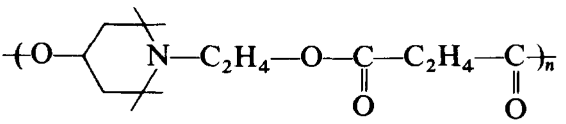
Tinuvin-770
(770)



(PDS)



(944)
Chimasorb-944



Tinuvin-622
(622)

Sensitized photo-oxidation in solution

The sensitized photo-oxidation of PB was carried out in a mixture of methanol and benzene (v/v = 1:9), containing PB($1{\cdot}9 \times 10^{-2}$M), rhodamine-B ($0{\cdot}63 \times 10^{-3}$M) and hindered amine ($2$–$6 \times 10^{-3}$ N). The irradiation of the solution was as described in the literature[14] and the change of viscosity of the solution was determined using Rabek's viscometer.[15] A 1000 W tungsten lamp was used as light source, the distance between lamp and sample being 28 cm, the intensity of light 1 mW/CM^2 and the reaction temperature 30°C.

The determination of the UV-spectrum was carried out on a Unicam-1750 UV-spectrometer, the change in the rhodamine-B being determined by the change in the peak at 546 nm.

The determination of ESR was carried out at 22°C, as described in the literature.[14]

The quenching rate constant of $^1O_2$ by HALS was determined using Monroe's method.[17] Chloroform was used as solvent. A 1000 W tungsten lamp was used as light source, the distance between lamp and cell being 42 cm, the intensity of light 0·5 mW/CM^2 at a temperature of 20°C. A 1 cm quartz cell was used both as reactor and determination cell. The change in concentration of rubrene was determined by the change of the peak at 446 nm. The irradiation time was 3 min for every sample.

The GPC determination was carried out on a LC-10 liquid chromatograph with tetrahydrofuran as solvent and mobile phase. The column was model-80, 500 × 8 mm (packed with polystyrene gel), the flow rate of THF being 1·5 ml/min.

RESULTS AND DISCUSSION

It has been reported that PB can be oxidized in solution by $^1O_2$ formed from dyes.[8,14] Rhodamine is the best sensitizer for $^1O_2$ oxidation because it is able to form $^1O_2$ without side effects.[7,8] The viscosity changes of polybutadiene solutions during irradiation by visible light are shown in Figs 1–5. Figure 1 shows that in the presence of rhodamine a rapid change of solution viscosity occurs, while without rhodamine there is no change during irradiation by visible light. In the presence of hindered amine, the $^1O_2$ oxidation of polybutadiene solution was inhibited. Obviously, the inhibiting effect of hindered amine for the $^1O_2$ oxidation at equal mole concentrations is in the order $944 > \text{PDS} > 770 > 622$.

The inhibiting effect of $^1O_2$ oxidation by HALS at equal piperidine functional group concentrations is shown in Fig. 2. The effect is in the order $944 \approx \text{PDS} > 770 \approx 622$. Because there are two piperidine groups in one

