Polymer Bulletin 21, 341–345 (1989)

Polymer Bulletin

# Photooxidation of poly(styrenesulfonic acid) and its Sodium salt

**A. Cabello and I.F. Piérola***

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense,
E-28040 Madrid, Spain

## SUMMARY

The ultraviolet irradiation of poly(styrenesulfonic acid) (HPSS) and its sodium salt (NaPSS) in aqueous solution produces spectral changes in both cases . The total intensity of the fluorescence spectra decreases, the fluorescence ratio ($I_E/I_M$) increases and a red shiftted new band grows up at about 370 nm. In the absortion spectra, new bands appear at both sides of the non irradiated spectra. The rate of appearance or disappearance of any band is different for HPSS or NaPSS and depends on the presence of oxygen in the solution.

## INTRODUCTION

The photodegradation of polymers has been investigated for several groups in the past decades. The main reason for the interest in this research is the control of photodegradation of plastic materials. Photodegradation of polymers remains of paramount importance as polymeric material is used more and more frequently in conditions where such photodegradation could occur.

The degradation of polyolefins and polypropylene has been the subject of an important investigation for many years (1). Recent works on the photooxidation mechanisms and kinetics of polyolefins have been reviewed by Garton et al. (2).

The photodegradation of polystyrene in various solvents has been investigated by several authors (3,4).

In this paper, an investigation of the photodegradation of polystyrenesulfonic acid and its sodium salt in aqueous solution has been carried out. Photochemical reactions were initiated by irradiating the sample with UV light and they were studied by means of the UV absorption and the fluorescence spectra of the solutions.

## EXPERIMENTAL PART

NaPSS was synthesized by radical polymerization in

---

*To whom offprint requests should be sent nitrogen purged aqueous solution at 20 °C. The redoxinitiator employed was potassium persulfate($5\times10^{-3}$ M)-triethanolamine ($1\times10^{-2}$ M). The monomer (0.24 M) was from Dupont. The resulting polymer was purified by repeated precipitations in acetone and finally, it was vacuum dried. The total yield was about 20%. The molecular weight of this sample viscometrically determined in 0.1 M NaCl aqueous solution at 25.0 °C by making use of the MHS equation from ref. 5, was $3.8\times10^{5}$. NaPSS was converted to HPSS by dialysis of a $6\times10^{-3}$ M solution with HCl 0.25 N during forteen days.

The concentration of NaPSS and HPSS solutions was in any case $6\times10^{-3}$ M with O.D. less than 1 at 260 nm.

The polymer solutions were irradiated with the light from a low pressure mercury lamp, model Pen-Ray 11SC-1 from Ultraviolet Products. A filter model G-275 also from Ultraviolet Products was inserted between the cell and the lamp; this filter absorbs visible light while transmitting ultraviolet at 253.7 nm as the most intense line. The irradiations of solutions were carried out in a square quartz cuvet 1 cm thick in the presence of air at atmospheric pressure or in the presence of nitrogen.

UV absorption spectra were recorded with a Shimadzu UV 240 spectrophotometer. Fluorescence spectra were recorded using a Perkin Elmer LS-3 spectrofluorimeter.

## RESULTS AND DISCUSSION

Fluorescence spectra of NaPSS and HPSS in dilute solution shows (Fig. 1) monomer and excimer emission

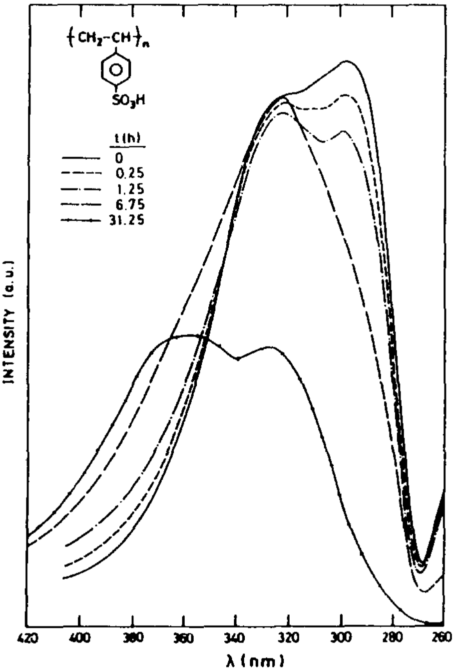

Figure 1.- Fluorescence spectra of HPSS aerated ($6\times10^{-3}$ M) aqueous solution after various irradiation times with λ = 253.7 nm.

