

Ionomers: The Sodium Salt of Poly(ethylene-co-Methacrylic Acid)

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Synopsis

A chemical method and an improved absorbance ratio method are presented to determine the degree of neutralization of poly(ethylene-co-methacrylic acid). Compared to the chemical method, the absorbance ratio method is simple and fast. It can be used also to determine the degree of neutralization when the chemical method is not suited to the system. By means of this absorbance ratio method, the influences of various reaction conditions on the rates of neutralization were observed. In the neutral system at the optimal water content a maximal rate of neutralization is obtained. The rate of neutralization is increased by increasing the temperature or the concentration of metal hydroxide or by decreasing the concentration of the copolymer.

INTRODUCTION

Polybutadiene was modified by including a few mole percent of acrylic acid to yield an ion-bearing copolymer which could be cured, for example, by a zinc compound.^{1,2} Later the term "ionomer" was used to describe a similar copolymer of ethylene with methacrylic acid which could be cured or crosslinked by a divalent cation.³ The methacrylic acid content was limited to a few percent and the preferred product was neutralized by zinc and sodium ions. This was produced with the trade name Surlyn. (E. I. duPont de Nemours & Co. Inc.).

In the course of time⁴ the term ionomer came to be applied to many hydrocarbon backbones carrying pendant acid or other groups, usually less than 10% which were partially or completely neutralized to form salts.

Such an attractive system has resulted in several lines of study. The change in physical properties relative to the parent polymer^{4,5} include increases in the glassy transition temperature, modulus, viscosity, rigidity, yield strength, and ultimate tensile strength. These properties can be changed by altering the parent copolymer, the nature and concentration of the reactive groups, the cations, and the degree of neutralization.

Other studies have been on the methods of synthesis of the ionomer salt form from the parent copolymer, whether by an homogeneous or heterogeneous technique, with or without a solvent for one or both of the reactants.

One problem is the precipitation of a crystalline or insoluble polymer at reduced temperature or when water or methanol solvents are used with sodium hydroxide or methoxide respectively. These problems are overcome by a modification to be described.

Particular emphasis has been placed on the aggregation of the carboxyl or carboxylate group into dimers, multiplets, or clusters.⁵⁻⁸

For the above investigations a means of analysis for the amount of ionic group present and the degree of neutralization is desirable. A chemical method^{6,9,10} for analysis of the acid groups which have not been neutralized has been used. When this technique is applied to the ionomer from ethylene and methacrylic acid, some difficulties may arise.

Infrared techniques have been used to identify carboxyl and carboxylic groups.¹¹⁻¹³ Of particular interest is that used by MacKnight et al.¹³ to measure the degree of neutralization. The technique involved the integrated absorbance per centimeter of sample thickness of the 1700 cm^{-1} carbonyl band. The method requires an accurate measurement of sample thickness and the absence of overlap of the neighbouring bands. An alternative infrared technique is described later. In this technique the degree of neutralization is calculated from the ratio of the integrated absorbance of the carbonyl vibration at 1700 cm^{-1} to the methylene vibration at 1465 cm^{-1} using a Fourier transform infrared spectrometer, i.e., the methylene vibration acts as an internal standard. This method assumes that Beer's law holds and analyses are confined to the concentrations over which the law is obeyed.¹⁴

Based on this integrated absorbance ratio method, the influences of different reaction conditions on the degree of neutralization within a fixed reaction time were observed.

Continuing studies with cations other than sodium will be reported later and include elemental analyses for cation concentrations.

EXPERIMENTAL

Preparation of Poly(ethylene-co-Methacrylic Acid) from the Ionomer

Copolymer preparation

Surlyn 1650 was used to prepare poly(ethylene-co-methacrylic acid). Surlyn 1650 is an ionomer based on poly(ethylene-co-methacrylic acid) and it is neutralized with sodium and zinc ions. It is reported to contain 4.1 mol % methacrylic acid.

The Surlyn 1650 pellets were finely ground in a grinder (C. W. Brabender Instruments Inc.) and then refluxed in tetrahydrofuran with 1*N* hydrochloric acid for 24 h to produce the completely unneutralized copolymer. The acid form was then precipitated with cold methanol-deionized water (1:1), filtered, washed with more methanol-deionized water mixed solvent, and then freeze-dried at -50°C for more than 24 h.

The purity of the poly(ethylene-co-methacrylic acid) was checked by its infrared spectrum.¹⁵

Sodium Ionomer Preparation

The poly(ethylene-co-methacrylic acid) was refluxed with tetrahydrofuran containing a little (or no) deionized water and sodium hydroxide to obtain the neutralized copolymer solution. This copolymer solution was precipitated in

cold methanol solvent with agitation using a magnetic stir bar, then filtered, washed several times with more cold methanol, and freeze-dried for more than 24 h.