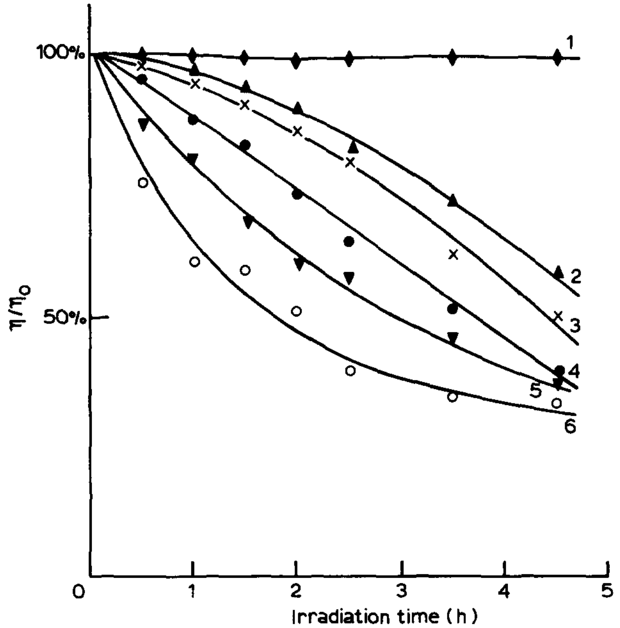


Fig. 1. The inhibiting effect of hindered amine on the $^1O_2$ oxidation of PB ([HA] = 2×10^{-3} M). 1, PB; 2, PB-Rh-944; 3, PB-Rh-PDS; 4, PB-Rh-770; 5, PB-Rh-622; 6, PB-Rh.

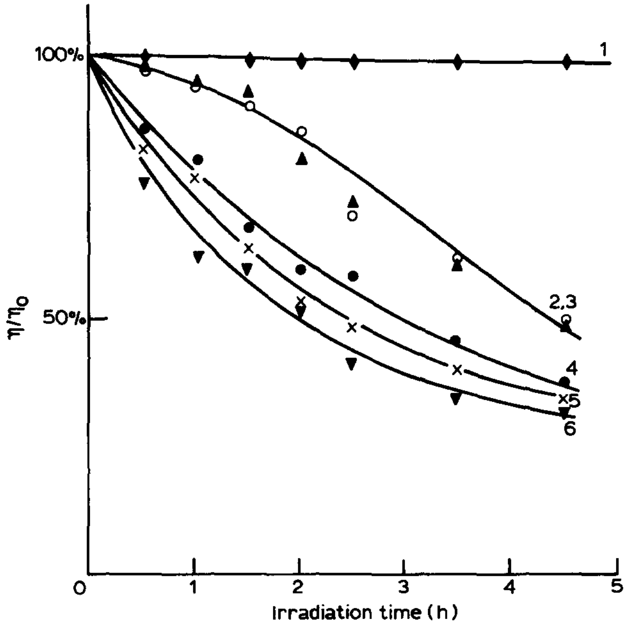


Fig. 2. The inhibiting effect of hindered amine on the $^1O_2$ oxidation of PB ([HA] = 2×10^{-3} N). 1, PB; 2–3, PB-Rh-944 (PDS); 4, PB-Rh-622; 5, PB-Rh-770; 6, PB-Rh.

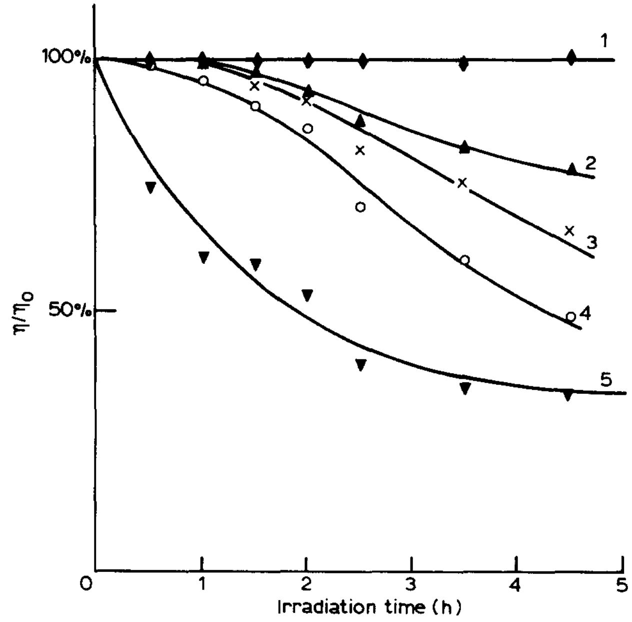


Fig. 3. The inhibiting effect of PDS on the $^1O_2$ oxidation of PB. 1, PB; 2, PB-Rh-PDS (6×10^{-3} N); 3, PB-Rh-PDS (4×10^{-3} N); 4, PB-Rh-PDS (2×10^{-3} N); 5-PB-Rh..

