Sulfonation Degree Determination of Polystyrene Ionomers by Using Adiabatic Bomb Calorimeter

Cemil Alkan,[1] Ahu Gümrah Dumanlı,[2] Leyla Aras[2]

[1]*Department of Chemistry, Gaziosmanpasa University, Tokat 60240, Turkey*
[2]*Department of Chemistry, Middle East Technical University, Ankara 06531, Turkey*

ABSTRACT: Sulfonation degree determination of sulfonated polystyrene and the corresponding ionomers are performed by adiabatic bomb calorimeter. The theoretical calculations from the band energies for the combustion enthalpy values (calorific values) and the experimental values are compared, and a linear relation between the values is found. Sulfonation and neutralization processes are examined by elemental sulfur analysis and atomic absorption spectroscopy (AAS). It was obvious that increasing sulfonation degree yields a decrease in the combustion enthalpy values, as it is expected from the theoretical calculations. In addition, metal ion incorporation to the structure deviates the experimental combustion enthalpy values especially for the ionomers which have higher sulfonation degrees. This is due to the formation of a higher degree aggregation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4684–4688, 2006

Key words: ionomer; sulfonated polystyrene; adiabatic bomb calorimeter; atomic absorption spectroscopy; calorific value

INTRODUCTION

For the last 30 years, polymer scientists have been examining an interesting group of the polymer family: ionomers. Most ionomers consist of two phases: one, a matrix phase containing dispersed ionic multiplets, i.e., nanosized aggregates of interacting ion pairs, and the other, an ion rich, more chain entangled cluster "phase" that consists of regions of restricted chain mobility surrounding the multiplets.[1,2]

The ionic group attached to the polymer backbone is generally a functional group of sulfonate, carboxylate, or phosphonate in ionomers, and these types of structures are called as anionic ionomers.

Sulfonation reaction is a substitution reaction to insert SO_3H group via chemical bond to carbon.[3,4]

Calorimetry is the measurement of the flow of heat or energy arising from chemical or physical changes in a material. The reaction is followed by the measurement of a temperature change as a function of time.[5] The standard method of adiabatic bomb calorimetry, including igniting and burning the sample, is performed under pressurized excess oxygen atmosphere to reach complete combustion. This is a reliable method for the determination of heat content of many fuels and some materials.[6–8]

This study investigates the use of adiabatic bomb calorimeter for the determination of sulfonation degree of the sulfonated polystyrene (SPS) samples. Bomb calorimeter obeys the regulations of the standard test method of ASTM D 2015–93 (dry basis). The common methods for the determination of sulfonation degree are NaOH titration method or AAS sulfur determination.[3,9,10] As a result of this study, bomb calorimetry is found to be an advantageous method because of its good reproducibility and the rapidness of the analysis.

Generally, SPS samples are assumed to be completely neutralized by applying metal cation salt; thus, the degree of metal neutralization is accepted equal to the sulfonation degree. AAS was used to determine the neutralization amount of metal neutralized ionomers.

EXPERIMENTAL

Materials

Polystyrene (Aldrich; M_W = 118,000 gmol^{-1}), sulfuric acid (98%; Riedel de Hein), 1,2 dichloro ethane (Rathburn Chemicals), acetic anhydride (reagent grade), magnesium acetate (Fischer), zinc acetate (Merck), aluminum trichloride (Merck), toluene (Merck), methanol (Merck) are used without further purification. 1.7% NaSPS, 2.6% NaSPS, and 4.2% NaSPS are obtained from Exxon laboratories.

