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# Thermal Degradation of Blends of Polystyrene and poly(sodium 4-styrenesulfonate) and the copolymer, poly(styrene-co-sodium 4-styrenesulfonate)

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# Thermal degradation of blends of polystyrene and poly(sodium 4-styrenesulfonate) and the copolymer, poly(styrene-co-sodium 4-styrenesulfonate)

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## Abstract

The thermal degradation of blends and copolymers of styrene with styrenesulfonic acid has been studied using thermogravimetric analysis, TGA/FTIR, and cone calorimetry. The blends have enhanced thermal stability relative to virgin polystyrene but there is no enhancement in thermal stability for the copolymers. Apparently, it is necessary to have adjacent sulfonic acid groups in order to permit the formation of a graphite-like char which can provide thermal

protection to the polymer. It is necessary to have a good match in degradation temperatures of the two components if one is to have significantly enhanced thermal stability.

# 1. Introduction

Graft copolymerization of char-forming monomers, such as sodium (meth)acrylate and acrylonitrile, onto various polymers has been the subject of increasing interest over the past several years [1], [2], [3], [4], [5]. In such systems, the polymer will produce non-volatile char upon thermolysis and these chars can act as physical barriers to heat and provide protection to the underlying polymers [6], [7]. One particular advantage of these char-forming systems is that they do not evolve the toxic gases usually released from traditional flame retardants, such as halogen-based compounds. These char-forming systems are a promising alternative for conventional halogen or phosphorous-based flame retardants.

Our laboratory has been focusing on the flame retardancy of polymers with the inherent ability to form inorganic non-volatile chars for some time. We have successfully grafted copolymerized sodium methacrylate onto ABS and SBS resin and found that the char was significantly increased and offered substantial protection to the underlying polymer as evidenced by Cone calorimetry data and thermogravimetric analysis [8], [9]. We have also studied in detail the thermal degradation of poly(sodium 4-styrenesulfonate), PSSNa, and found that the degradation of this polymer produces a large amount of non-volatile char with substantial content of the inorganic salts, sodium sulfate and sodium sulfite. Approximately 55% of PSSNa is non-volatile at 800°C [10]. This large amount of char suggests that sodium 4-styrenesulfonate may be useful to enhance the thermal stability of polymers. Our interest in sodium 4-styrenesulfonate was further sparked by the observation that the thermal degradation of poly(sodium 4-styrenesulfonate) produces foam.

In this paper, the thermal degradation of blends of poly(sodium 4-styrenesulfonate) and polystyrene and the chemical combination of the monomeric components, poly(styrene-co-sodium 4-styrenesulfonate), will be examined by a combination of techniques including thermogravimetric analysis, TGA, and Cone calorimetry in order to ascertain whether sodium 4-styrenesulfonate will provide protection to inhibit the degradation and combustion of polystyrene.

# 2. Experimental
## 2.1. Materials

All chemicals were purchased from Aldrich Chemical Company and used as received except as otherwise noted. The inhibitor was removed from styrene by passing the monomer through an inhibitor remover column (Aldrich).

## 2.2. Instruments

Thermogravimetric analysis (TGA) was performed using an Omnitherm 1000 unit, and thermogravimetric analysis coupled to Fourier transform infrared spectroscopy, TGA/FTIR,

was performed using a Cahn TG-131 thermogravimetric analyzer interfaced to a Mattson Galaxy infrared spectrometer. The TGA data reported herein is an average of three determinations; the uncertainty in temperature is ±3°C. Infrared spectroscopy was recorded on a Mattson Galaxy 4020 infrared spectrometer at 4 cm$^{-1}$ resolution. NMR spectra were recorded on a GE 300 MHz unit. Cone calorimetry was performed per ASTM E 1354-92 using a Stanton Redcroft/PL Thermal Sciences instrument at 35 KW/m$^2$ in the horizontal orientation. The samples were 6.3 mm thick and mounted using the edge retainer frame and wire grid; the mass was approximately 35 g. Exhaust flow was set at 24 l/s and the spark was continuous until the sample ignited. All reported Cone data is from duplicate determinations; the uncertainty in the data is ±10%.