Film Preparation

To prepare a film for infrared measurement, each sample was pressed in a laboratory press using an especially prepared mold at 190°C and 24,000 psi for several minutes. These films were thin enough to be within the range in which Beer's law is obeyed.¹⁴

After each pressing, the mold with the film sample was quenched in liquid nitrogen in a desiccator over anhydrous CaSO₄ to avoid moisture. The films were stored in the desiccator over silica gel or anhydrous CaSO₄ prior to infrared spectral measurements.

Method

Chemical Analysis Method

In the ionomer based on poly(ethylene-co-methacrylic acid) the main portion of the segments are ethylene. It is a semicrystalline system and not easy to dissolve. To dissolve this ionomer, heating should be used with a suitable solvent. On the other hand, it is easy to precipitate the polymer during titration with sodium hydroxide solution or sodium methoxide solution because both water and methanol are precipitating agents for this copolymer. In order to avoid the appearance of a precipitate during titration, sodium methoxide solution was chosen as a titration agent because it can be evaporated to dryness with a flow of nitrogen¹¹ at a temperature above the boiling point of methanol (64–65°C).

About 0.02 g of poly(ethylene-co-methacrylic copolymer) was refluxed in 30 mL toluene-isobutyl alcohol (75 mL:25 mL) mixed solvent with heating and stirring under nitrogen in a three-neck flask. After the polymer dissolved completely, titration of the acid groups was conducted with 0.0225*N* sodium methoxide solution at 70°C under nitrogen using phenolphthalein as indicator, at the same time leaving a gap in the flask for escaping methanol vapor. The sodium methoxide solution was standardized by standard acid. A blank titration for 30 mL toluene-isobutyl alcohol mixed solvent is necessary under the same conditions mentioned above before calculating the degree of neutralization.

FTIR

The infrared spectrum of each sample was obtained on a Nicolet 60SX FTIR spectrometer. The spectrum was scanned between 1400 and 1800 cm⁻¹ at a resolution of 4 cm⁻¹. The spectra were stored on a magnetic tape system. The absorbance ratio was calculated by integrated peak areas in the ranges 1750–1635 cm⁻¹ for the carbonyl vibration and 1495–1426 cm⁻¹ for the methylene vibration. Studies of dichroism of the polymer¹³ were not included. The films should be completely relaxed and isotropic.

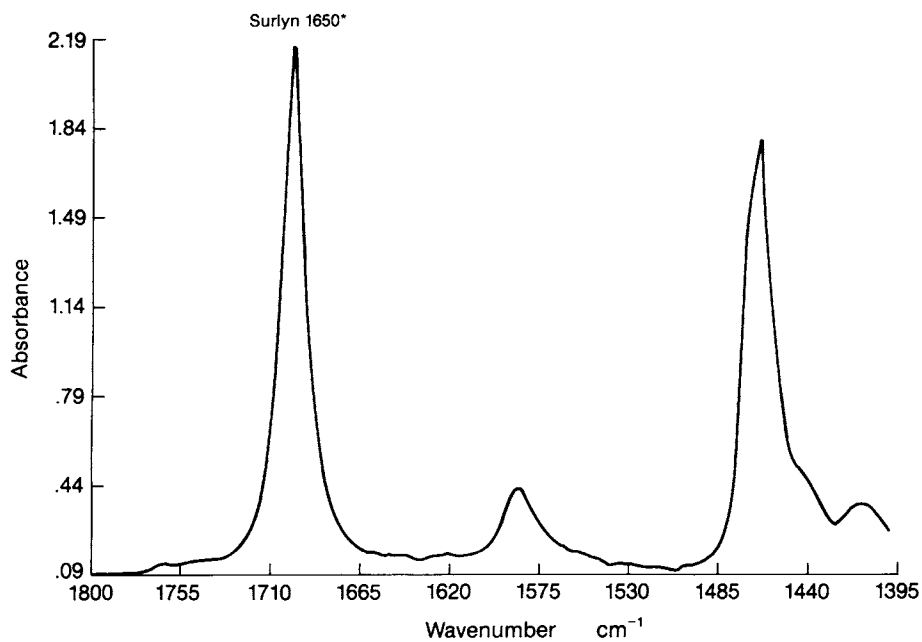


Fig. 1. Infrared spectrum of Surlyn 1650.