Sulfonation of polystyrene

The sulfonation method is a standard procedure performed by forming acetyl sulfonate from sulfuric acid

TABLE I
Demonstration of Theoretical and Experimental-Adiabitic Bomb Calorimeter Combustion Enthalpy Values for SPS

SD mol % (titration)	Theoretical combustion enthalpy (cal/g)	Bomb calorimeter combustion enthalpy (cal/g)
Polystyrene	−10,714	−10,056
3.28	−10,401	−9777
4.38	−10,292	−9521
6.51	−10,089	−9387
7.29	−10,022	−9154

Figure 2 Calorific values versus sulfonation degree of Na-neutralized SPS ionomers.

and acetic anhydride in 1,2-dichloroethane solution of polystyrene.[11]

Neutralization of sulfonated polystyrene ionomer

Neutralization of sulfonated polystyrene was performed in tetrahydrofuran (THF). Zinc, aluminum, and magnesium salts are dissolved in THF and added to SPS solution in the same solvent. The molar ratio of the metal salts to the sulfonic acid groups was 1.5/1.0.[12] The resultant solution is mixed for 2 h at 50°C. It is transferred to deionized water. The ionomers are precipitated, filtered, and dried at room temperature. The solution obtained from filtration is used in AAS measurements to determine the residual metal.

SPS samples in a mixture of toluene/methanol (1/9 v/v) solution, with phenolphthalein indicator, are titrated with 0.02M NaOH solution. NaOH solution is standardized with primary standard potassium hydrogen phthalate according to ASTM E 200–91.[13,14]

Determination of heat of combustion (calorific) value

An IKA-Calorimeter System-C4000 Adiabatic is used for the determination of calorific values. The thermal and thermochemical corrections applied were in accordance with the ASTM D 2015. 30 bar pure oxygen
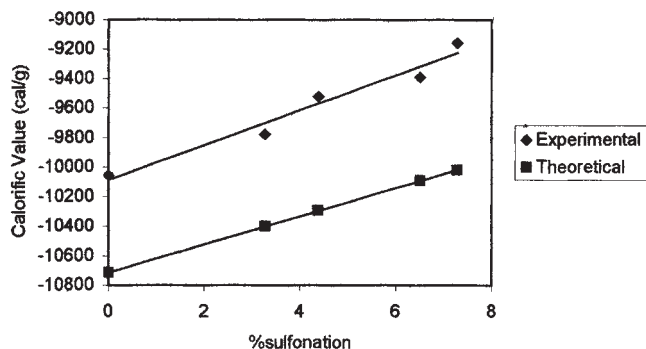

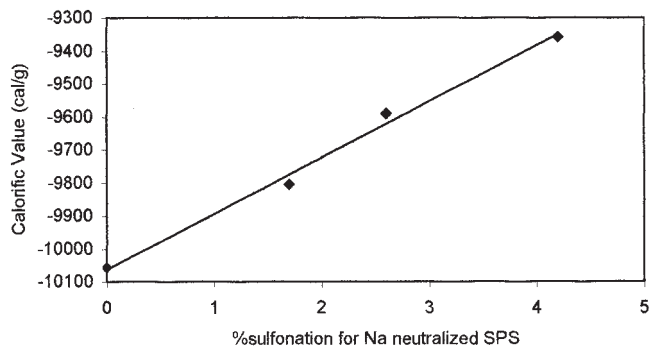**Figure 1** Calorific values versus sulfonation degree of SPS ionomers.

is applied for complete combustion. The heat of combustion produced increases the temperature of the calorimeter. The temperature rise is then measured and serves to calculate the gross calorific value H_o[15,16]. The measurements are corrected according to the equation below

$$Q_v = [(tC) - e_1 - e_2 - e_3] \,/\, g \qquad (1)$$

where

Q_v: gross calorific value (cal/g)

t: corrected temperature rise (°C)

C: heat capacity (cal/°C)

e_1 : correction for the formation of nitric acid (1 mL Na_2CO_3 = 5.56 cal).

e_2 : correction for heat of combustion of ignition wire (1 cm = 0.7 cal).

e_3 : correction for heat of formation of sulfuric acid ($[23.7*S\%*m_{sample}]$/1.8 cal).

g : mass of sample (g)

Sample preparation for atomic absorption spectroscopy

The filtrate solutions are analyzed with AAS. A Varian AA-110 atomic absorption spectrophotometer is used to determine the residual metal, which does not incorporate in ionomer structure. The metal percentage in ionomer structure is calculated according to the equation below

Neutralizing cation%

$$= ((w_{initial} - w_{residual}) \,/\, w_{initial}) \times 100 \quad (2)$$

where

$w_{initial}$: Initial mass of neutralizing cation

$w_{residual}$: Weight of neutralizing cation obtained from residual solution of neutralization by AAS.