## 2.3. Preparation of polymers, copolymers, and blends

Poly(sodium 4-styrenesulfonate), PSSNa, was polymerized using potassium peroxydisulfate as initiator (0.75% w/w of monomer) in water and the polymer was purified by precipitation several times using a deionized water (solvent)/methanol (non-solvent) system and dried overnight in vacuum at 120°C. $^1$H NMR spectrum proves that PSSNa is monomer free.

## 2.4. Emulsion copolymerization

Emulsion copolymerization of styrene and sodium 4-styrenesulfonate was performed according to published preced ures [11], [12]. Emulsifier-free emulsion copolymerizations were conducted employing potassium persulfate as the initiator. In a typical procedure, 100 g styrene, 10 g sodium 4-styrenesulfonate, 0.505 g potassium persulfate, and 310 g water were combined in a 500 ml three-necked flask equipped with magnetic stirring bar and condenser and the mixture was allowed to react at 70°C for 8 h. The copolymer was recovered by precipitation by adding acetone into the latex and the precipitate was purified by extraction with water and tetrahydrofuran to remove any homopolymer. Emulsion copolymerization of styrene and sodium 4-styrenesulfonate was also carried out using sodium dodecyl sulfate, SDS, as the emulsifier and 2,2′-azobisisobutyronitrile, AIBN, as the initiator at 70°C. The amount of AIBN was 0.5% (w/w) of styrene and the amount of SDS was varied. The composition of the copolymers was determined by sulfur analysis, which was done by Midwest Microlabs, and the results are shown in Table 1.

Table 1. Emulsion copolymerization of styrene and sodium 4-styrenesulfoante[a]

| $f_{NaSS}$[b] | Initiator | SDS [m] | Latex | $F_{NaSS}$[c] |
|---|---|---|---|---|
| 3.03 | K$_2$S$_2$O$_8$ | 0 | Stable | 2.85 |
| 4.94 | K$_2$S$_2$O$_8$ | 0 | Stable | 5.72 |
| 5.51 | K$_2$S$_2$O$_8$ | 0 | Stable | 7.65 |
| 5.28 | AIBN | 0 | Non-stable | 0 |
| 2.42 | AIBN | 0.017 | Non-stable | 0 |
| 2.45 | AIBN | 0.035 | Stable | 0 |

[a]Total weight 420g, H$_2$O 310 g.

Blends of [polystyrene](#) and poly(sodium 4-styrenesulfonate) were obtained by mechanical mixing in a Brabender mixer at 150°C for 30 min.

## 2.5. Foam expansion

Poly(sodium 4-styrenesulfonate) expanded in volume upon heating, the amount of volume expansion was noted by placing a quantity of the polymer in a small tube and heating the sample slowly in a sand bath to elevated temperatures. The samples were heated to the desired temperatures between 200 and 500°C and the temperature was maintained for 30 min in order to ensure that the volume had completely expanded before a reading was taken. The height after volume expansion was compared to that of the unexpanded sample to give the volume expansion. The amount of expansion which is observed in air is recorded in [Table 2](#).

Table 2. Volume expansion during thermal degradation of poly(sodium styrenesulfonate) in air

| Temperature (°C) | 200 | 250 | 300 | 350 | 380 | 400 | 420 | 430 |
|---|---|---|---|---|---|---|---|---|
| Expansion (times) | 1 | 1 | 1 | 1 | 1.3 | 8.3 | 3.3 | 1.4 |