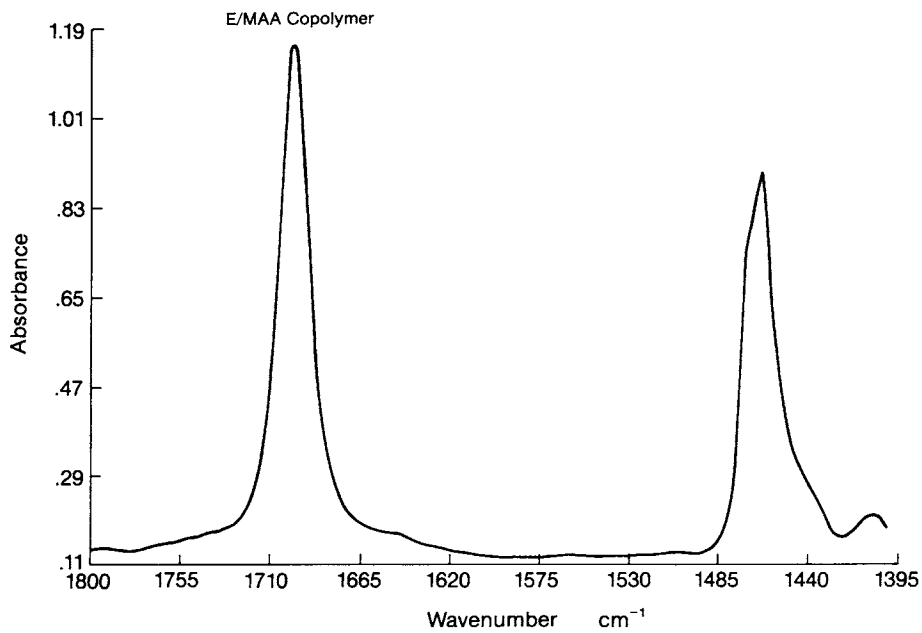


Fig. 2. Infrared spectrum of poly(ethylene-co-methacrylic acid).

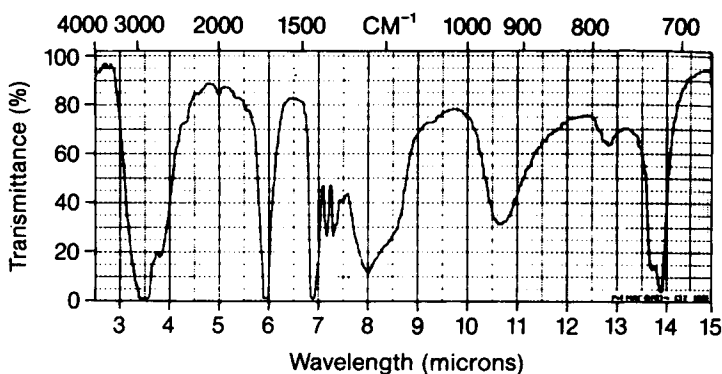


Fig. 3. Infrared spectrum of poly(ethylene-co-methacrylic acid).¹⁵

Procedure

In order to observe the influence of different reaction conditions on the degree of neutralization within a fixed time, the components or the reaction conditions of the reacting system were changed while following the procedure mentioned above.

In order to study the relationship between the integrated absorbance ratio of $1700\text{ cm}^{-1}/1465\text{ cm}^{-1}$ and the degree of neutralization, the degree of neutralization of different samples was measured both by the infrared ratio method and by the chemical method.

RESULTS AND DISCUSSION

Preparation of Poly(ethylene-co-Methacrylic Acid)

Figures 1 and 2 show the infrared spectra of Surlyn 1650 and of prepared poly(ethylene-co-methacrylic acid) respectively, and Figure 3 shows the standard spectrum of poly(ethylene-co-methacrylic acid).¹⁵ By comparing these figures it can be seen that the copolymer obtained from Surlyn 1650 is pure.

Absorbance Ratio Method to Determine the Degree of Neutralization

The Relationship between the Degree of Neutralization and the Absorbance Ratio of $1700\text{ cm}^{-1}/1465\text{ cm}^{-1}$

Figure 4 shows the FTIR spectra of samples which were neutralized to different degrees. The absorbance by the carbonyl vibration at 1700 cm^{-1} decreases gradually with neutralization while the absorbance by the methylene vibration at 1465 cm^{-1} remains almost the same during the neutralization. The peak for the carbonyl group vibrations which have not been neutralized shifts to the right.