TABLE II
Adiabatic Bomb Calorimeter Results for Ionomers

Experimental calorific values of neutralized SPS ionomers (cal/g)			
Sulfonation percentage	Zn-neutralized SPS	Mg-neutralized SPS	Al-neutralized SPS
Polystyrene	10,056	10,056	10,056
3.28	9737	9445	9810
4.38	9497	9359	9746
6.51	9202	8870	9558
7.29	9377	9035	9705

RESULTS AND DISCUSSION

According to NaOH titration results, the degree of sulfonation of SPS species is found as 3.28, 4.38, 6.51, and 7.29 mol % SPS.

Applicability of adiabatic bomb calorimeter for the determination of degree of sulfonation is checked by comparing the titration results with that of theoretical combustion enthalpies from bond energies.

$$\Delta H_{combustion} = \Delta H_{bonds\ formed} - \Delta H_{bonds\ broken} \quad (3)$$

Bond energies of each bond are taken from literature.[17,18] The results of both theoretical and experimental combustion enthalpy values of SPS ionomers are represented in Table I and Figure 1. Figure 2 represents the corresponding enthalpy values of Na neutralized 1.7, 2.6, 4.2% SPS ionomers.

The main reason for choosing adiabatic bomb calorimeter for the determination of the degree of sulfonation was that the adiabatic bomb calorimeter results are expected to reflect how strongly the atoms are held to each other. The results of the theoretical calculations show that as the sulfonation degree increases, $\Delta H_{combustion}$ value increases. It is clearly observed that calculated $\Delta H_{combustion}$ values are less than the experimental values, and they both show the same trend as mentioned earlier. Another important observation is that both curves have the same slope, which indicates that adiabatic bomb calorimeter can be used for this
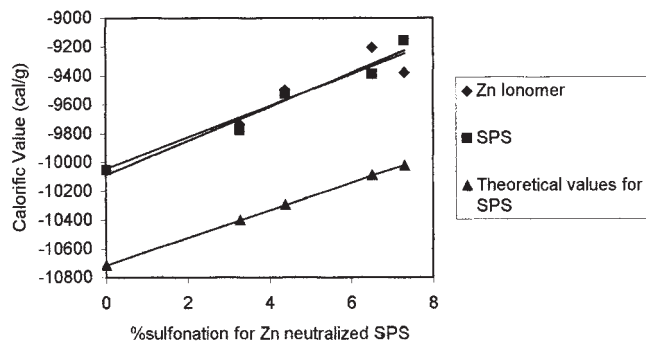
purpose. The difference between theoretical and experimental calorific values is mainly caused by the chemical nature of each bond in the molecule. Structural features of ionic polymers and completely covalent polymers are quite different from each other. The concentration of bound ions is an important parameter for ionomer enthalpies, and the most interesting features of ionic polymers is the state of aggregation of the ionic bonds. Thus, decomposition of ion pairs, ion multiplet, ion-clusters, and aggregates certainly will require more energy and this is why experimental calorific values are higher than the calculated ones.

The effect of different metal cation neutralizations on calorific values is also investigated. Results are shown in Table II and Figures 3, 4, and 5.

It is clearly seen in Figures 3–5 that SPS and Zn-SPS have similar combustion enthalpy values, while Mg-SPS need lower energy to decompose and has a higher combustion enthalpy, and Al-SPS needs higher energy to decompose, thus have a lower combustion enthalpy curve. This behavior is determined by many studies on the basis of different experimentations.[8,18–24] The main parameter that causes the difference between the calorific values of ionomers is the characteristic of the counterions. Their charge to size ratio is an important factor to account for the multiplet size and the strength of the bonds holding the ions together. Al^{3+}
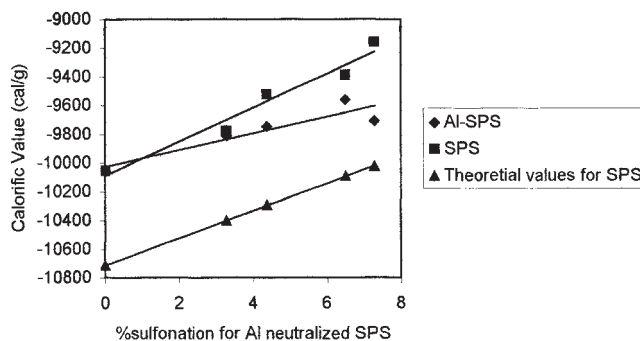