# 3. Results and discussion

## 3.1. Polystyrene and poly(sodium 4-styrenesulfonate) blends

### 3.1.1. Thermogravimetric analysis

The TGA curves of blends of [polystyrene](#), PS, and poly(sodium 4-styrenesulfoante), PSSNa, are shown together with the rate of mass loss of blends in [Fig. 1](#) (this figure begins at 400°C in order to better show the features which are discussed herein) and the numbers which have been extracted from these TGA curves are compiled in [Table 3](#). The onset temperature, $T_d$, is defined as the temperature at which 5% mass loss occurs, and $T_{50\%}$ is the temperature at which 50% mass loss occurs. The maximum rate of mass loss, $r_{max}$, and $T_{max}$, the temperature at which $r_{max}$ occurs, are obtained from the derivative. Very similar terminology has been used by [Van Krevelen](#) [13]. As seen in the TGA curves, there are two main degradation steps for the blends. The first occurs between 350 and 500°C and corresponds to polystyrene degradation while the second, at higher temperature, 470–505°C, is correlated with the degradation of PSSNa. The derivative clearly shows this differentiation and confirms that the second step is correlated with the amount of PSSNa in the blend. This suggests that the two components of the blend are degrading independently. One can normalize the rate of mass loss of polystyrene to its fraction in a blend and this is reported in the column in [Table 3](#) headed $r_{max}$ of PS. This value of $r_{max}$ is unchanged for samples ranging from pure polystyrene to a blend with 21.86 mol% PSSNa. The rate of decay of polystyrene does not depend on the composition of the blend while the rate of mass loss of the blend drops significantly as the amount of PSSNa increases. Since the fraction of polystyrene, the component which undergoes the easier degradation, is decreased, the rate of mass loss must also decrease.
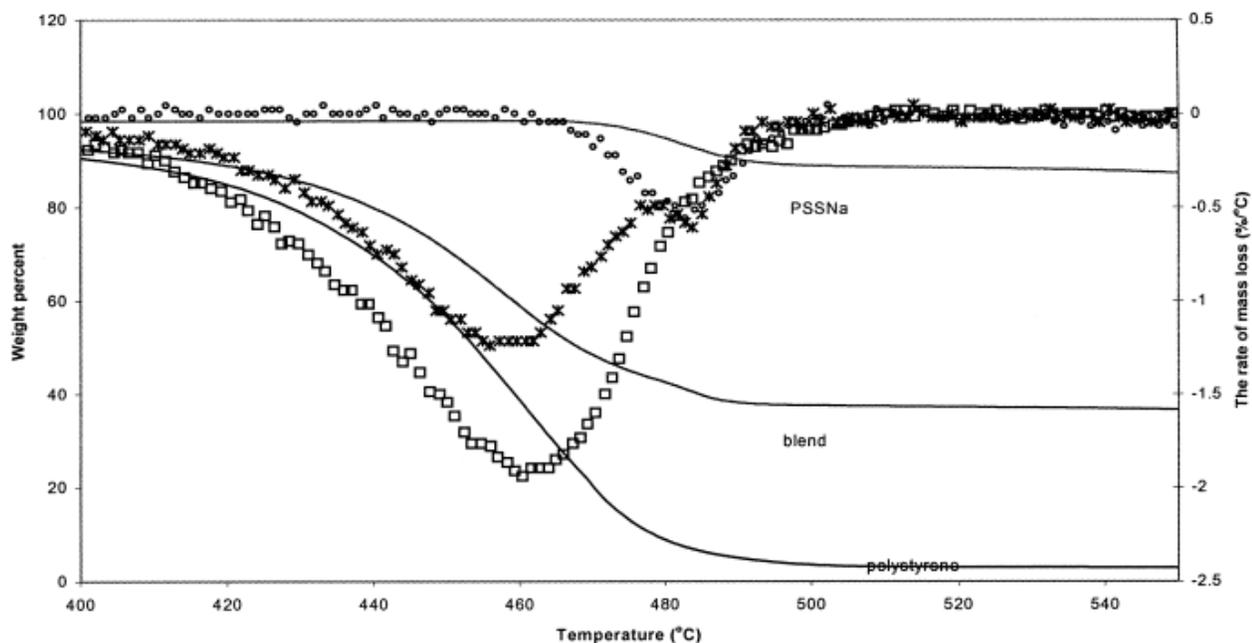
Fig. 1. Thermogravimetric analysis of blends of PS and PSSNa at 20°C/min under $N_2$.