A relationship between the degree of neutralization and the absorbance ratio of carbonyl to methylene can be obtained. In Figures 5 and 6 A_1 and A_3 are the absorbance of the carbonyl vibration and the methylene vibration, respectively, in each sample which was neutralized partially or completely; A_1'

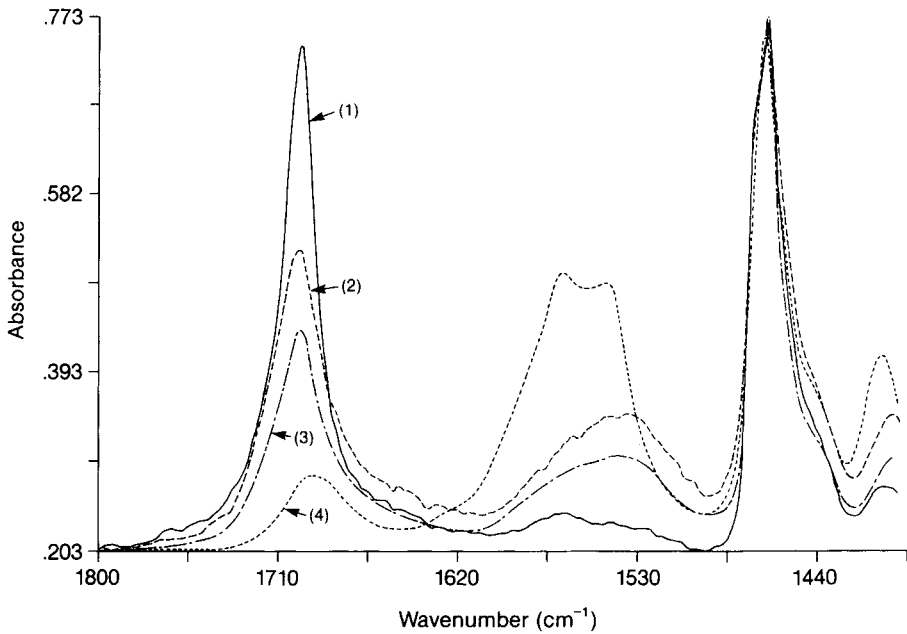


Fig. 4. Infrared spectra of poly(ethylene-co-methacrylic acid) neutralized to different extents with sodium: (1) 10.0%; (2) 28.8%; (3) 44.6%; (4) 80.8%.

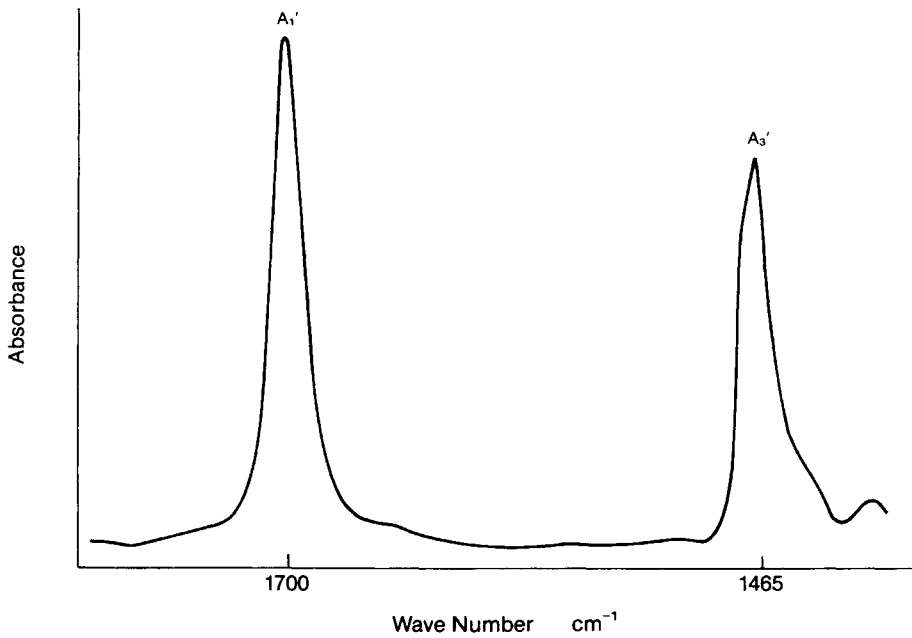


Fig. 5. The absorbance vs. wave number for poly(ethylene-co-methacrylic acid).

