

Notes on modification of polystyrene by sulphonation: Some properties of poly(styrenesulphonic acid)

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(Received 2 October 1985)

Polystyrene is sulphonated by use of sulphonic acid at three different temperatures (85, 100 and 125°C). The maximum percentage sulphonation and energy of activation for the process are found to be 61.59% and 8.85 kg mol⁻¹, respectively. During the sulphonation process, considerable degradation is observed, which varies between 10 and 70%, depending on the temperature and duration of treatment.

(Keywords: polystyrene; sulphonation; poly(styrenesulphonic acid); modification)

INTRODUCTION

Poly(styrenesulphonic acid) and its copolymers have received considerable attention for years and still there is growing interest in the subject because of the variety of applications in industry, including the probability of immobilization of catalyst on polymer¹.

Sulphonation is usually done by use of either concentrated sulphuric acid, fuming sulphuric acid or chlorosulphonic acid. Owing to the existence of the (CH-CH) group on the benzene ring, the sulphonic acid group is directed to the *para* position during sulphonation. It has been established² that the nature of the sulphonating agent as well as the physical properties and molecular weight of the polymer to be sulphonated are important parameters that affect the characteristics of the product and the extent of sulphonation. In addition, the duration of sulphonation and the temperature are two important factors. The effect of some reaction conditions, e.g. the speed of stirring of the system, is also shown to have an effect to some degree on the extent of reaction³.

The study of sulphonation by concentrated sulphonic acid involves a number of complications. In this study, by keeping several polymerization parameters constant, sulphonation by concentrated sulphonic acid is achieved while keeping duration and temperature of the reaction as the main parameters, with the aim of gaining more understanding of the process.

EXPERIMENTAL

The polystyrene (PS) used is a Petkim (Turkish Petrochemical Ind. Inc., Yarımca) product (K.500 crystal PS, with $\bar{M}_v = 1.70 \times 10^5$ g mol⁻¹). It is powdered by precipitation from solution (solvent, toluene; non-

solvent, ethanol) and carefully dried by application of vacuum. Since sulphonation initiates and proceeds via a heterogeneous reaction, powdering is necessary to keep the interface at a maximum⁴. Owing to the highly hygroscopic nature of poly(styrenesulphonic acid) (PSSA), special care is needed during storage of the polymer as well as during the sulphonation reaction.

Sulphonation is done in a balloon fitted with a condenser, a CaCl₂ tube and a thermometer. After reaching the desired temperature with sulphonic acid in the system, powdered PS is added (ratio 2 g PS/20 ml acid) while stirring the system at a constant rate. After a certain period of time, the reaction is slowed down by cooling the balloon, and its contents are poured into 100 ml of cold water (10°C). The precipitate is filtered without shaking the system, and the precipitate is then dissolved in 20 ml cold water by vigorous stirring. Excess unreacted PS (which amounts to less than 1%) is separated from the solution by filtering carefully through glass wool. The solution, which contains water, PSSA and a trace amount of sulphuric acid, is concentrated by evaporation until a PSSA gel is separated. The gel is isolated and pressed. To remove the trace of sulphuric acid that may still exist in the bulk, extraction is done using acetic acid (99.9%, Merck) for 4 h. This is followed by ion-exchange treatment, which is carried out by dissolving the PSSA in water that contains Amberlite IR-45-OH form anionic resin. In this treatment, sulphonic acid is expected to penetrate selectively into the ion-exchange resin and be neutralized⁴. We test for any remaining possible sulphuric acid trace by use of excess BaCl₂ at 50°C. PSSA solution is concentrated by solution evaporation and drying.

Viscosity-average molecular weights are obtained by using either toluene (for PS) or NaCl solutions (at an optimum concentration of 0.52 M (ref. 5) for PSSA) at

25°C, employing the following Mark-Houwink equation⁶:

$$[\eta] = 8.48 \times 10^{-3} \times M_v^{0.748} \quad (\text{for PS})$$

$$[\eta] = 0.312 \times 10^{-3} \times M_v^{1.0} \quad (\text{for PSSA})$$

RESULTS AND DISCUSSION

I.r. (from KBr disc) and n.m.r. (in CDCl₃) spectra of PSSA are given in Figures 1 and 2. In Figure 1, the peak at 830 cm⁻¹ is characteristic of disubstituted benzene.