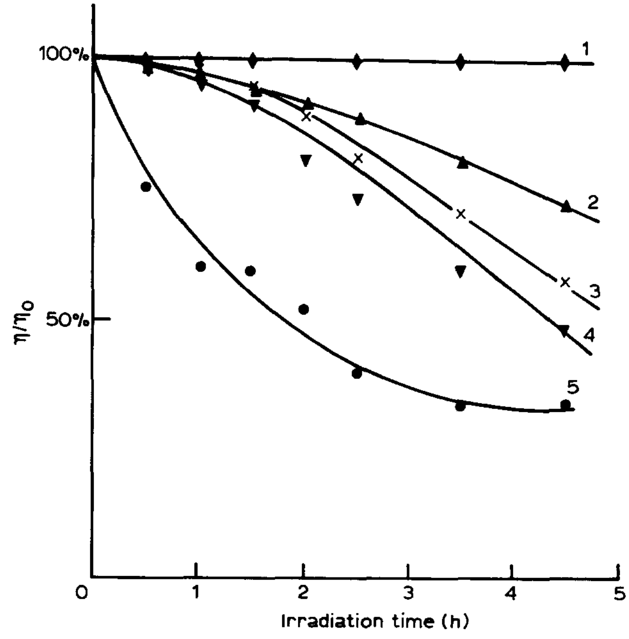


Fig. 4. The inhibiting effect of 944 on the $^1O_2$ oxidation of PB. 1, PB; 2, PB-Rh-944 (6×10^{-3} N); 3, PB-Rh-944 (4×10^{-3} N); 4, PB-Rh-944 (2×10^{-3} N); 5-PB-Rh..

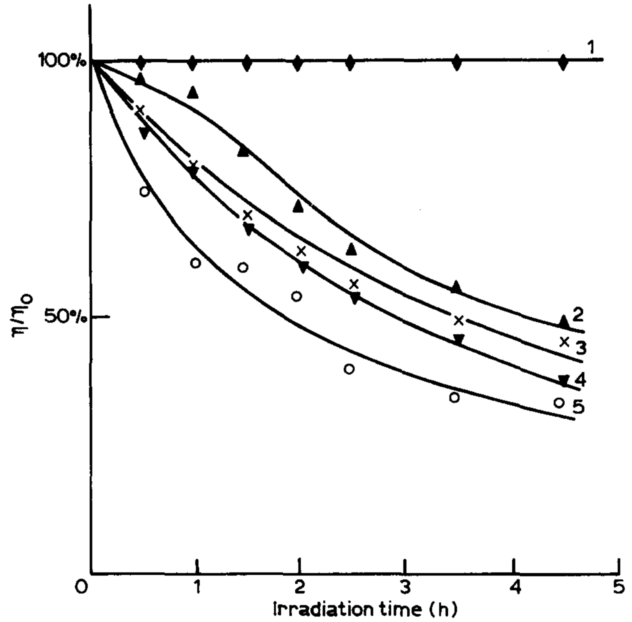


Fig. 5. The inhibiting effect of 622 on the $^1O_2$ oxidation of PB. 1, PB; 2, PB-RH-622 (6×10^{-3} N); 3, PB-Rh-622 (4×10^{-3} N); 4, PB-Rh-622 (2×10^{-3} N); 5-PB-Rh..

molecular segment of 944 while PDS has only one, the effectiveness of 944 is greater than that of PDS for equal molar concentration(M), but it is the same for equal piperidine functional group concentrations(N). It has also been reported that bis(hindered piperidines) are better than mono-hindered piperidine.[8]

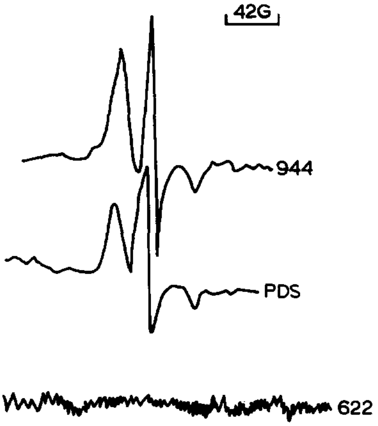


Fig. 6. The ESR signal from the sensitized photo-oxidation in solution of rhodamine–HALS–PB–benzene–methanol (W-lamp, 5 h).