Table 3. The effect of poly(sodium 4-styrenesulfonate) on the thermal degradation of polystyrene

| $f_m$ (mol%) | $T_{50\%}$ (°C) | $T_{max}$ (°C) | $r_{max}$ of blends (%/°C) | $r_{max}$ of PS (%/°C) | Actual char 800°C (%) | Theoretical char (%) |
|---|---|---|---|---|---|---|
| 0[a] | 454 | 463 | −1.97 | −1.97 | 2.8 | 2.8 |
| 2.74 | 455 | 463 | −1.88 | −1.98 | 5.9 | 5.7 |
| 5.57 | 454 | 461 | −1.79 | −1.99 | 10.0 | 8.6 |
| 7.16 | 454 | 461 | −1.72 | −1.96 | 11.3 | 10.1 |
| 21.86 | 453 | 459 | −1.24 | −1.96 | 29.2 | 23.0 |
| 27.60 | 453 | 459 | −1.08 | −1.89 | 32.5 | 26.6 |
| 100 | | | | | 58.0 | 58.0 |

[a]PS (Mn 45,000) from Aldrich.

The thermal degradation of poly(sodium styrenesulfonate) begins at about 470°C. Before degradation commences, no effect on the thermal degradation of polystyrene is expected and this is reflected in the constancy of the $r_{max}$ values for polystyrene. Above 470°C, PSSNa degrades and produces a carbonaceous foam along with inorganic salts which can inhibit the thermal degradation of polystyrene. At 470°C 80% of the polystyrene has completely degraded and 20% is still remaining. At low PSSNa content, the amount of char is very close to the theoretical values and one concludes that the presence of PSSNa offers little protection to the polystyrene. Apparently the quantity of foam and char is too small to cover the entire surface and polystyrene degradation continues. At higher PSSNa content, for example, 27.6 mol%

PSSNa, the actual char amount, 32.5%, is clearly greater than the theoretical value, 26.6%. This indicates that some polystyrene or its degradation products must be retained in the residue, buried inside the foam and inorganic salts. This 6% increase in the amount of char is a relatively low retention of polymer; the degradation of the char-forming monomer occurs at too high a temperature and too much of the underlying polymer has been able to escape before it can have an effect.

3.1.2. Cone calorimetry

One requirement for a flame retardant by the char-forming process is that it must be formed in a timely manner before the polymer which it is to protect has undergone extensive degradation. PSSNa thermally degrades at a higher temperature than most polymers and this will inhibit its utility to enhance the thermal stability of polymers. However, for a large sample, surface PSSNa may degrade before bulk PS and this may offer some thermal protection. PSSNa degrades at a lower temperature in an air atmosphere than in nitrogen so there is a better match in the degradation temperatures of PS and PSSNa in air. Cone calorimetry shows this effect; the data for unmodified PS, blends of PS and PSSNa and copolymers is presented in Table 4. This data show that the combustion properties of PS are altered by the combination with PSSNa. The peak heat release rate for the blends is always less than for polystyrene and it decreases as the fraction of PSSNa increases. Likewise the time to reach this peak heat release rate is increased in the blends. The blend clearly shows enhanced thermo-oxidative stability relative to polystyrene but these effects only become important at relatively high amounts of PSSNa. As noted above from the TGA data, a relatively large amount of char-former must be present in order to provide thermal-oxidative protection.

Table 4. The Cone calorimetry data of PS[a], blends of PS and PSSNa and P(S-co-NaSS) at 35 kW/m$^2$

| | mol% SSNa | Time to ignition, s | Time to burnout, s (S) | Peak heat release rate, kW/m$^2$ | Time to peak HRR, s | Energy rel. through S, kJ | Specific ext. area average through S, m$^2$/kg | Extinct. area through S, m$^2$ | Mass loss rate mg/s |
|---|---|---|---|---|---|---|---|---|---|
| PS | 0 | 45 | 223 | 795 | 200 | 940 | 1163 | 37 | 198 |
| Copolymer | 2.9 | 55 | 249 | 740 | 273 | 917 | 1098 | 40 | 197 |
| | 6.0 | 45 | 229 | 696 | 210 | 788 | 1098 | 36 | 192 |
| | 7.7 | 55 | 250 | 712 | 210 | 849 | 1128 | 39 | 188 |
| Blends | 2.8 | 33 | 219 | 668 | 193 | 845 | 1156 | 36 | 184 |
| | 6.4 | 45 | 276 | 485 | 238 | 859 | 1166 | 36 | 143 |
| | 8.2 | 33 | 332 | 462 | 253 | 928 | 1061 | 33 | 110 |
| | 23.8 | 40 | 375 | 293 | 315 | 783 | 1160 | 32 | 84 |
| | 29.9 | 40 | 378 | 294 | 303 | 759 | 985 | 26 | 78 |

[a]PS (M$_w$ 280,000) from Aldrich.

