# Analysis of Bisphenol A Sulfonate–Carboxylate Polymer

JOHN E. FORRETTE,* JAMES E. BURROUGHS, and CHRISTINE
C. BOOKER,† *Roy C. Ingersoll Research Center, Borg-Warner Corporation,
Des Plaines, Illinois 60018*

Synopsis

The method of analysis for a polycondensation polymer containing the carboxylate and sulfonate functional groups has been devised. A combination of infrared spectroscopy and combustion analysis provides a simple and accurate determination of the monomeric units and their molar distribution in the polymer.

The interfacial polycondensation reaction of the difunctional compounds; bisphenol A, biphenyl disulfonyl chloride, and isophthalyl and terephthalyl chlorides resulted in a polymeric system containing, in the linear chain, the sulfonate and carboxylate functional groups.[1] In conjunction with the studies of the physical properties of this polymer, it was necessary to develop an analytical method for determining the ratios of the sulfonate and carboxylate units.
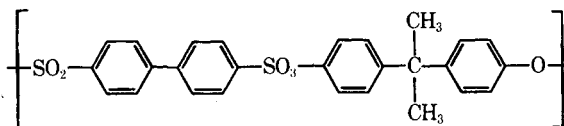
Sulfonate Unit
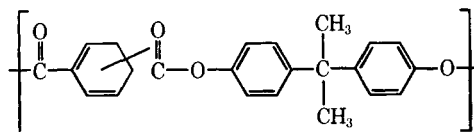
Carboxylate Unit

From the infrared spectrum of the polymer (Fig. 1), assignments could be made for the carboxylate and the sulfonate groups at 5.75 and 7.25 μ, respectively. By using these absorption bands, it was possible to determine the molar ratios of these units in the polymer molecule. A combustion method was also developed for the analysis of total sulfur content of the polymer by use of an induction furnace. This provided an independent

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* Present address: Velsicol Chemical Corp., Chicago, Ill. 60611.
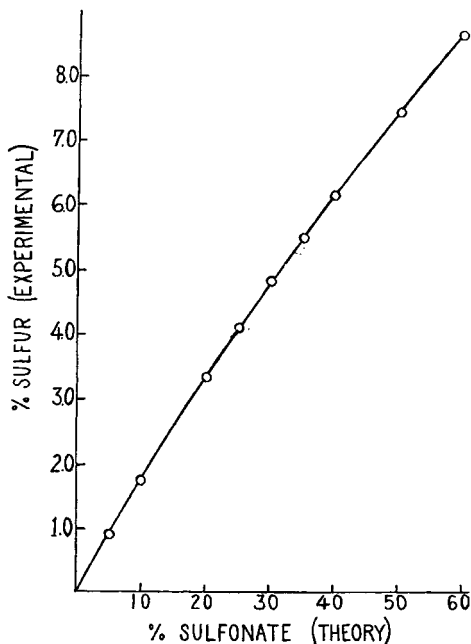† Present address: Zenith Radio Corp., Chicago, Ill. 60639.

Fig. 1. Standard calibration curve.

measure of the sulfonate content, assuming that all the sulfur present was in the form of the sulfonate unit.

EXPERIMENTAL

Apparatus and Reagents

A Beckman Model IR-8 spectrophotometer was employed for the infrared measurements. The instrument settings were: slow scan speed with balance control off and a gain setting of 5. The normal slit program was used during the scan. The polymer was dissolved in reagent grade tetrachloroethane (Fisher Scientific Company), and transmission measurements were made with the use of matched 0.15-mm sealed sodium chloride cells.

The total sulfur analyses were performed by the use of a Leco Model 521 induction furnace in conjunction with a Leco Model 518 semiautomatic sulfur titrator.

Infrared Analysis

Calibration. Two standards were synthesized to contain identical repeat units as were found in the original copolymer. The pure polysulfonate standard was made by polymerizing bisphenol A and biphenyl disulfonyl chloride,[2] which yielded the sulfonate unit (unit weight = 506.5). Likewise, the pure polycarboxylate standard was prepared from bisphenol

A and a mixture of isophthalyl and terephthalyl chloride,[2] which gave the carboxylate unit (unit weight = 358.4).

Solutions of each were prepared using tetrachloroethane as solvent. A plot of absorbance versus concentration of these standards showed that adherence to the Lambert-Beer law was maintained in the range of 1.2–8.2 g/l for the polysulfonate and 0.7–9.1 g/l for the polycarboxylate.

Analysis. The samples were prepared for analysis by weighing 0.25 g into a 25-ml volumetric flask. About 10 ml of tetrachloroethane was then added and the samples allowed to stand for 2 hr. Shaking was avoided during this period because the polymer became jellylike and was difficult to remove from the neck of the flask. When the polymers were dissolved after the initial solvent addition, the remainder of solvent was added to the mark. The flask was then inverted several times for complete mixing.