The inhibiting effects of $^1O_2$ oxidation of PB by HALS at different concentrations are shown in Figs 3–5, from which it can be seen that the inhibiting effect increases with increasing concentration of HALS, 622 being less effective.

The ESR signals obtained during oxidation of solutions of the system rhodamine–HALS–PB are shown in Fig. 6. Obviously, 944 and PDS can form stable nitroxy free radicals while 622 cannot. It is very interesting that a very strong ESR signal can be observed in the solid state system rhodamine–HALS–PB under ambient visible light for 3 months as shown in Fig. 7. This result shows that the $^1O_2$ can be formed by energy transfer from the excited molecule of rhodamine to the oxygen molecule in air and the stable nitroxy free radicals of 944 and PDS can be formed by $^1O_2$ oxidation.

It has been reported that the quenching of $^1O_2$ by low molecular HALS is

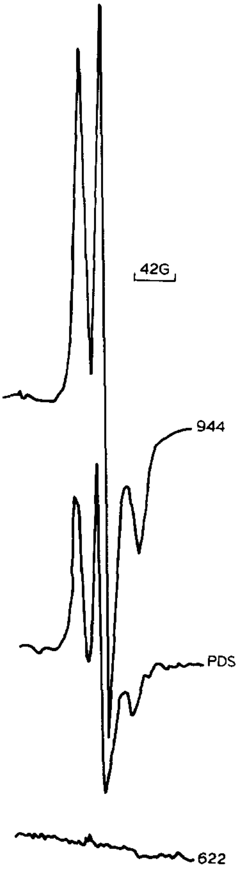
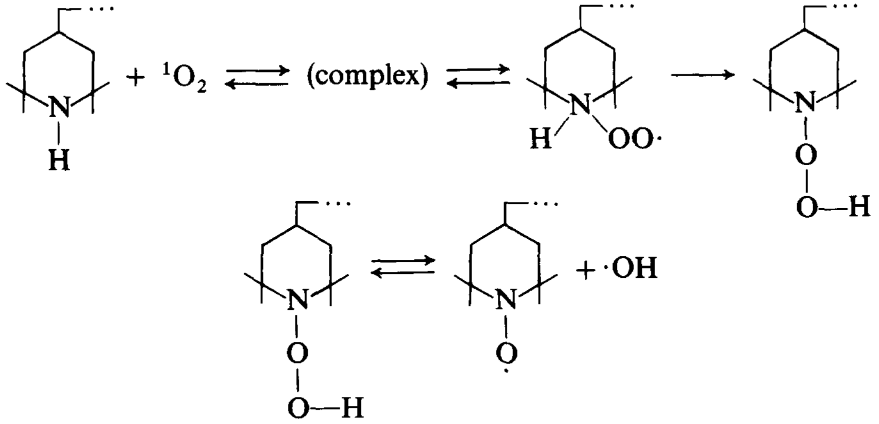


Fig. 7. The ESR signal from the system rhodamine–HALS–PB in the solid state (under ambient visible light for 3 months).

a chemical process and involves the processes of complex formation and oxidation:[8]



Therefore, quenching of $^1O_2$ by polymeric HALS and the formation of stable nitroxy free radicals should occur in the same way. Obviously, the processes of complex formation and the formation of stable nitroxy free radicals can consume or deactivate $^1O_2$. Therefore, the polymeric HALS can protect PB against oxidation by singlet oxygen. The 622 cannot complex with $^1O_2$ owing to its steric hindered effect.[9,16] so cannot be oxidized by $^1O_2$ and cannot form stable nitroxy free radical. For this reason the inhibiting effect of $^1O_2$ oxidation by 622 is poor.

