

## SURFACE MODIFICATION OF POLYMERS—II. PHOTO-OXIDATION OF SBS CONTAINING ANTHRACENE AND GRAFTING INITIATED BY PHOTO-GENERATED HYDROPEROXIDES

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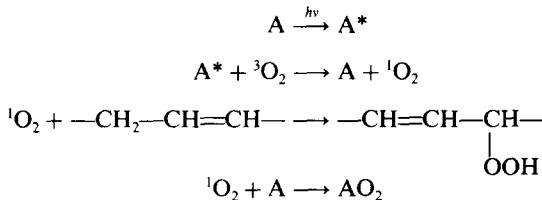
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**Abstract**—Diffusion of anthracene at room temperature from a methanolic solution into a styrene–butadiene–styrene block copolymer (SBS) follows Fick's law with a diffusion coefficient of  $3.4 \times 10^{-12} \text{ m}^2 \text{ sec}^{-1}$ . The equilibrium concentration of anthracene in SBS is 2.8 times the solution concentration. Irradiation around 350 nm of SBS films containing anthracene results in the sensitized production of singlet oxygen that competitively reacts with anthracene to give the 9,10-endoperoxide and with double bonds of SBS to form polymeric hydroperoxides. Quantum yields of both processes have been measured: they depend on anthracene concentration and are of the order of  $10^{-2}$  and 1 respectively. Their ratio increases linearly with anthracene concentration. Thermal decomposition of polymeric hydroperoxides in the presence of an aqueous solution of methacrylic acid initiates the grafting. This actually occurs in the film and not at the surface because diffusion of the monomer in SBS is faster than the grafting. Nevertheless contact angle measurements reveal surface modifications due to hydroperoxidation and subsequent grafting.

### INTRODUCTION

In a recent paper [1] we have shown that grafting of methacrylic acid from an aqueous solution onto a styrene–butadiene–styrene block copolymer (SBS) can be initiated by thermal decomposition of photo-generated hydroperoxides. These were obtained by reaction of the polymer with singlet oxygen, the production of which can be photo-sensitized by anthracene. The sensitizer itself reacts with singlet oxygen and is progressively converted to the 9,10-endoperoxide. The sequence of reactions is the following:



In our previous work, films of SBS containing anthracene were obtained by casting from solutions of both the polymer and the sensitizer at the appropriate concentration. In the present paper, we describe and discuss a convenient and more general technique (in principle applicable to samples of any shape and thickness) to introduce anthracene into SBS. It consists in sorption of the additive by the polymer from a methanolic solution. We have also studied more quantitatively the decay of anthracene and the production of hydroperoxides on irradiation. The kinetics of grafting is found independent of the way anthracene is introduced in the film but we have obtained further information by studying the diffu-

sion of the monomer into the film and the influence of grafting on contact angles.

### EXPERIMENTAL PROCEDURES

The polymer used is a SBS block copolymer containing 28 wt% styrene, supplied by Shell as Cariflex TR 1102. Films, about 0.01–0.03 cm thick, are obtained by compression of polymer crumbs at 160° and a pressure of 8 GPa. Anthracene is introduced into the films by sorption from methanolic solutions of various concentrations. The additive concentration in the films is measured by spectrophotometry at 374 nm (molar decadic absorption coefficient 8900 l mol<sup>-1</sup> cm<sup>-1</sup> [2]). Films are irradiated at a distance of 4 cm from a Philips TL 20 lamp that is a polychromatic light source with an emission spectrum extending from 300 to 420 nm, a maximum of intensity at 350 nm and a half-intensity bandwidth of about 35 nm. The total incident intensity at the surface of the films is measured with the benzophenone–benzhydrol actinometer [3] and found to be  $1.34 \times 10^{-5} \text{ E m}^{-2} \text{ sec}^{-1}$ . The decay of anthracene on irradiation is monitored either by u.v. absorption at 374 nm or by fluorescence emission at 423 nm (excitation at 365 nm). The concentration of hydroperoxide produced is measured by i.r. spectroscopy at 3470 cm<sup>-1</sup> using a value of 701 mol<sup>-1</sup> cm<sup>-1</sup> [4] for the absorption coefficient. Ultraviolet and i.r. spectra are recorded with a Perkin–Elmer Lambda 3A and with a Perkin–Elmer mod. 177 spectrophotometer respectively. Multiple attenuated total reflection spectra are obtained with a Wilks mod. 9 ATR unit equipped with a KRS-5 crystal (25 reflections). The fluorescence spectrophotometer is a Perkin–Elmer MPF 2A. Grafting is performed by dipping hydroperoxidized SBS films into aqueous solutions of methacrylic acid at 100° for 1–10 min. After grafting they are washed for 10 min in water to remove unreacted monomer and dried at room temperature in air for one night. The concentration of methacrylic acid grafted is measured by i.r. spectroscopy at 1710 cm<sup>-1</sup>