## 3.2. Poly(styrene-co-sodium 4-styrenesulfonate)

### 3.2.1. Preparation of the copolymer

Completely different materials are obtained when one uses AIBN versus potassium persulfate as the initiator. With AIBN initiation, the entire polymer is soluble in tetrahydrofuran, THF, while with $K_2S_2O_8$ initiation, highly swollen gels are produced The infrared spectrum of these gels shows the characteristic peaks of a sulfonate at 1224 and 1199 cm$^{-1}$, due to the splitting of the doubly degenerate ($E$) asymmetric stretching mode of the sulfonate [14]. These sulfonate bands are completely absent in the AIBN-initiated copolymerization. In the case of potassium persulfate, copolymerization first occurs in the aqueous phase to incorporate the sodium 4-styrenesulfonate [12]. On the other hand, if one employs AIBN as the initiator, the reaction site will be the oil phase, and the entry of water-soluble monomer into the oil phase is difficult, due to the very low solubility of sodium 4-styrenesulfonate in styrene, so homopolymerization of styrene dominates the reaction. In the experimental section of this paper, the results for the analysis of sulfur are shown and they indicate that there is no copolymerization when AIBN is used as the initiator.

### 3.2.2. Thermogravimetric analysis

The TGA curve for thermal degradation of poly-(styrene-co-sodium 4-styrenesulfonate) is shown in Fig. 2 together with the derivative of this TGA curve; the data is also collected in Table 5.
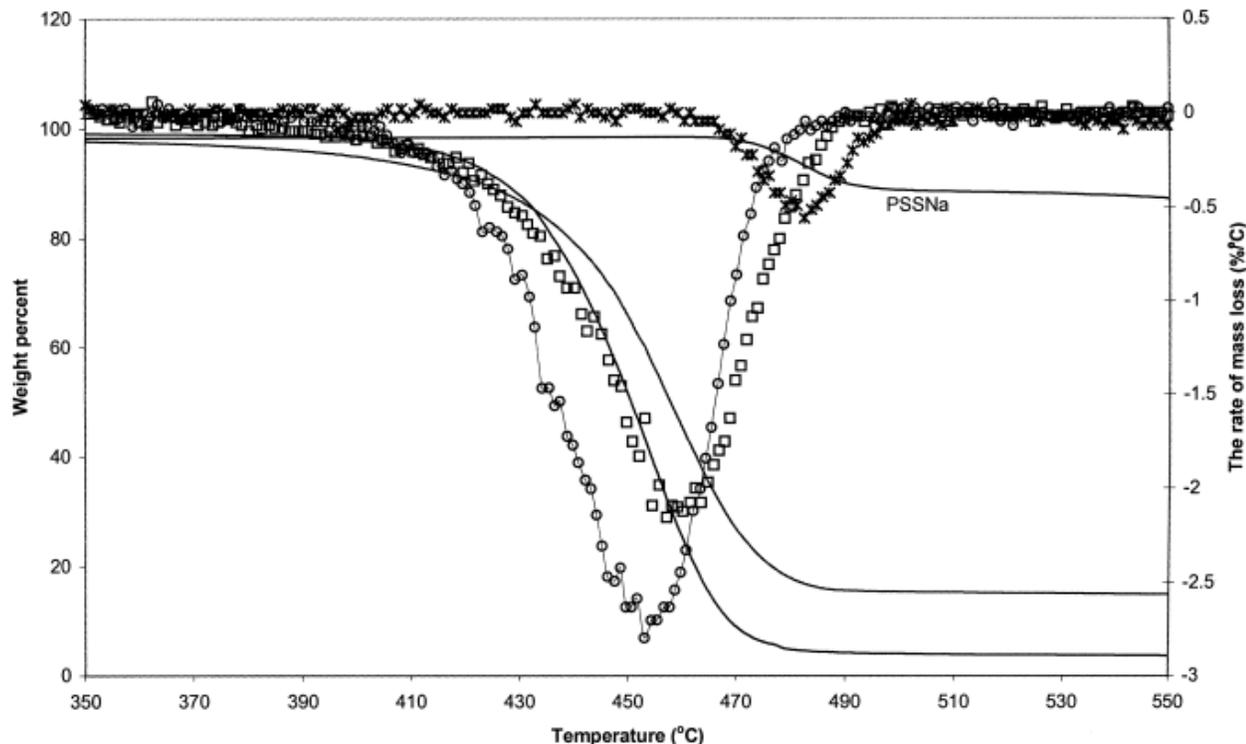