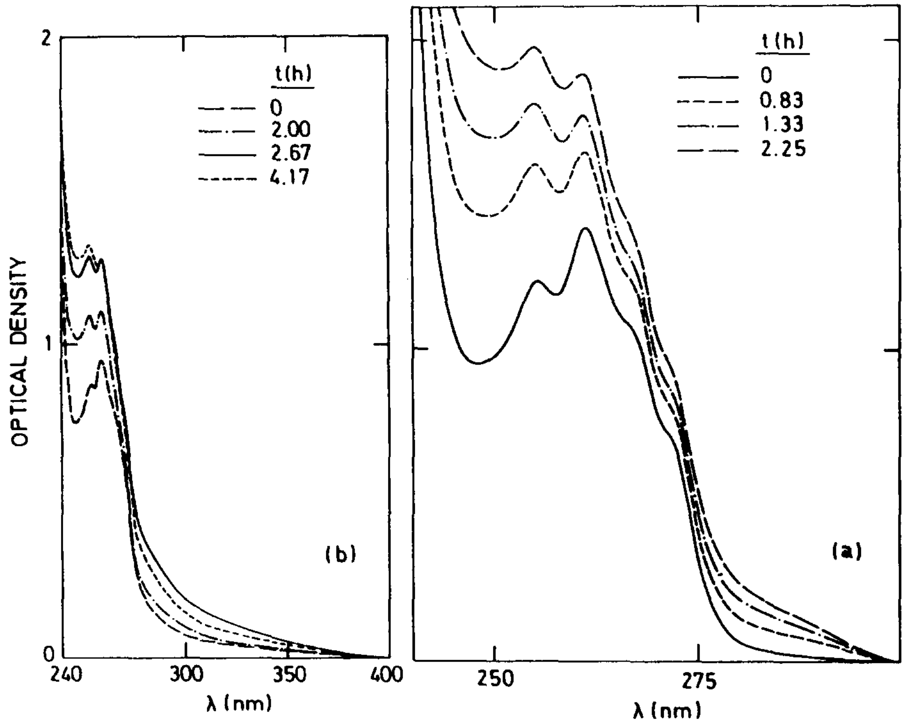

Figure 2.- Absorption spectra of (a) NaPSS in aerated solution and of (b) HPSS aqueous solution with nitrogen, after various irradiation times with λ = 253.7 nm.

centered at 295 and 325 nm respectively (6,7).

The absorption spectra of both samples is essentially identical (Fig. 2a and 2b). It shows a band peaking at 261 nm for HPSS and 0.3 nm red shifted for the polysalt. The vibrational resolution is about the same for both samples, however, the polyacid shows a small tail which extends to 300 nm on the long wavelength side of the band. In polystyrene-like polymers and according to some authors (8,9), that tail is due to charge transfer complexes with oxygen but in our case it is not modified by nitrogen bubbling. On the other hand, nitrogen bubbling does not modify the fluorescence intensity in more than 2%, suggesting that the chromophore is protected for oxygen quenching. We conclude that HPSS and NaPSS do not form charge transfer complexes with oxygen, typical of polystyrene like polymers.

Upon irradiation with UV light, absorption and emission spectra suffer of some spectral changes for both polymers (Figs. 1 and 2). Fig. 1 shows the changes in the fluorescence spectra of an aerated HPSS solution after irradiation at λ = 253.7 nm. Monomer emission decreases very efficiently, excimer emission remains practically constant but becomes broader in the red side. After irradiation during a very long time a new band peaking at about 370 nm appears clearly. The appearance of the new band is made at the expenses of excimer emission which decreases very much. Light scattering at the excitation wavelength ( $\lambda$ = 260 nm) do also decreases appreciably (Fig. 1); in principle, it may be due to chain scission or to the increment of optical density at that wavelength.

