

Characterization of Ionomer Solutions. I. Division of the Concentration Region and Viscosity–Concentration Functions

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ABSTRACT: The solution behavior of metal maleate low density polyethylene graft ionomers (LDPE-*g*-MAMe) in extremely dilute and dilute solutions was investigated in this study. The concentration region was divided into three parts because of the different viscosity–concentration relations of these ionomers. The η_{sp}/C – C relations of zinc maleate low density polyethylene graft ionomers (LDPE-*g*-MAZn) were studied in detail and compared with those of low-density polyethylene and low-density polyethylene-*g*-maleic anhydride. Finally, the viscosity–concentration relations of LDPE-*g*-MAMe (Na, K, La) were also studied and compared with one another. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1481–1486, 2001

Key words: ionomers; solution behavior; extremely dilute solution; reduced viscosity

INTRODUCTION

Ionomers are an interesting class of high polymers that have been widely studied over the last few decades. In the course of time, the term *ionomer* has come to refer to many hydrocarbon backbones carrying pedant acid or other groups, usually less than 15 mol %, that are partially or completely neutralized to form salts. Such an attractive system has resulted in several lines of study. The presence of ionic groups and their interactions produces a physical type of crosslinking between chains; and the induced changes that occur in the microstructure and physical properties have received considerable attention in the literature.

Many different experimental techniques have been used for investigating the structure of ionomers. These include small-angle X-ray scattering, small-angle neutron scattering, dynamic mechan-

ical thermal analysis, electron spin resonance, transmission electron microscopy, Raman spectra, annealing results, Fourier transform infrared spectra, and theoretical analysis. Reviews of these studies and the possible influence of the altered microstructure on such phenomena as the glass-transition temperature, melt viscosity, rheological behavior, and mechanical behavior are available.^{1,2}

However, relatively little attention has been given to the solution behavior of ionomers, especially with respect to their viscometric properties.^{3,4} This is surprising given the importance of ionomers and the relative ease with which the acid forms dissolve in nonpolar solvents. Dilute solution viscosity and light-scattering experiments have indicated that the aggregation of the acid groups is weaker than that of the salt groups. A detailed study on the effect of the temperature and concentration on the mechanism of aggregation in these systems has not been done, although it would be of particular interest not only because of its direct application but also because of its fundamental role in our understanding of poly-

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mer segment–segment and segment–solvent interactions.

In recent years, experimental and theoretical works have established the existence of three concentration regimes of macromolecular solutions: dilute, semidilute, and concentrated.^{5–7} Dondos and coworkers⁵ obtained viscometric results with various polymer–solvent systems. They introduced a concept of a critical concentration in macromolecular solutions, which they called C^{**} and which separates very dilute and dilute solutions. The well-known critical concentration C^* , which lies above the concentration C^{**} , separates dilute and semidilute solutions. Lundberg and coworkers⁸ observed that at low polymer concentrations, the reduced viscosity of salts of sulfonated polystyrene (SPS) in nonpolar solvents was lower than that of unmodified polystyrene. A crossover in the viscosities of the two solutions was observed at a certain polymer concentration and interpreted as a changeover from intramolecular association at low concentration to intermolecular association at higher concentrations.

In this article, we mainly report on the very dilute and dilute solution behavior of ionomers based on metal maleate low density polyethylene graft ionomers (LDPE-*g*-MAMe). A detailed viscometric study of very dilute solutions of LDPE-*g*-MAMe permitted us to observe a crossover of the variation of the reduced viscosity of the polymer solution as a function of the concentration of the ionomers. At the same time, several other factors that influenced the viscosity of the solution were also investigated.

EXPERIMENTAL

Material

The low-density polyethylene (LDPE; 1I2A-1, $M_n = 9.2 \times 10^4$) and maleic anhydride (MAH) employed in this work were commercial products. The mixed solvent was a mixture of tetrahydronaphthalene (**A**), 1,1,2,2-tetrachloroethane (**B**), and *N,N*-dimethyl acetamide (**C**).

Solution Preparation

The detailed preparation method and the determination of the grafting degree (G) have been described elsewhere.⁹ Different metal hydroxides were used to neutralize MAH to obtain metal ionomers. Samples with various degrees of neu-

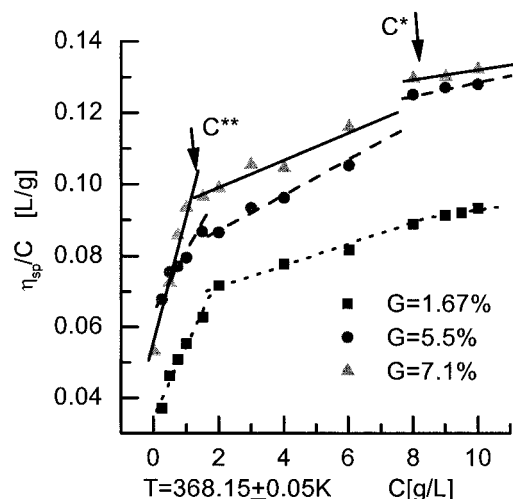


Figure 1 Variation of reduced viscosity as a function of concentration for LDPE-*g*-MAZn ($T = 368.15 \pm 0.05$ K).

tralization were collected during the process of chemical reactions. Each sample was precipitated in acetone, filtered, washed several times with more acetone, and dried *in vacuo* at 70°C for more than 24 h. The samples were characterized by infrared, and characteristic peaks of maleate ($1500\text{--}1680\text{ cm}^{-1}$) were found instead of characteristic peaks of MAH ($1700\text{--}1900\text{ cm}^{-1}$), which implied that the samples were purely ionomers.