Fig. 2. Thermogravimetric analysis of p(st-co-NaSS) at 20°C/min under N$_2$.

Table 5. The thermal degradation of poly(styrene-co-sodium 4-styrenesulfonate)

| Entry | NaSS (%mol) | $T_{5\%}$ (°C) | $T_{50\%}$ (°C) | $T_{max}$ (°C) | $r_{max}$ (%/°C) | Char (%) | Theoretical char (%) |
|---|---|---|---|---|---|---|---|
| 1[a] | 0 | 417 | 441 | 454 | −2.70 | 3.4 | 3.4 |
| 2 | 2.9 | 417 | 457 | 461 | −2.45 | 6.3 | 6.9 |
| 3 | 6.0 | 399 | 459 | 462 | −2.37 | 7.7 | 10.6 |
| 4 | 7.7 | 399 | 459 | 462 | −2.29 | 9.3 | 12.4 |

[a]PS obtained by emulsion polymerization.

It is noteworthy that there is only one apparent degradation step for the copolymers between 300 and 500°C. This is in contrast to the thermal degradation of blends which clearly show two independent degradation steps.

Both $T_{50\%}$ and $T_{max}$ of copolymers are increased relative to pure polystyrene; again this may be contrasted to the blends, which show values that are quite similar to those of polystyrene. The onset temperature of the degradation, as measured by the temperature at which 5% mass loss occurs, $T_{5\%}$, decreases. This is likely to be due to the presence of some solvent or other impurity in the sample. It has also been suggested by Suchocka-Galas [15] that ionomeric copolymers of polystyrene undergo degradation at lower temperatures than does polystyrene. The increase in $T_{max}$ indicates that the thermal stability of copolymers is enhanced relative to pure polystyrene. The increased $T_{max}$ may be attributed to the reduced mobility of copolymer molecules caused by aggregation. The decrease in $r_{max}$ as the fraction of sodium styrenesulfonate in the copolymers increases is expected since this degrades at a higher temperature than polystyrene. The reduced $r_{max}$ indicates that the copolymer is more thermally stable than polystyrene.

Suchocka-Galas [15] has compared the thermal stability of poly(styrene-co-sodium acrylate) with polystyrene, and found that the ionomers, poly(styrene-co-sodium acrylate), have somewhat lower thermal stability than polystyrene as measured by the onset temperature of the degradation. It must be pointed out that Suchocka-Galas was mainly concerned with the thermal stability in the initial step, not the entire process. As far as the entire degradation process is concerned, the thermal stability of poly(styrene-co-sodium 4-styrenesulfonate) is a little enhanced relative to polystyrene; this is reflected in the increased $T_{50\%}$, $T_{max}$ and reduced $r_{max}$.