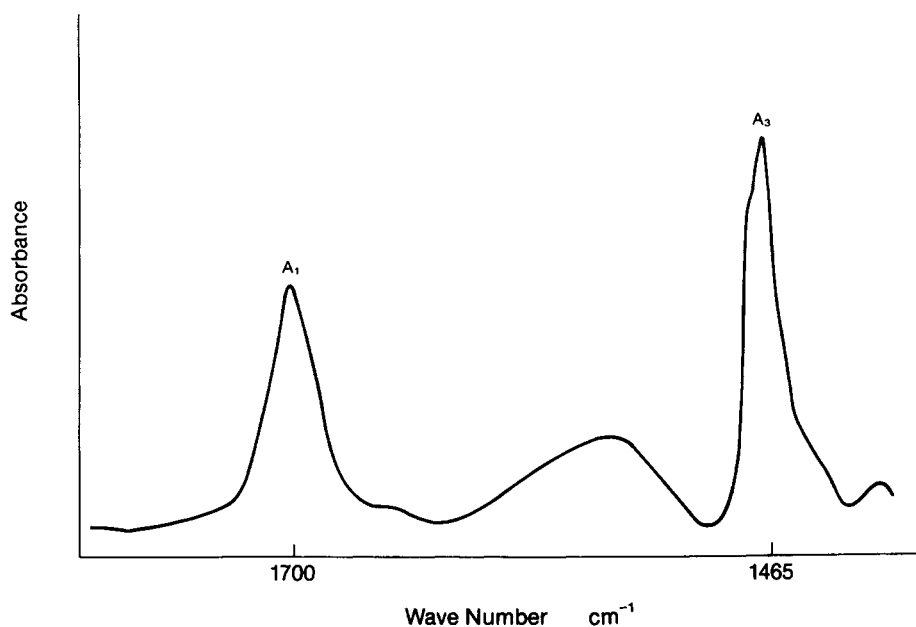


Fig. 6. The absorbance vs. wave number for the samples which were neutralized partially or completely.

and A'_3 are the absorbance of the carbonyl vibration and the methylene vibration respectively for the sample of poly(ethylene-co-methacrylic acid). $A = abc$ is Beer's law, where A is absorbance, a is a constant specific for the substance at a particular frequency, b is the thickness of the sample, and c is the concentration of the substance. Therefore,

$$A'_1 = a'_1 b'_1 c'_1, \quad A'_3 = a'_3 b'_3 c'_3,$$

$$\text{and } b'_1 = b'_3 \quad (\text{for the same thickness of sample})$$

$$A_1 = a_1 b_1 c_1, \quad A_3 = a_3 b_3 c_3,$$

$$\text{and } b_1 = b_3 \quad (\text{same thickness})$$

Then

$$\frac{A_1}{A_3} = \frac{a_1}{a_3} \cdot \frac{c_1}{c_3} \quad \text{and} \quad c_1 = \frac{A_1}{A_3} \cdot \frac{a_3}{a_1} \cdot c_3 \quad (1)$$

$$\frac{A'_1}{A'_3} = \frac{a'_1}{a'_3} \cdot \frac{c'_1}{c'_3} \quad \text{and} \quad c'_1 = \frac{A'_1}{A'_3} \cdot \frac{a'_3}{a'_1} \cdot c'_3 \quad (2)$$

The degree of neutralization (DN) is

$$DN = \frac{c'_1 - c_1}{c'_1}$$

where c'_1 is the concentration of carbonyl group in the poly(ethylene-co-methacrylic acid), and

$$DN = 1 - \frac{c_1}{c'_1}$$

where c_1 is the concentration of carbonyl group in the poly(ethylene-co-methacrylic acid) sodium ionomer.

Replacing c_1 and c'_1 by (1) and (2), respectively,

$$DN = 1 - \left(\frac{A_1}{A_3} \cdot \frac{a_3}{a_1} \cdot c_3 \right) / \left(\frac{A'_1}{A'_3} \cdot \frac{a'_3}{a'_1} \cdot c'_3 \right)$$

Because a'_1, a_1 and a'_3, a_3 represent the same specific substance (carbonyl group and methylene group, respectively), a_1/a_3 should be equal to a'_1/a'_3 .

c'_3 and c_3 represent, respectively, the concentration of methylene groups in the poly(ethylene-co-methacrylic acid) and in the samples which were neutralized to different degrees. It is supposed that c_3 is equal to c'_3 because the methylene vibration at 1465 cm^{-1} will not be affected significantly during the neutralization. Thus

$$DN = 1 - \frac{A_1/A_3}{A'_1/A'_3} \quad (3)$$

where the value of (A'_1/A'_3) is a constant for the poly(ethylene-co-methacrylic acid) which was obtained from Surlyn 1650. The value is 1.30 in this study.