With solvent in both the sample and reference cells, the transmission was adjusted to 90% at 4.8 μ. The spectrum was then scanned, and absorptions at 5.75 μ for the carboxylate and 7.25 μ for the sulfonate were calculated by using base lines drawn across the minimum absorptions on either side of the above maxima. The base line for the 5.75 μ absorption was drawn from the minimum at 5.6 μ to that at 6.2 μ while that of the 7.25 μ absorption was drawn from the minimum at 7.0 μ to that at 7.5 μ.

Calculations. Since there was essentially no interfering absorption from each group at the analytical wavelengths, it was not necessary to use a matrix solution. From the Lambert-Beer expression:

$$A = abc \tag{1}$$

where A is absorbance, a is absorptivity (in l/g-mm), b is cell path (in mm), and c is concentration (g/l).

The absorptivities of the polysulfonate and polycarboxylate standards were calculated and used for determining these units in the mixed polymer.

To determine the concentration of the sulfonate C_s and the carboxylate C_c in the polymer, the following equations were employed:

$$C_c = A_{5.75\mu}/ab \tag{2}$$

$$C_s = A_{7.25\mu}/ab \tag{3}$$

To check the results for possible errors, it was necessary to determine the total recovery. This was accomplished by adding the concentrations of the sulfonate and carboxylate and then determining the percentage from the original sample concentration.

$$\frac{(C_s + C_c)\,100}{C(\text{sample})} = \%\ \text{recovery} \tag{4}$$

The recovery should be at least 95%. As this value decreased, it indicated increasing sample contamination. Usual sources were impurities and residual solvent. These could be reduced by reprecipitation of the polymer

from methylene chloride solution into methanol and careful vacuum drying.

In order to determine the ratios of the sulfonate unit (SU) to the carboxylate unit (CU), it was necessary to determine the mole per cent of each. This was accomplished by the following:

$$C_c \times 1000/358.38 = CU \text{ (mmol)} \qquad (5)$$

$$C_s \times 1000/506.3 = SU \text{ (mmol)} \qquad (6)$$

$$CU + SU = T \text{ (Total mmol)} \qquad (7)$$

$$CU \times 100/T = \text{mol-\% CU} \qquad (8)$$

$$SU \times 100/T = \text{mol-\% SU} \qquad (9)$$

Combustion Analysis

Calibration. The KIO_3 reagent was prepared by dissolving 0.410 g of reagent KIO_3 in 1 liter of distilled water. The sulfur titer of this titrant was ascertained by analyzing known weights of reagent $AlK(SO)_4)_2 \cdot 12H_2O$ (S = 13.52%). Sample sizes were restricted to the range of 10–12 mg so that the final sulfur reading would be within the buret range. (The buret as supplied with the instrument had a calibration from 0–0.200% sulfur for a 1-g sample.) It was also necessary to employ a factor in order to correlate the buret reading with the true sulfur content of the standard. This factor was calculated from the following expression:

$$\text{Factor} = \frac{\% \text{ sulfur in standard}}{\% \text{ sulfur on buret} - \% \text{ sulfur in reagent blank}}$$

Normally, repetitive analyses were reproducible to within $\pm 0.02\%$ sulfur for a 10-mg sample of the standard.

Analysis. A 10–50 mg sample (depending on the sulfur content) of the finely ground polymer was accurately weighed into a clean, tared ceramic crucible (Leco No. 20). To the crucible were added 1 scoop (Leco) of low-sulfur iron powder and 1 scoop of tin accelerator. A micro nickel spatula was used to thoroughly blend the resulting mixture. The crucible was covered with a porous cover (Leco No. 528) and placed on the pedestal in the furnace. A reagent blank was prepared for each set of determinations. The samples were then analyzed by the conventional technique using an oxygen flow rate of 1.5 l/min. The sulfur content of the samples was calculated from the following expression:

$$\% S = \frac{(\% \text{ sulfur from buret}) \text{ (factor)}}{\text{Wt. sample, g}}$$

The combustion method is subject to interferences of all those elements which, in the process of decomposition, yield easily oxidizable or reducible species. Chief among these interferences would be chloride, nitrogen, and phosphorus, none of which were present in the polymer samples. To

further ascertain the validity of the results from the Leco combustion method, duplicate samples were analyzed by the Schöniger combustion method by using the barium perchlorate–thorin technique.[3] Both procedures yielded identical results, but the Leco method was much more rapid for repetitive analyses.

A test of the quantitative accuracy of the combustion method for organic sulfur compounds was made by analysis of reagents. The results are shown in Table I.

TABLE I
Combustion Analysis of Purified Reagents

| | Sulfur, % | |
Compound	Theory	Found
Bromthymol Blue	5.14	5.17
Phenylbenzene sulfonate	13.69	13.69

RESULTS AND DISCUSSION

Both of these methods of analysis were developed and used because each has inherent advantages not shared by the other. When it was possible to apply both, greater accuracy in the analytical data could be obtained.