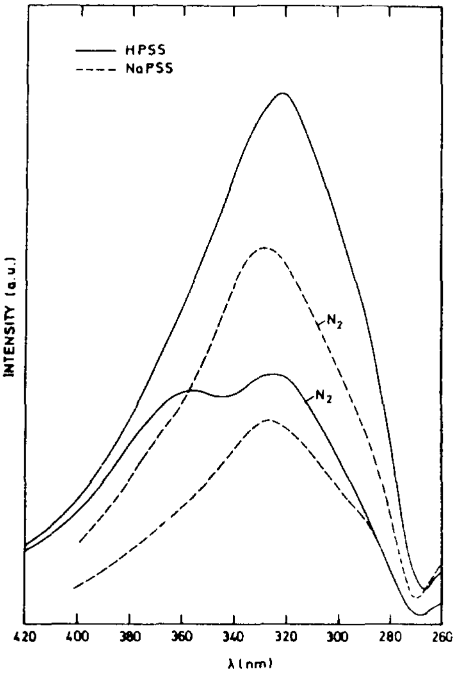

Figure 3.- Emission spectra of HPSS and NaPSS in aerated or nitrogen bubbled solutions after five hours of irradiation.

The irradiation of NaPSS and HPSS solutions with (Fig. 2a) or without oxygen (Fig. 2b) increases the absorption at both sides of the original band due to photochemical reactions. Similar UV absorption changes of polystyrene irradiated solutions have been adscribed to the formation of hydroperoxides followed by the production of carbonyl compounds (3) and conjugated polyene structures (4). In the case of HPSS and NaPSS, the appearance of the new emission band at 370 nm (in particular at long irradiation times) supports the existence of polyene structures, specially dienes (10). Carbonyl compounds do not show fluorescence and therefore they could be present at short irradiation times , when emission spectra changes only in the monomer band.

The rate of spectral changes is different for NaPSS and HPSS and it depends on the presence of oxygen in the solution. Fig. 3 illustrates that with very similar irradiation times, the fluorescence spectra of both samples, aerated or purged with nitrogen, differs in the relative intensity of excimer emission and the new band at 370 nm. The band adscribed to polyene structures increases more easily (i) for HPSS than for NaPSS solutions and (ii) in the absence of oxygen than in aerated solutions.

## ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support supplied by the CAICYT under grant n GG85/0013. Thanks are also due to Caja de Ahorros y Monte de Piedad de Madrid for research support and to Mrs. Elena Morales for determining the samples molecular weight.

## REFERENCES

1. D. M. Wiles and D. J. Carlson in "New Trends in the Photochemistry of Polymers", ed. by N. S. Allen and J. F.Rabek, Elsevier Applied Science Pub., New York 1985.
2. A. Garton, D. J. Carlsson and D. M. Wiles in "Developments in Polymer Photochemistry", Vol. I, ed. by N. S. Allen, Elsevier Applied Science Pub., New York 1980.
3. J. Kowal and M. Nowakowska, Polymer 23, 281 (1982).
4. J. Lucki, J. F. Rabek, B. Ranby and Y. C. Jiang, Polymer 27, 1193 (1986).
5. A. Takahashi, T. Kato and M. Nagasagwa, J. Phys. Chem. 71, 2001 (1967).
6. N. J. Turro and T. Okubo, J. Phys. Chem. 86, 1485 (1982).
7. M. D. Major and J. M. Torkelson, Macromolecules 15, 213 (1982).
8. J. F. Rabek and J. Sanetra, Macromolecules 19, 1679 (1986).
9. J.F. Rabek, J. Sanetra and B. Ranby, Macromolecules 19, 1674 (1986).
10. G. Geuskens, D. Baeyens-Volant, D. Delaunois, Q. Lu-Vinh, W. Piret and C. David, Eur. Polym. J. 14, 291 (1978).

Accepted January 16, 1989 C