Figure 4 Calorific value of magnesium-neutralized SPS samples.

Figure 3 Calorific value of zinc-neutralized SPS samples.

Figure 5 Calorific value of aluminum-neutralized SPS samples.

has the highest charge and the smallest size. Therefore, it needs the greatest energy to decompose. Then comes Zn^{2+} and SO_3^{2+} and the lowest one is Mg^{2+}.

The sulfonation degree 4.38 mol % SPS and 6.51 mol % SPS are 4.6 and 5.8 mol % according to Figure 1. This result brings us the point that, as long as the ion content of the ionomer is kept below 10%, the relation between sulfonation degree and calorific value obtained from the adiabatic bomb calorimeter results can be used to determine degree of sulfonation of polystyrene.

The ionomer calorific values show another interesting feature that all 7.29 mol % ionomers have a decreasing behavior for calorific value while the general trends of all relations show increasing behavior, as seen in Table II. It can be explained by the aggregation of highly SPS ionomers.

AAS measurements

The amount of metal cation in metal-cation-neutralized SPS is determined by AAS, according to the eq. (2). Table III represents these results.

The neutralization values are calculated according to the difference between the initial amount of metal salt and the final metal cation concentration of the residual solution (eq. (2)). It should be clear that obtained ionomer samples are analyzed with AAS by dissolving a small amount of sample in 1/1 H_2SO_4/H_2O solution. The dissolving attempts were made at 2 and 5 h time periods. The insolubility of metals in the metal-neutralized ionomers is due to the strong interactions inside the ionomer. In addition, metal ions are surrounded by the nonpolar hydrocarbon chain backbone, which has resistivity against acid attack.[25–29]

The average neutralization degree was found in good agreement with the AAS results. However, it is observed that some of the samples showed fluctuations.

CONCLUSIONS

Polystyrene is sulfonated and then neutralized by standard methods. Degree of sulfonation was deter-
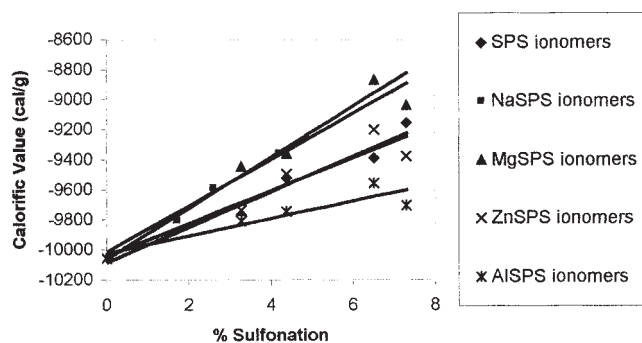

Figure 6 Neutralizing metal effect on calorific value of SPS ionomers.

mined by two methods: titration and adiabatic bomb calorimetry. The results showed that the two methods are in good agreement. As a result, it is concluded that, for the known molecular weight of polystyrene-based SPS samples, the adiabatic bomb calorimetry can be used as a method of sulfonation degree determination.

Metal cation used for neutralizations affected the combustion enthalpy, which lead to different relations between enthalpy and percent neutralizations. Figure 6 summarizes the results and effects of metal-neutralized SPS ionomers.

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TABLE III
AAS Results for Determination of Metal Atoms Involved in Ionomer Structure

Sample SD mol %	Neutralization Mg mol %	Neutralization Zn mol %	Neutralization Al mol%
328	113	83	96
4.38	113	135	95
6.51	96	105	106
7.29	85	97	101

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