The change in absorption of rhodamine solution at 546 nm is shown in Fig. 8. It can be seen that PDS and 944 effectively inhibit discoloration, and 622 is less effective. Although the mechanism of discoloration of rhodamine is not yet well understood, self-sensitizing $^1O_2$ oxidation of rhodamine may be the most important reason, as with rubrene.[16,17] The inhibition of discoloration of rhodamine by PDS and 944 shows that the $^1O_2$ can be quenched by PDS and 944, which is similar to the results presented previously.

The deactivation of $^1O_2$ by HALS can be illustrated by determination of the quenching rate constants of $^1O_2$ by HALS. Monroe's method[17] was used to determine the quenching rate constants of $^1O_2$ by HALS, $K_q^{^1O_2}$, which are as follows:

$$944(3{\cdot}2 \times 10^{6}),\ \mathrm{PDS}(8{\cdot}2 \times 10^{5}),\ 622\ \text{and}\ 770(2 \times 10^{5})\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$$

Obviously, the effectiveness is in the order $944 > \mathrm{PDS} > 622$. This is consistent with the results in Fig. 1. Because this method A can only be used to determine values up to about $2 \times 10^5\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, it is difficult to say whether 622 or 770 is the better.

When equal piperidine functional group concentrations are used, the

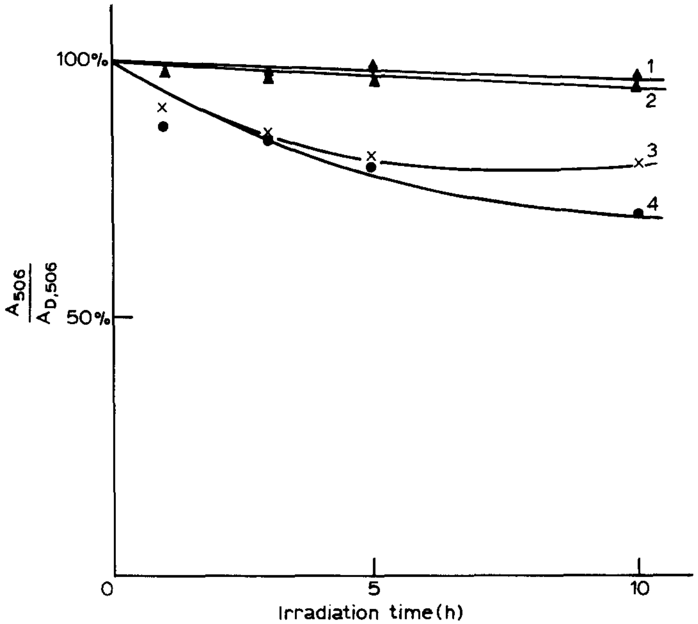


Fig. 8. Change of relative absorption of rhodamine solution at 546 nm. 1, PDS–Rhodamine; 2, 944–Rhodamine; 3, 622–Rhodamine; 4, Rhodamine.

inhibiting effects of PDS and 944 for self-sensitizing the $^1O_2$ oxidation of rubrene are the same, as shown in Table 1. This is consistent with the results in Fig. 2.