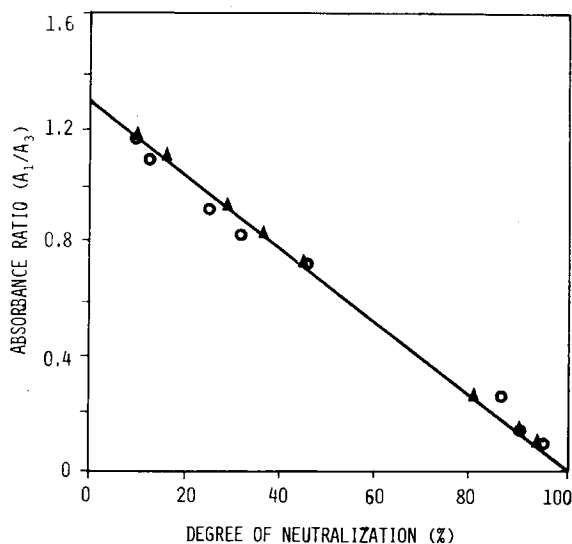


Fig. 7. Comparison of absorbance ratio and chemical analysis methods with theoretical line from Eq. (3): (Δ) degree of neutralization calculated from the absorbance ratio; (\circ) degree of neutralization determined by chemical analysis method plotted at the corresponding absorbance ratio.

TABLE I
The Degree of Neutralization of Different Samples Determined Using the Absorbance Ratio Method and Chemical Analysis Method

Ionomer sample	Degree of neutralization (%)		
	Absorbance ratio method		Chemical analysis method
	Ratio of A_1/A_3	Value	Value
1	1.17	10	10
2	1.10	16	13
3	0.93	29	25
4	0.83	36	32
5	0.72	45	45
6	0.25	81	85
7	0.12	91	91
8	0.08	94	95

When $DN = 0$,

$$A_1/A_3 = A'_1/A'_3 = 1.30$$

When $DN = 1$

$$A'_1/A'_3 \neq 0$$

then

$$A_1/A_3 = 0$$

The relationship between DN and (A_1/A_3) is a straight line according to eq. (3).

The absorbance ratio of the carbonyl vibration to methylene vibration vs. degree of neutralization is shown in Figure 7. The line is calculated from eq. (3). The degree of neutralization of the samples was calculated not only by the absorbance ratio method but also chemically. The results are presented in Table I and show that the absorbance ratio method can be used to determine the degree of neutralization accurately.

The Advantages of the Absorbance Ratio Method

There are many publications on the solvent shifts of the infrared absorption peaks, including the series of articles by Bellamy et al. and comments on them (cf. Ref. 16). Recently Fowkes et al.¹⁶ studied these concepts in relationship to "polymer shifts" of the infrared absorption peaks.

There are two interactions of polymers with neighbouring molecules, the London dispersion forces and the Lewis acid-base interactions. That the Lewis acid-base interaction in liquids is independent of dipole moment and is operative only when a basic site interacts with an acidic site has been found by Fowkes et al.¹⁶

In the sodium salt of poly(ethylene-co-methacrylic acid) the spectral shifts are also found. This phenomenon can be interpreted as follows: As the degree of neutralization increases the multiplets and clusters will be formed gradu-

ally.¹⁷ These multiplets and clusters form a local polar environment. They possess the ability to accept electrons because clusters and multiplets involve metal cations (Na^+). The unneutralized carboxyl groups are basic (electron donors) and they extend to complex with the acid (electron acceptors). The higher the percent neutralization, the stronger the acid so that they will become gradually sufficiently acidic to form significant acid-base complexes. Thus the phenomenon of the acid-base shift of the infrared absorption peaks in ionomers appears.

Since it is observed that spectral shifts exist in ionomers,¹⁸ it is reasonable to calculate the absorbance ratio by using integrated absorbance peak area rather than by using the integrated absorbance peak height for determining the degree of neutralization, because the integrated absorbance peak area calculated from 1750 to 1635 cm^{-1} includes all of the shifted peaks.

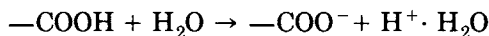
The method described above is a ratio method, independent of film thickness. All that is required is that the sample be in the form of a film which is easy to realize for this material. The time required for analyzing a sample for determining the degree of neutralization by this ratio method is about 10 min compared to about 2 h by chemical analysis. In addition to the advantages mentioned above, there are times when it is difficult to find a suitable solvent to dissolve the ionomer sample. Thus this absorbance ratio method is a good way to analyze the degree of neutralization quantitatively.

This ratio method to determine the degree of neutralization could be applied to any kind of ionomer but each ionomer needs to include two characteristic groups. One varies in absorbance and the other is unchanged in absorbance basically during the neutralization. The ratio method could be used for any reactive group in the raw material from which the ionomer was obtained.