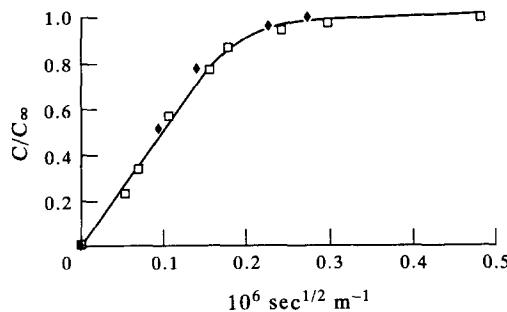


Fig. 1. Fickian diffusion isotherm of anthracene (from a methanolic solution) into SBS ( $C$  and  $C_\infty$  = conc. in the film at time  $t$  and at equilibrium respectively,  $x$  = film thickness).  $\blacklozenge$ ,  $x = 1.8 \times 10^{-4}$  m, solution conc.  $10^{-3}$  mol  $l^{-1}$ ,  $\blacksquare$ ,  $x = 1.25 \times 10^{-4}$  m, solution conc.  $2 \times 10^{-3}$  mol  $l^{-1}$ .

using a value of  $600 l \text{ mol}^{-1} \text{ cm}^{-1}$  for the absorption coefficient [5].

## RESULTS AND DISCUSSION

### 1. Sorption and desorption of anthracene in SBS

When SBS films 0.01–0.03 cm thick are dipped in methanolic solutions of anthracene the concentration of aromatic hydrocarbon in the film increases with time until it reaches an equilibrium value after about 20 min. Figure 1 shows a typical isotherm corresponding to Fick's second law of diffusion [6]. This is observed when the rate of diffusion of permeant molecules is much less than polymer segment mobility [7]. In the investigated range of anthracene concentration (about  $1$ – $4 \times 10^{-3}$  mol  $l^{-1}$ ) the diffusion coefficient of anthracene is independent of concentration and can be calculated from Fig. 1 using the relation [6]:

$$D = \frac{0.049x^2}{t_{0.5}}$$

where  $x$  is the film thickness and  $t_{0.5}$  the time required to reach half the equilibrium concentration of anthracene in the film.

The value found,  $3.4 \times 10^{-12} \text{ m}^2 \text{ sec}^{-1}$ , is typical for polymers in the rubbery state well above  $T_g$ . It indicates that sorption of anthracene occurs only in the polybutadiene phase of SBS since the diffusion coefficient in the polystyrene phase is expected to be at least eight orders of magnitude smaller [7]. Moreover, it has been checked that in the experimental conditions used, no anthracene can be detected in a polystyrene film. The equilibrium concentration of

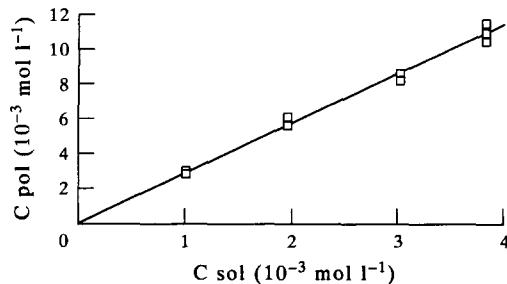


Fig. 2. Equilibrium concentration of anthracene in SBS ( $C_{\text{pol}}$ ) as a function of anthracene concentration in methanol ( $C_{\text{sol}}$ ).