The change of molecular weight distribution of PB is shown in Fig. 9. It can be seen that after irradiation, the average molecular weight has decreased and a shoulder has been formed. The largest molecular weight of PB increased from 110 000 to 200 000. This phenomenon of increasing molecular weight with increasing irradiation time may be related to the effect of grafting–crosslinking of PDS,[18,19] which contains about 20 piperidine groups in one molecule of PDS.[18]

PB—OOH can be formed by $^1O_2$ oxidation of PB, and PB macro-free radical can be formed by decomposition of PB—OHH using heat or light. It

TABLE 1

The Inhibiting Effect of Self Sensitizing Oxidation of Rubrene by PDS and 944 at Equal Piperidine Function Groups

	A_{446}, *before irradiation*	A_{446}, *after 3 min*	*Retention of rubrene*
Rubrene-10^{-4}M, 944-10^{-2}N	1·66	0·55	34%
Rubrene-10^{-4}M, PDS-10^{-2}N	1·62	0·56	34·6%

From this Table, it can be seen that the inhibiting effect of PDS and 944 is the same.

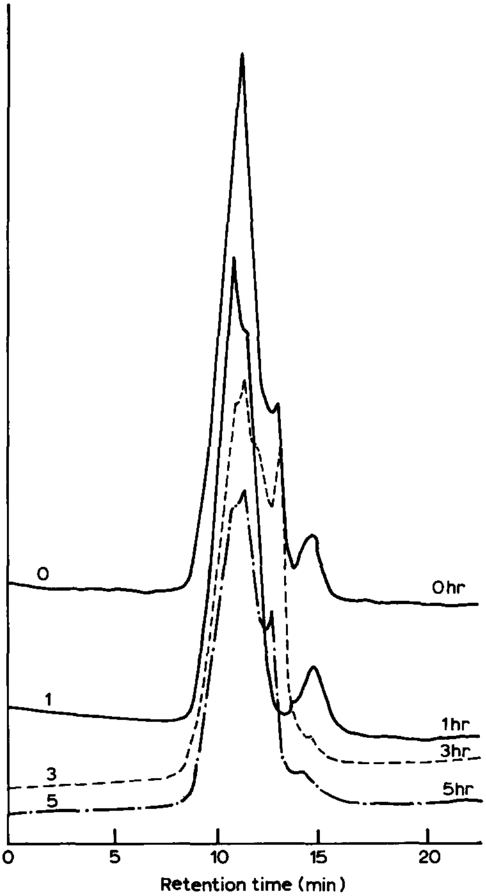
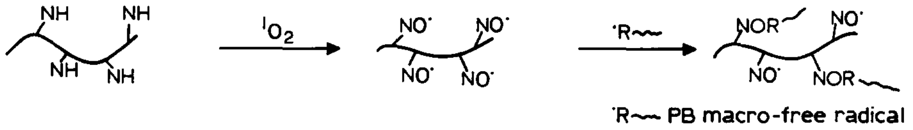


Fig. 9. GPC curves of PB during $^1O_2$ oxidation in presence of PDS.

has been shown that PDS can form PDSNO$^{\cdot}$ in these experimental conditions. Therefore, the grafting reaction can be occurring when PDSNO$^{\cdot}$ combines with PB. When one PDSNO$^{\cdot}$ combines with more than two PB macro-free radicals, (R~~~) crosslinking of PB has occurred and the molecular weight increases:



Because 622 cannot produce stable nitroxy free radicals, no crosslinking of PB is observed under these experimental conditions. The grafting–crosslinking effect of 944 is not so serious as of PDS, because there are less piperidine groups in one molecular chain of 944 4–6 piperidine groups exist in one molecular chain of 944).

CONCLUSIONS

(1) Viscosity, ESR and UV results, and determination of $K_q^{^1O_2}$ show that polymeric HALS 944 or PDS are efficient deactivators of $^1O_2$ and protect *cis*-1,4-polybutadiene against oxidation by singlet oxygen. 622 is less effective for the deactivation of $^1O_2$. This may be related to the steric hindered effect of 622.

(2) It has been observed that there is a crosslinking effect in the sensitized photo-oxidation of PB solution when PDS is added. The mechanism of this cross-linking may be related to the grafting of PDSNO$^\cdot$ onto PB.

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