The Influence of Reaction Conditions on the Rate of Neutralization

Water Content

The mole ratio of $\text{H}_2\text{O}/-\text{COOH}$ was changed from 0, 25, 50, 75, and 100 and other conditions were unchanged. There are three functions of water in the neutral system. The carboxyl groups can be ionized by water:



It is easier for ($-\text{COO}^-$) than ($-\text{COOH}$) to combine with sodium cation. Thus water favors the neutralization. From Figure 8 it can be seen that a little water is very helpful in increasing the rate of neutralization.

On the other hand, water is a poor solvent for the poly(ethylene-co-methacrylic acid) polymer. The shape of the macromolecule will be more coiled in the presence of water. In this case the reactive groups may be screened. This would not be favorable for neutralization. Thus there is an optimal amount of water that is not only favorable for carboxyl group ionization but also favorable for macromolecule shape in the solution. From

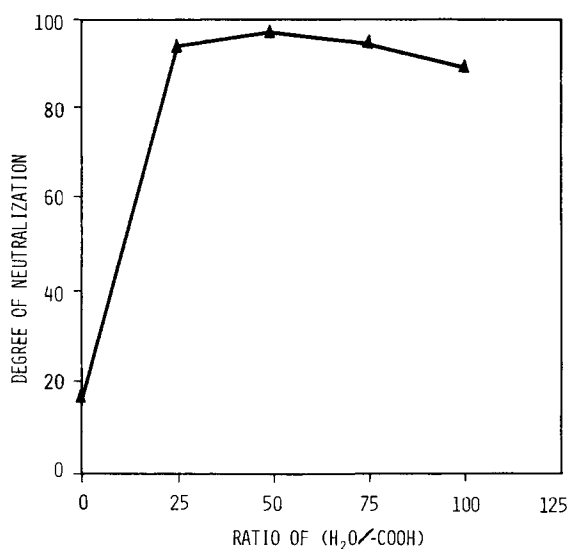


Fig. 8. The influence of mole ratio of water on the rate of neutralization.

Figure 8 it can be seen that the mole ratio of water to carboxyl group is optimal in the range of about 50.

Of course, sodium hydroxide can be ionized in water in this system, but the solubility of sodium hydroxide in hot water is 347 g/100 cc. Accordingly it can be estimated that all the sodium hydroxide in these systems will be ionized by the smallest amount of water. It means that the influence of water on the rate of neutralization is dependent on the ionization of the carboxyl group and on the macromolecular shape in the solution.

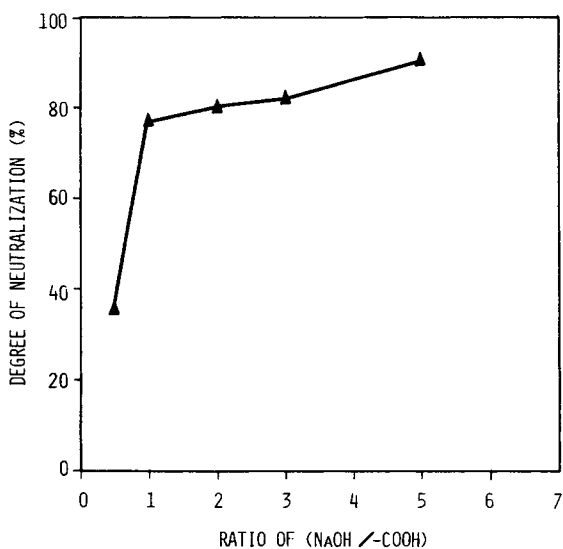


Fig. 9. The influence of mole ratio of sodium hydroxide on the rate of neutralization.

Sodium Hydroxide Content

The mole ratio of sodium hydroxide to carboxylic group was varied from 0.5 to 1, 2, 3, and 5 while other conditions were unchanged. The results of the influence of sodium hydroxide content on the rate of neutralization are shown in Figure 9. From Figure 9 it can be seen that the higher the concentration of sodium hydroxide, the faster the rate of neutralization. Sodium hydroxide is a small molecule. If the concentration of sodium hydroxide is high, it will increase the chances of collision with the carboxyl group, thus increasing the rate of neutralization.

The Local Concentration of Copolymers

In this reaction system it was of interest to know the effect of polymer concentration on the rate of neutralization. The experiments were done by changing only the concentration of copolymer, keeping other reaction conditions unchanged for the same reaction time, to get the absorbance ratios A_1/A_3 , shown in Figure 10. It was found that the concentration of copolymer influenced the rate of neutralization. The higher the concentration of copolymer, the lower the rate of neutralization if the concentration of copolymer is above 0.5%.