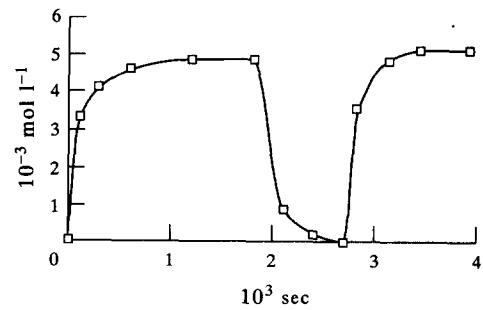


Fig. 3. Sorption and desorption of anthracene in the system SBS-methanol as a function of time.

anthracene in SBS is 2.8 times the concentration of anthracene in the methanolic solution, as shown on Fig. 2. Such a simple type of sorption law arises when polymer-permeant interactions are weak. It also indicates that anthracene molecules are homogeneously distributed in the polybutadiene phase of SBS because sorption in some specific sites or clustering would result in more complex sorption isotherms [7]. Sorption–desorption cycles are perfectly reversible as shown on Fig. 3.

### 2. Photo-oxidation of SBS containing anthracene

When SBS films containing anthracene are irradiated around 350 nm polymeric hydroperoxides are formed, as evidenced by the growth of a new absorption band at  $3470 \text{ cm}^{-1}$  in the i.r. spectrum. Simultaneously anthracene is progressively converted to the 9,10-endoperoxide the absorption of which is shifted to shorter wavelengths with respect to the parent hydrocarbon and does not interfere with a quantitative analysis of anthracene decay at 374 nm. In our previous paper [1] we measured about 150 polymeric hydroperoxides formed per anthracene molecule converted to endoperoxide. This results from the competition between anthracene and double bonds in the polybutadiene phase of SBS to react with singlet oxygen. As we shall see that competition is dependent on anthracene concentration in SBS.

(a) *Anthracene conversion to 9,10-endoperoxide.* The decay of anthracene by oxidation can be monitored from the decrease of its typical absorption in the near u.v. It follows a first order law (Fig. 4) that

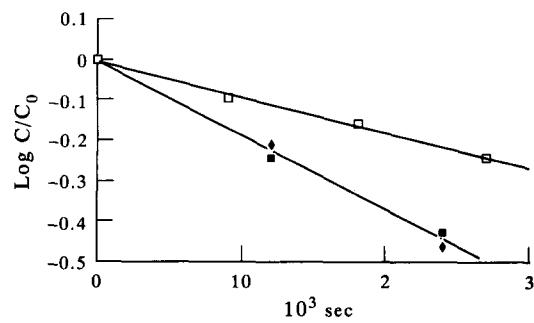


Fig. 4. Decay of anthracene in SBS as a function of irradiation time in air. Initial anthracene concentration  $C_0$ :  $\blacksquare$ ,  $6.5 \times 10^{-4}$  mol  $l^{-1}$ ;  $\blacksquare$ ,  $10^{-2}$  mol  $l^{-1}$  (absorption measurements at 374 nm);  $\blacklozenge$ ,  $10^{-2}$  mol  $l^{-1}$  (fluorescence measurements at 423 nm).

Table 1. Quantum yields of anthracene conversion to endoperoxide and of polymeric hydroperoxide production (incident intensity:  $1.34 \times 10^{-5} \text{ E m}^{-2} \text{ sec}^{-1}$ )

Anth. conc. $\times 10^3 \text{ mol l}^{-1}$	Film thickness $\times 10^4 \text{ m}$	Rate of anth. decay $\times 10^8 \text{ mol l}^{-1} \text{ sec}^{-1}$	Intensity absorbed $\times 10^7 \text{ E m}^{-2} \text{ sec}^{-1}$	Q. yield anth. decay $\times 10^2 \text{ mol E}^{-1}$	$r^*$	Q. yield hydroperox. prod. $\text{mol E}^{-1}$
0.449	0.8	9.33	5.82	1.28	285	3.65
0.655	1.2	14.6	12.4	1.41	182	2.56
3.03	1.2	105	47.7	2.56	72	1.84
3.12	1.1	95.0	45.8	2.29	89	2.04
5.84	1.0	187	67.5	2.78	52	1.45
6.05	1.3	223	81.3	3.57	38	1.36
8.67	1.3	347	97.8	4.59	26	1.19
10.7	1.2	385	103	4.47	27	1.20
11.5	1.2	437	106	4.93	26	1.28