Although the resolution is poor, the peaks at 1250–1150 and 1060–1010 cm⁻¹ are characteristic of sulphonic acid^{7–9}. In Figure 2, although spin-spin splittings are not too clear, CH₂ groups (at 1.3 ppm) and benzene ring (at 7 ppm for PS and 7.4 ppm for PSSA) can still be identified. In addition, owing to the inductive effect of the -SO₃H group, the electron density at C_b is expected to decrease and H_b protons are expected to shift to a lower field. Hence, there is a shift of 0.4 ppm between the absorption signals of H_b protons and similar protons in PS, which is a clear indication of addition of a substituent at the *para* position.

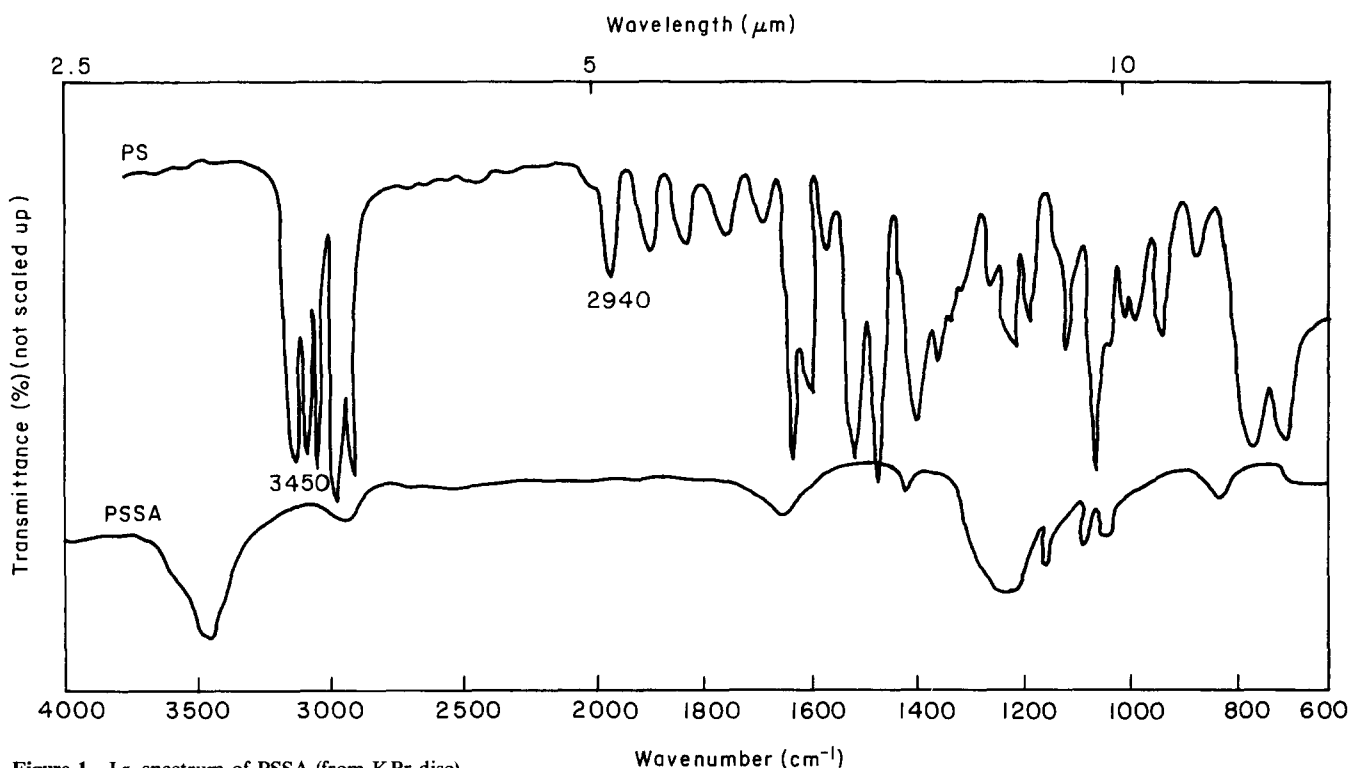


Figure 1 I.r. spectrum of PSSA (from KBr disc)