In general, it was found that the combustion method gave greater accuracy (Table II) with samples which were essentially free of interferences. One difficulty which was discovered and overcome was that the sulfur content was not linearly related to the sulfonate unit content. Known blends of 100% sulfonate and 100% carboxylate polymers were prepared and analyzed for total sulfur. A working curve was then obtained by plotting the percent sulfur versus the per cent sulfonate as shown in Figure 2.

TABLE II
Comparison of Methods for Sulfonate Content

| Sample sulfonate, % | Sulfonate found, % | |
	Combustion	Infrared
30	29.3	31.6
35	36.0	36.6
40	39.8	42.1

Though the infrared method was somewhat less accurate, it did provide a direct measurement of the carboxylate as well as the sulfonate units. Use of the total recovery data provided a means of determining the purity of the polymer. This was not possible with the combustion method. Residual solvent was found to be the usual impurity; however, some cases were found where reactants and other products were present. The infrared method was superior for detecting these undesirable components.
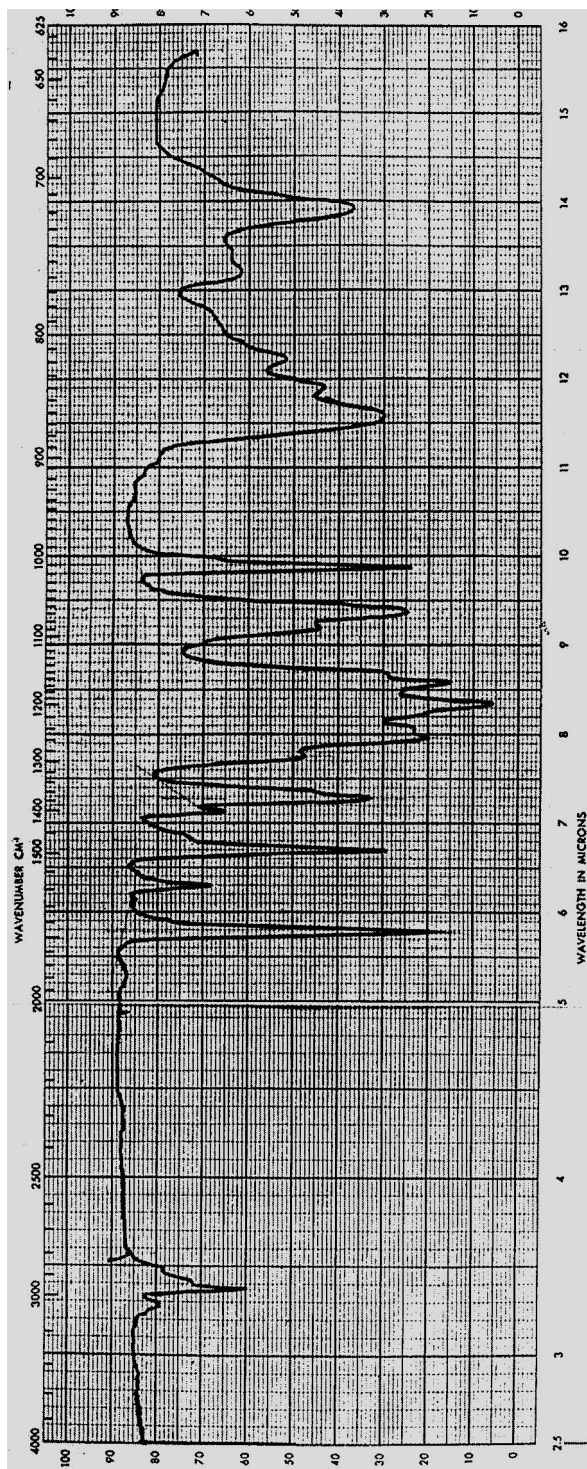
Fig. 2. Infrared spectrum of bisphenol A sulfonate–carboxylate polymer.

To compare both methods, some specially prepared condensation polymers were highly purified by reprecipitation and careful drying. These samples were analyzed and the results are shown in Table II. As can be seen, the combustion method gave values nearer to the expected sulfonate contents. Precision studies by combustion showed a value of $\pm 0.03\%$ sulfur (ca. 0.3% sulfonate) while infrared gave $\pm 0.5\%$ sulfonate.

A series of 29 condensation polymers which were prepared to contain 30% sulfonate were analyzed by both methods. The average difference between the two methods for these samples was 0.6%.

Both methods have been applied to many samples of these condensation polymers and have been useful in following the progress of the reaction. The infrared method was employed generally for all samples with combustion analysis used in cases where supplemental data were desired.

References

1. E. P. Goldberg and F. Scardiglia (assigned to Borg-Warner Corporation), U.S. Pat. 3,262,914 (1966).

2. P. W. Morgan, *Condensation Polymers: By Interfacial and Solution Methods*, Interscience, New York, 1965.

3. J. M. Corliss, GRDLR 3130 U.S. Army Chem. Corps R&D Comd., Army Chemical Center, Md. (April 1, 1952).