\* $r$ , Polymeric hydroperoxide to endoperoxide ratio.

can be easily explained. Indeed, the rate of any photochemical reaction is proportional to the quantum yield of the reaction and to the absorbed intensity that is a function of the incident intensity and of the absorbance of the sample, as shown below. In the present case, the absorbance is proportional to anthracene concentration and to the thickness of the sample. If the absorbance is small the rate of decay should be approximately proportional to the anthracene concentration.

$$-\frac{dC}{dt} = \Phi I_a = \Phi I_0 (1 - 10^{-A}) = \Phi I_0 (1 - e^{-2.303A})$$

if  $A = \epsilon x C$  is small:

$$-\frac{dC}{dt} \approx \Phi I_0 2.303 \epsilon x C \approx k C$$

where  $C$  = anthracene concentration,  $\Phi$  = quantum yield of anthracene decay,  $I_a$  = absorbed intensity,  $I_0$  = incident intensity,  $A$  = absorbance, 2.303 = conversion factor of decimal to neperian log,  $\epsilon$  = molar decadic absorption coefficient,  $x$  = thickness of sample.

Figure 4 shows that the slope of the logarithmic decay increases with anthracene concentration: the quantum yield of anthracene conversion is thus not constant. Knowing the incident intensity (determined by actinometry to be  $1.34 \times 10^{-5} \text{ E m}^{-2} \text{ sec}^{-1}$ ), it can be calculated in each case from the rate of decay, provided the absorbance of the sample is measured. A problem arises because the light source is not monochromatic. It has been solved by dividing the emission spectrum of the light source (plotted with an abscissa linear in wavenumber from 2.4 to  $3.3 \times 10^4 \text{ cm}^{-1}$ ) in six zones of  $1500 \text{ cm}^{-1}$  each. The fraction of the incident intensity corresponding to each zone is estimated from the ratio of its area to the total area of the emission spectrum. Taking an average value for the absorbance of anthracene in each zone, the absorbed intensity in each zone is calculated and, by summing up, the total intensity absorbed by the sample is obtained. The initial rate of decay of anthracene divided by the total intensity initially absorbed gives the quantum yield of anthracene reaction with singlet oxygen. The experimental data are collected in Table 1.

The experimental values indicate that the quantum yield of anthracene conversion to 9,10-endoperoxide increases with anthracene concentration. This is due

to the increased probability for singlet oxygen to react with anthracene as its concentration increases. Because of the competition to react with the same reagent, singlet oxygen, the quantum yield of conversion of double bonds to hydroperoxides decreases as anthracene concentration increases.

(b) *Production of polymeric hydroperoxides.* Polymeric hydroperoxides result from the reaction of singlet oxygen with double bonds in the polybutadiene phase of SBS. Until their concentration is about  $0.1 \text{ mol l}^{-1}$  (corresponding to 40–60% conversion of anthracene to endoperoxide) no other oxidation products can be detected by i.r. spectroscopy. Figure 5 shows that the polymeric hydroperoxide to anthracene endoperoxide ratio (as measured from the decay of anthracene) decreases as the initial anthracene concentration increases. From the lowest to the highest concentration used it drops from about 285 to 25. This results from the increasing probability for singlet oxygen to react with anthracene to the detriment of double bonds in SBS, the concentration of which remains constant. Quantum yields of hydroperoxide production can be calculated from the rate of increase of their absorbance at  $3470 \text{ cm}^{-1}$ . We have used for the absorption coefficient of polymeric hydroperoxides a value of  $70 \text{ l mol}^{-1} \text{ cm}^{-1}$  quoted in the literature and obtained by extrapolation of the absorption coefficient of t-butyl hydroperoxide to infinite concentration to take into account hydrogen-bonding [4]. This brings up quantum yield values  $> 1$ , as shown in Table 1, that are unexpected if polymeric hydroperoxides are formed exclusively by reaction with singlet oxygen. A trivial explanation would be to consider the value of the absorption coefficient as

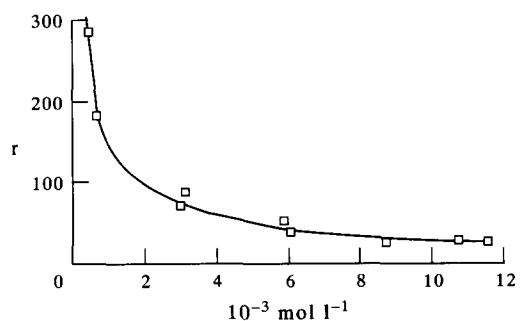


Fig. 5. Polymeric hydroperoxide to endoperoxide ratio ( $r$ ) as a function of anthracene concentration.