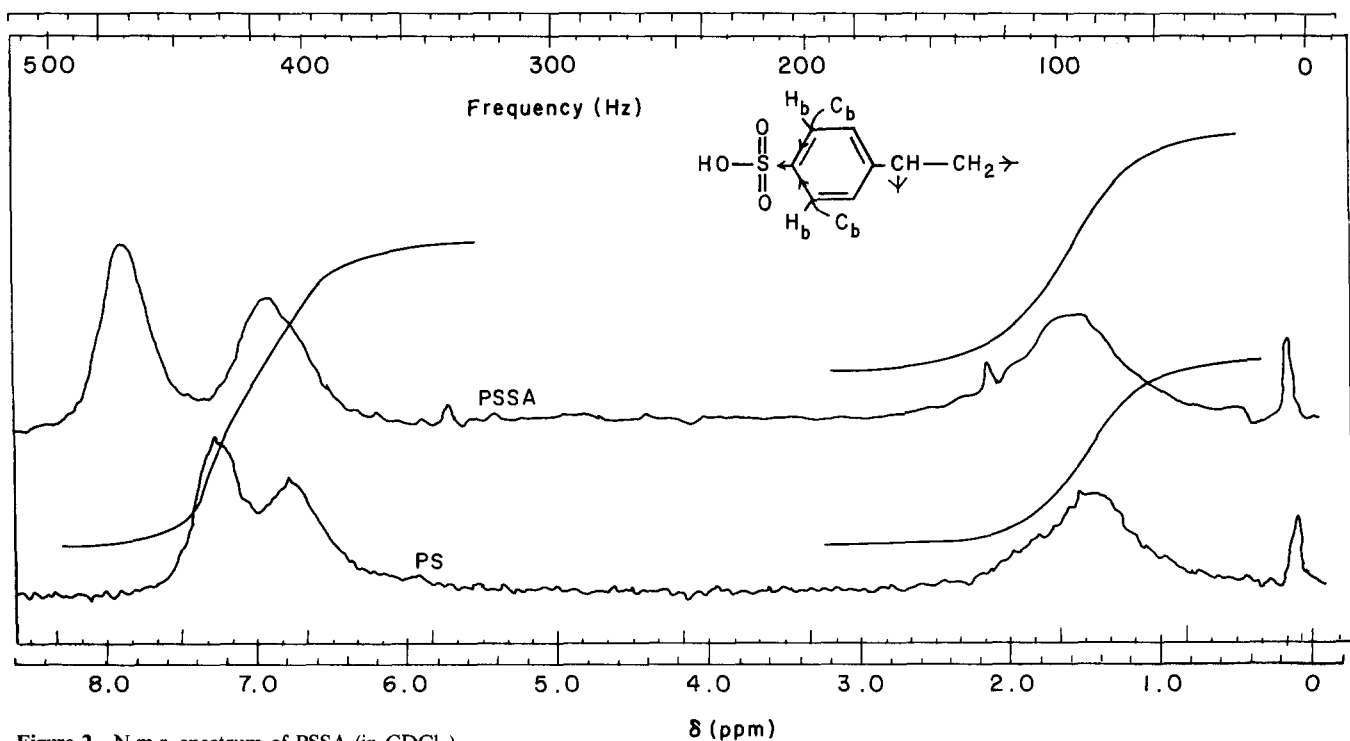


Figure 2 N.m.r. spectrum of PSSA (in CDCl₃)

Table 1 presents percentage sulphonation, at different temperatures and times. Percentage sulphonation is calculated by use of the titration method (titration with NaOH solution against phenolphthalein indicator). Results are plotted in Figure 3. As shown, percentage sulphonation ranges between 26.59 and 61.59, which means that, as a minimum, 26.59 SO₃H groups are added to 100 styrene units and, as a maximum, this number can be increased roughly three times by increasing temperature and time within the ranges used here.

Results of viscosity studies are presented in Figures 4 and 5, and are summarized in Table 2. It is seen that there is a considerable amount of chain degradation during sulphonation, which increases as a function of time and temperature of treatment. Percentage chain degradation is calculated* by using data and Table 1. Although the effect of PS molecular weight and molecular weight distribution on the extent of percentage degradation is not yet known completely, it is obvious that sulphonation should be carried out at lower temperatures or at high temperatures for a short period of time if the molecular weight distribution of the product is important and if a catalyst will not be used⁹. The energy of activation for the sulphonation process (Figure 6) is calculated as 8.85 kJ mol⁻¹.

D.t.a. thermograms of several PSSA samples are presented in Figure 7. As shown in the figure, the peaks shift slightly to lower temperatures as percentage sulphonation increases. No further speculation will be made on the trend and the system, which is under current investigation.

Table 1 Percentage sulphonation

<i>t</i> (°C)	Time (h)	Sulphonation (%)
85	1	26.59
	2	34.95
	3	38.88
	4	42.65
	5	46.69
100	1	32.69
	2	38.20
	3	45.26
	4	49.35
	5	52.30
125	1	35.72
	2	46.72
	3	54.79
	4	57.16
	5	61.59