Temperature

In general, neutralization is an exothermic reaction. Raising the temperature should not favor the reaction. On the other hand, the ionomer based on poly(ethylene-co-methacrylic acid) is semicrystalline. Generally semicrystalline polymers dissolve more easily at temperatures close to their melting points. Thus raising the reaction temperature is favorable for dissolving this kind of copolymer. It was of interest to determine the influence of temperature on the rate of neutralization.

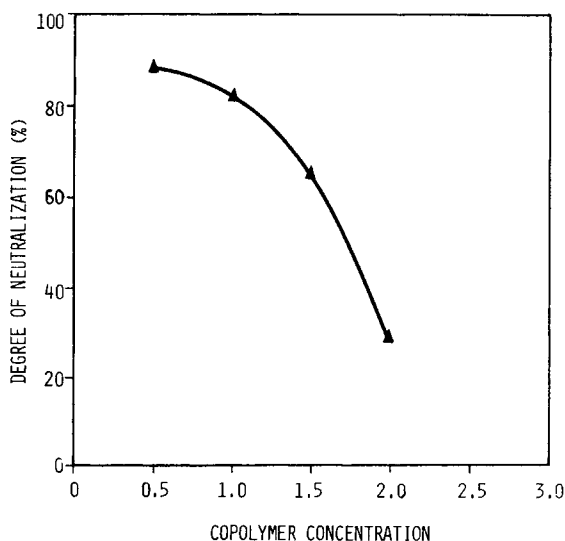


Fig. 10. The influence of concentration of copolymer on the rate of neutralization.

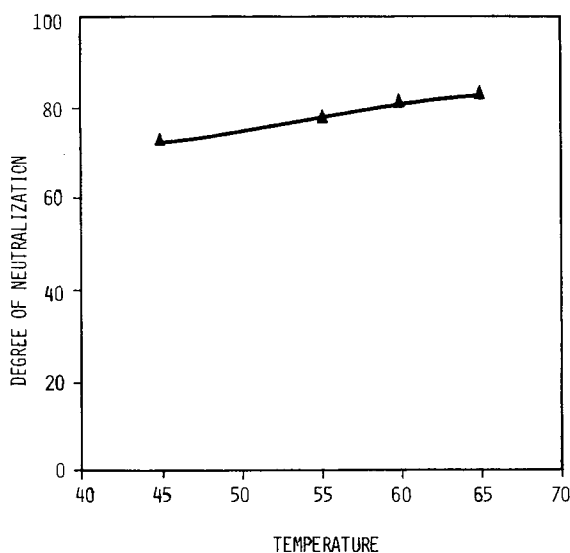


Fig. 11. The influence of temperature on the rate of neutralization.

The experimental results are that the rate of neutralization increased with temperature increase and the exothermal effect can be ignored. These results are shown in Figure 11.

In this system THF was chosen as a solvent. Its boiling point is 65°C. Thus the highest reaction temperature at atmospheric pressure is 65°C. The melting point of the copolymer is 100°C. Although it would be impossible to raise the temperature above 65°C to increase the rate of neutralization, there were several reasons to choose THF as solvent.

(1) The solubility parameter of THF is close to that of the copolymer. Thus it will dissolve this copolymer.

(2) Although the solubility parameters and polarities of several mixed solvents, for example, toluene and isobutyl alcohol (75 mL:25 mL) and benzene and dioxane (80 mL:20 mL), are close to that of THF, the boiling temperatures are higher than that of THF, which suggests that, although the reaction temperature could be raised, it would not be as easy to choose precipitating agents for these complex copolymer systems as it would be to choose a method for precipitation from THF.

(3) The toxicity is lower for THF than for the other solvent systems mentioned above.

Thus THF is favored as solvent and the highest reaction temperature is 65°C for this reaction system.

CONCLUSIONS

In order to determine the degree of neutralization of the ionomer based on ethylene and methacrylic acid, a chemical method and an absorbance ratio method are presented. Compared to the chemical method, the absorbance ratio method is simple and fast. It can be used to determine the degree of neutralization when the chemical method is not suitable.

By means of this ratio method it is easy to compare different reaction systems in order to determine their influence on the rate of neutralization. These results are:

1. In the neutral system when the water content is optimal (the mole ratio of water to carboxyl group is about 50) a maximal rate of neutralization can be obtained.
2. The rate of neutralization was increased by increasing the temperature or concentration of metal hydroxide or by decreasing the concentration of copolymer.

The authors wish to thank Francis V. Lambert for valuable suggestions on infrared analysis. This study was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

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Received March 10, 1988

Accepted July 29, 1988