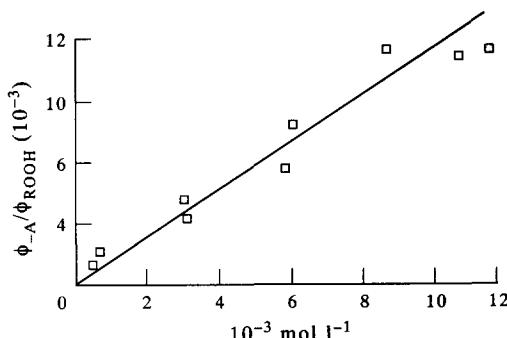


Fig. 6. Endoperoxide to polymeric hydroperoxide quantum yield ratio as a function of anthracene concentration.

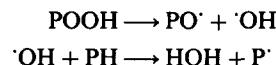
inaccurate. However, if photo-sensitized decomposition of hydroperoxides occurs to some extent free radicals are produced that can initiate a chain reaction. Indeed, it is well established by fluorescence quenching experiments that energy transfer occurs from aromatic hydrocarbons to hydroperoxides and that such a process can initiate the photo-oxidation of polymers [8, 9]. This proceeds, in air at atmospheric pressure, as a very short chain reaction involving no more than about 2 propagation steps [10]. Evidence for a free radical oxidation of SBS is obtained for long exposure times (see below). It is important to notice that the ratio of the quantum yield of anthracene decay (by conversion to endoperoxide) to the quantum yield of hydroperoxide production increases linearly with anthracene concentration (Fig. 6). This is to be expected since it is the ratio of the rates of reaction of singlet oxygen with anthracene and with double bonds in SBS: the former increases with anthracene concentration while the latter remains practically constant.

(c) *Formation of other oxidation products.* After about 40 min irradiation in our experimental conditions, when the concentration of polymeric hydroperoxides is about  $0.1 \text{ mol l}^{-1}$ , a new absorption band due to carbonyl compounds appears at  $1710 \text{ cm}^{-1}$  and progressively increases with irradiation time. This is evidence for a free radical oxidation initiated by photo-decomposition of hydroperoxides. However, it cannot be the consequence of direct absorption of light by hydroperoxides since, at that moment, the concentration of anthracene in the film is at least  $3 \times 10^{-4} \text{ mol l}^{-1}$  (depending on the initial concentration) resulting in an absorbance at 350 nm (maximum intensity of the light source) at least 1000 times larger than that of hydroperoxides. This can be checked from the absorption coefficients at that wavelength ( $9000 \text{ l mol}^{-1} \text{ cm}^{-1}$  for anthracene [2] and  $0.031 \text{ mol}^{-1} \text{ cm}^{-1}$  for t-butyl hydroperoxide [4]). Photo-decomposition of polymeric hydroperoxides is thus sensitized by energy transfer from anthracene. This supports the assumption that quantum yields larger than one for hydroperoxide production are due to a contribution of free radical oxidation. At high anthracene concentration, Table 1 shows that the quantum yield of hydroperoxide production tends to the expected value of one. This is because energy transfer from anthracene to hydroperoxides is less likely when 25 (instead of 285) such groups are

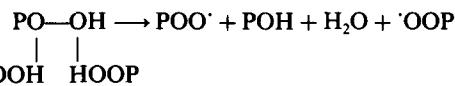
formed around each anthracene molecule before it is converted to endoperoxide. Indeed, Fig. 4 shows that, in those conditions, energy transfer is negligible since anthracene decay is the same whether measured by u.v. absorption and or by fluorescence emission.