*For data at 85°C, 5 h, for example, we have:

$$\text{Number of mers (sulphonated)} = \frac{170600}{104} \times 0.4669 = 765.9$$

$$\text{Number of mers (not-sulphonated)} = \frac{170600}{104} - 765.9 = 874.5$$

$$\begin{aligned} \text{Percent degradation} &= \frac{\text{mol.wt of (sulphonated + not sulphonated)} - \bar{M}_v}{\text{mol.wt of (sulphonated + not sulphonated)}} \times 100 \\ &= \frac{(765.9 \times 184 + 874.5 \times 104) - 149000}{765.9 \times 184 + 874.5 \times 104} \times 100 = 35.7 \end{aligned}$$

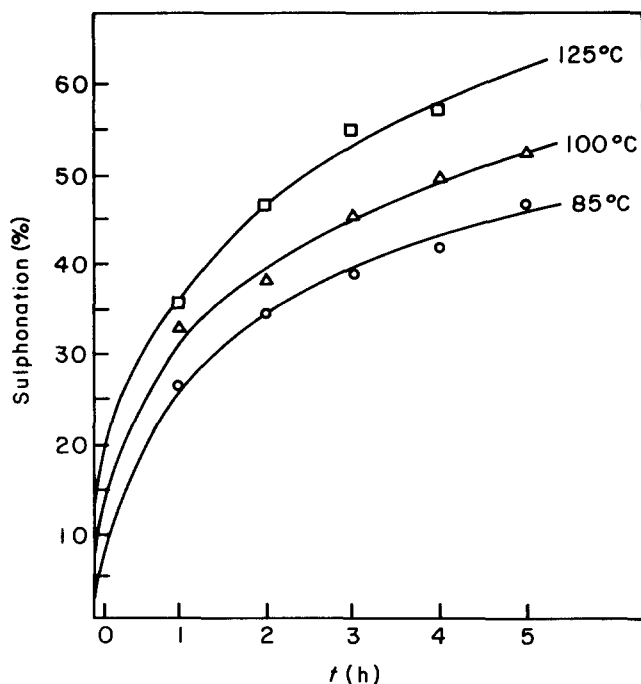


Figure 3 Percentage sulphonation of PS as a function of time and temperature

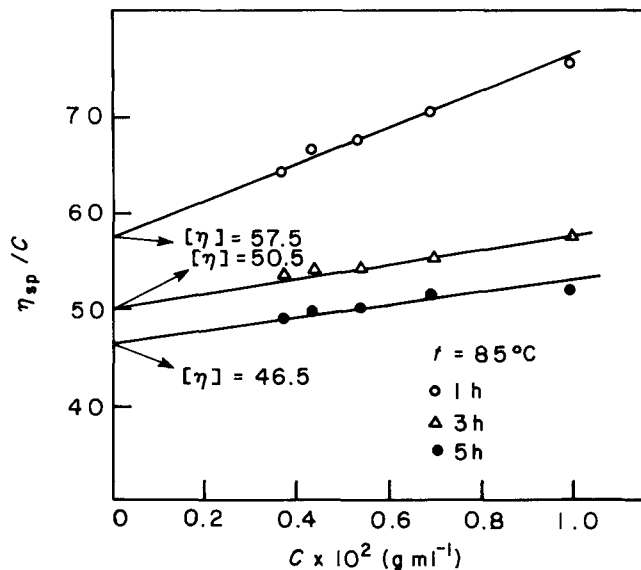


Figure 4 Results of viscosity studies on sulphonation of PS at 85°C for various durations

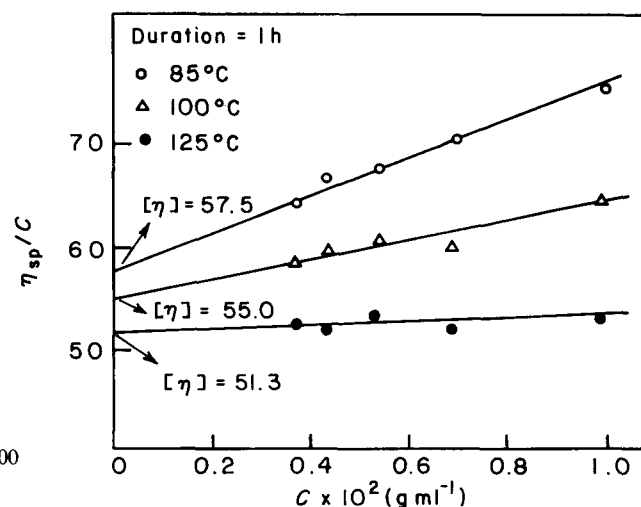


Figure 5 Results of viscosity studies on sulphonation of PS for 1 h at various temperatures