The actual amount of char is always less than that expected from the fraction of sodium styrenesulfonate in the copolymer. Turner et al. [12] have shown that emulsion copolymerization of styrene and sodium 4-styrenesulfonate produces random copolymers and, therefore, sodium styrenesulfonate groups are not adjacent in these copolymers. The degradation of poly(sodium styrenesulfonate) produces $SO_2$ as one of the first products of its degradation. In a TGA/FTIR study of the degradation of the copolymer, only a very small amount of $SO_2$ is produced. In previous work [10], we have suggested that $SO_2$ may be formed via two pathways. Both begin by the loss of an $SO_3Na$ moiety; in one case this can hydrogen abstract to give the mono-sodium salt of sulfurous acid which can then disproportionate while in the other case the products arise from a displacement on sulfur reaction of this moiety. The absence of $SO_2$ from

the products suggests that its production arises by the interaction of nearby sulfonate units which are absent in the copolymers. The loss of sulfur dioxide also leads to the formation of a graphite-like char [10]; the small amount of char which is produced is taken to mean that this reaction also does not occur to any significant extent.

### 3.2.3. Cone calorimetry

The Cone calorimetry data for the copolymers is presented, together with data on blends and PS, in Table 4. The peak heat release rate is little changed for the copolymers, regardless of the fraction of sodium styrenesulfonate that is present. None of the Cone parameters show any significant improvement relative to pure polystyrene. The enhanced thermal-oxidative stability which was found in the blends can be attributed to the formation of the graphite-like char which arises from the interaction of adjacent sulfonate units, since the adjacent sulfonate units are not present, graphite-like char cannot form and the copolymers do not have enhanced thermal-oxidative stability.

## 4. Conclusion

The thermal degradation of blends of polystyrene with poly(sodium 4-styrenesulfonate) occurs in two completely independent steps; there is no interaction between these components. When the fraction of poly-(sodium styrenesulfonate) is small, there is little inhibition of the degradation of polystyrene. When larger amounts of the salt are present, the fraction of char is increased and this is reflected in decreased heat release rate in a Cone calorimetric study. On the other hand, copolymers degrade in only a single step but, since the copolymers are random, the graphite-like char is not produced and there is no improvement in the degradation of polystyrene. It appears that blends of poly(sodium styrenesulfonate) with polymers may enhance the thermal stability of the polymer. However, this is likely to only be successful when the degradation temperature of the polymer to be protected has some match with the fairly high degradation temperature of poly(sodium styrenesulfonate).

## Acknowledgements

## References

1 I.C. McNeil Develop. Polym. Deg., 7 (1987), p. 1
2 I.C. McNeil, M. Zulfiqar Polym. Degrad. Stab., 1 (1979), p. 89
3 I.C. McNeil, M. Zulfiqar Polymer. J. Polym. Sci., Polym., Chem. Ed., 16 (1978), p. 2465
4 I.C. McNeil, M. Zulfiqar Polymer. J. Polym. Sci., Polym., Chem. Ed., 16 (1978), p. 3201
5 M. Suzuki, C.A. Wilkie Polym Degrad. Stab., 47 (1995), p. 223
6 D.W. Van Krevelen Polymer, 16 (1975), p. 615

7 Well ED, Hansen RH, Patel N. In: Nelson GL, editor. Fire and polymers: hazards identification and prevention, ACS symposium series (425). Washington DC, 1990. p. 97.

8 C.A. Wilkie, M. Suzuki, X. Dong, C. Deacon, J.A. Chandrasiri, T.J. Xue Polym. Degrad. Stab., 54 (1996), p. 117

9 J.A. Chandrasiri, C.A. Wilkie J. Polym. Sci. Part A. Polym. Chem., 34 (1996), p. 1113

10 Jiang DD, Yao Q, McKinney MA, Wilkie CA. Polym Degrad Stab 1999;63:423.

11 J.H. Kim, M. Chainey, M.S. El-Aasser, J.W. Vanderhoff J. Polym. Sci. Part A Polym. Chem. Ed., 37 (1989), p. 3187

12 S.R. Turner, R.A. Weiss, R.D. Lundberg J. Polym. Sci. Polym. Chem. Ed., 23 (1985), p. 535

13 Van Krevelen DW. Properties of polymers. 3rd ed. Amsterdam: Elsevier, 1990. p. 643–44.

14 S. Yang, K. Sun, W.M. Risen Jr. J. Polym. Sci. Part B Polym. Phys. Ed., 28 (1990), p. 1688

15 K. Suchocka-Galas J. Therm. Anal., 35 (1989), p. 1423