### 3. Grafting of methacrylic acid initiated by photo-generated hydroperoxides

We have checked that grafting of methacrylic acid from an aqueous solution onto irradiated SBS is independent of the way anthracene is introduced provided it is homogeneously distributed. Indeed, the rate of grafting is the same whether anthracene has been introduced by sorption from a methanolic solution, as in the present work, or by casting from a solution containing both SBS and anthracene, as in our previous work. In our previous paper [1] we assumed that grafting occurs at the surface of hydroperoxidized SBS films. In this work we have observed that the monomer diffuses very quickly into SBS and that the equilibrium concentration, reached after dipping a non irradiated film for 1 min in a 10 wt% aqueous solution at 100°, is  $> 0.2 \text{ mol l}^{-1}$  i.e. more than the largest concentration of grafted monomer that we have measured. This means that diffusion is faster than grafting and that grafting actually occurs *in* the film and not at the surface. We have checked that the unreacted monomer diffuses out very quickly also and that it can no more be detected after washing for 10 min in water at room temperature. However, no change of the i.r. absorbance at  $1710 \text{ cm}^{-1}$  can be detected if a grafted film is washed in boiling water for 2 hr. This rules out the presence of homopolymer that could result from initiation by hydroxyl radicals. Most probably they very quickly abstract allylic hydrogen from the polymer in such a way that only macroradicals remain.



Another possibility could be that clustered hydroperoxides, formed around sites initially occupied by anthracene molecules, decompose by a concerted mechanism that is thermodynamically more favourable [11]. This would result in macroradicals exclusively.



Grafting in the film and not at the surface nevertheless results in modification of some surface properties of the material.

#### 4. Surface modification of SBS grafted with methacrylic acid

We have mentioned earlier [1] that films irradiated through a mask and subsequently grafted with methacrylic acid get coloured by crystal violet selectively on irradiated areas. This, however, is not a clear evidence for surface modification because the dye can diffuse into the sample. In the present work we have checked that, though methacrylic acid is grafted mainly in the bulk of the film, carboxylic acid groups can also be detected in i.r. reflection spectra

Table 2. Contact angles of water droplets at the surface of SBS films (unless otherwise stated both sides of the films are identical)

Hot pressed SBS	90°
After sorption of anthracene	88°
After hydroperoxidation	
dry (kept one night in air)	85°
wet (kept one night in water)	78°
After grafting of methacrylic acid	
dry (kept one night in air)	82°
wet (kept one night in water) front side	65°
	71°

of both dry and wet films. Contact angles of water droplets laid down at the surface of SBS films provide evidence for surface modification due to photo-oxidation and subsequent grafting. Values reproducible to plus or minus 2° are collected in Table 2.

The difference observed between front side (facing the light source during hydroperoxidation) and back side originates from the inhomogeneous absorption of light in the sample (the fraction of incident energy absorbed varies from about 4 to 80% in the anthracene concentration range investigated). This results in a concentration gradient in hydroperoxides that has no influence on contact angles. A concentration gradient of grafted methacrylic acid also probably arises but apparently without influence on contact angles measured on dry films. Quite clearly the surface of the grafted films is strongly influenced by the environment: after one night in water more polar groups come to the surface thanks to the mobility of the grafts. If shorter grafts are formed at the front side, because the hydroperoxide concentration is larger than at the back side, one could expect their influence on contact angles to be more pronounced, as observed. Presently, this is just an assumption and more experimental results are required before a valid explanation can be provided.

### CONCLUSION

Sorption of anthracene from a methanolic solution is a convenient way to introduce a photo-sensitizer in the polybutadiene phase of SBS selectively. In principle, the depth of penetration can be controlled and hence the thickness of the layer in which polymeric hydroperoxides will be generated by irradiation.

Photo-generated hydroperoxides can also be produced in well defined areas if irradiation is performed through a mask. Their localization in SBS films can thus be controlled in three dimensions. Simultaneously anthracene is converted to endoperoxide but this can be easily extracted together with eventual excess of photo-sensitizer since sorption and desorption of low molecular weight compounds is rather fast in SBS. Thermal decomposition of polymeric hydroperoxides, possibly catalysed at low temperature, initiates the grafting of methacrylic acid or other water soluble vinyl monomer without production of homopolymer. The technique of grafting described in the present paper is thus simple, convenient and versatile. It offers the possibility to control the localization and probably the length of the grafts. This makes quite interesting a study of their influence on surface properties of the polymer as a function of environmental conditions. Research along that line is in progress in our laboratory.

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