Table 2 Some data for the polymers used

t (°C)	Time (h)	$[\eta]$ (25°C) (ml g ⁻¹)	\bar{M}_v (g mol ⁻¹)	Degradation (%)
85	1	57.5	1.843×10^5	10.3
	3	50.5	1.619×10^5	27.0
	5	46.5	1.490×10^5	35.7
100	1	55.0	1.763×10^5	17.4
	3	42.5	1.362×10^5	40.7
	5	34.5	1.106×10^5	53.8
125	1	51.3	1.644×10^5	17.4
	3	28.5	0.913×10^5	62.3
	5	23.0	0.737×10^5	70.7
PS (base polymer)		69.5	1.706×10^5	-

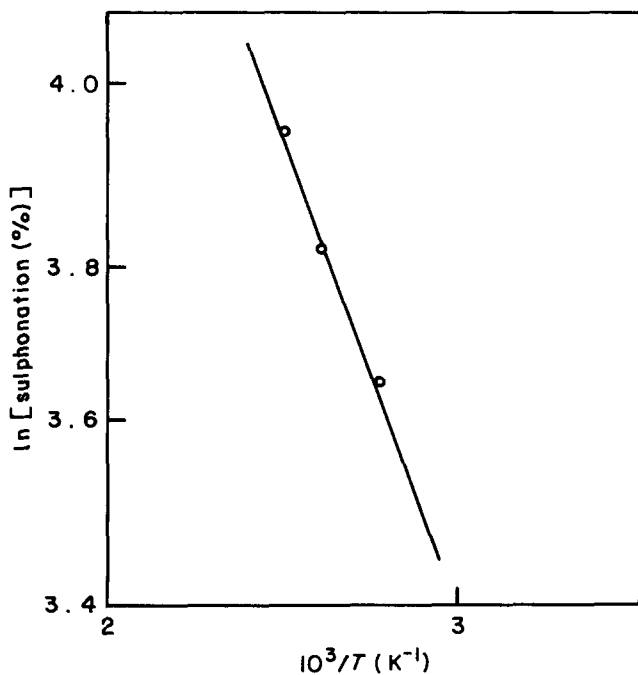


Figure 6 Plot of percentage sulphonation on log scale versus $1/T$, in order to calculate the energy of activation for the sulphonation process

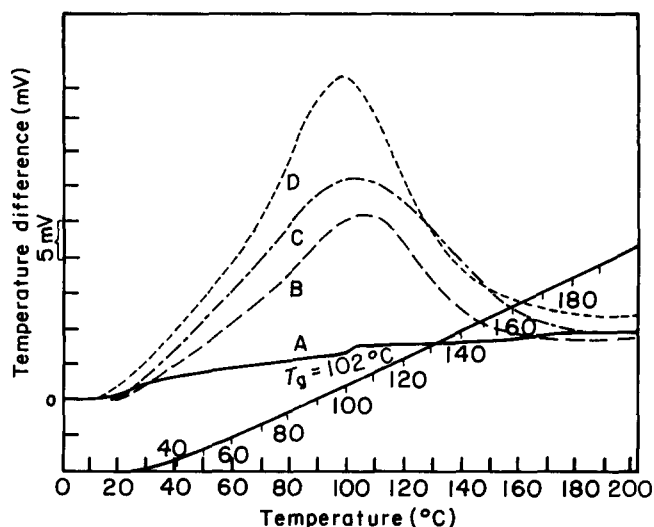


Figure 7 D.t.a. thermograms of various PSSA samples: heating rate, $50^\circ\text{C min}^{-1}$; range, ± 50 mV; gas, nitrogen; flow rate, 25 ml min^{-1} ; curves as on figure. A, base polymer, PS; B, sulphonated at 85°C , 1 h; C, sulphonated at 100°C , 2 h; D, sulphonated at 125°C , 5 h

ACKNOWLEDGEMENTS

This work is supported by TÜBİTAK (Turkish National and Scientific Research Council) through TUMKA.

REFERENCES

- 1 Widdecke, H. *Chem. Ing. Tech.* 1980, **52**, 825
- 2 Roth, H. H. *Ind. Chem. Eng.* 1957, **49**, 1820
- 3 Özkan, A. M.Sc. Thesis, Fırat University, Elazığ
- 4 Hart, R. and Timmerman, O. *Chim. Belge Suppl.* 1959, **2**, 312
- 5 Kato, M., Nakagawa, T. and Akamatu, H. *Chem. Sci. Japan* 1960, **33**, 332
- 6 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', Wiley Interscience, New York, 1975
- 7 Hart, R. and Janssen, R. *Macromol. Chem.* 1961, **43**, 242
- 8 'CRC Handbook of Chemistry and Physics', CRC Press, New York
- 9 Carrol, W. R. and Eisenberg, H. *J. Polym. Sci.* 1966, **4**, 599