Viscosity Measurements

Ionomers of different G (mmol/100 g of LDPE) and different cations were dissolved in the mixed solvent (**A**:**B**:**C** = 65.8:15:19.2); then, they were diluted to different concentrations.

Viscosity measurements were carried out in a high-temperature Ubbelohde-type capillary viscometer. The temperature was controlled to within 0.05°C with a high-isotemperature apparatus that was made in our lab. The reproducibility of the flow times was almost perfect, and the errors were about $\pm 0.01\%$.

RESULTS AND DISCUSSION

Division of the Concentration Region of Ionomers

It is extremely difficult to find an appropriate solvent for ionomers. We tried many solvent systems and empirically chose the mixture of **A**, **B**, and **C** (**A**:**B**:**C** = 65.8:15:19.2) as the solvent system for the LDPE-*g*-MAMe ionomers.

In Figures 1 and 2, we display the variation of

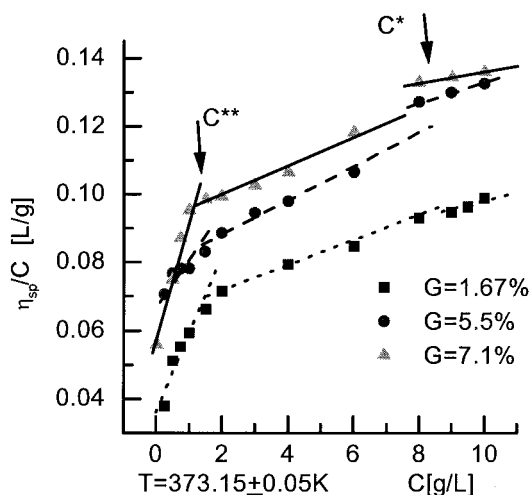


Figure 2 Variation of reduced viscosity as a function of concentration for LDPE-*g*-MAZn ($T = 373.15 \pm 0.05$ K).

reduced viscosity, η_{sp}/C , as a function of concentration, C , of ionomers of different G in the mixed solvent at two different temperatures.

We observed two special crossover points in the concentration regions $C = 1.5\text{--}2.0$ g/L and $C = 8.0\text{--}9.0$ g/L. The two crossover points were then defined as C^{**} for the crossover point in the lower concentration region and C^* for the crossover point in the higher concentration region. The crossover point in the lower concentration region was attributed to a critical concentration C^{**} . Dondos⁷ thought that at this concentration, the chains of the polymer first come into contact, and the coils occupy the entire volume of the solution (it was evident that we had additional volume between the coils in contact). Above this concentration, a compression of the macromolecular coils occurs, and this must be attributed to the resistance of the macromolecular coils to mutual interpenetration. For ionomers, with the concentration increasing, the ion pairs aggregate to form quadruplets, sextuplets, and higher aggregates, collectively called *multiplets*. At any G , there is always a certain ion-pair aggregation form that will predominate. Therefore, at each G there is always a crossover point. This does not exclude the existence of other aggregation forms, which involve different numbers of ion pairs, but these aggregation forms are not dominant. For transition-metal and rare-earth-metal ionomers, there may also exist coordinated effects that include coordination in the coil and between the coils. We considered that at the first crossover point, that is, at the concentration C^{**} , the coordination in the coil would predominate.

The crossover point that appeared in the relatively higher concentration region was called C^* , which was the limit between two regimes: (1) the regime of dilute solutions below C^* , where we had no complete interpenetration of macromolecules, and (2) the regime above C^* , where the coils overlapped and the individuality of the molecules disappeared. For ionomers, more and more multi-plets aggregated together; thus, clusters formed. For transition-metal and rare-earth-metal ionomers, the coordination between coils predominated.

According to these two critical concentrations, we divided the concentration region of ionomers into three parts: $C < C^{**}$, very dilute solution; $C^{**} < C < C^*$, dilute solution; and $C > C^*$, semi-dilute solution.

To explain abnormal behavior of reduced viscosity, someone proposed a hypothesis of adsorption, yet it was short of a quantitative description.¹⁰ Recently, Liu⁴ explained the systematic effect of adsorption on the viscosity of extremely dilute solutions of polymer. However, our results show that the crossover observed in viscosity-concentration curves cannot be attributed to adsorption phenomena because the curves below the critical concentration increased in slope.

Viscosity-Concentration Relations of LDPE-*g*-MAZn Compared with Pure LDPE

The results of a detailed viscometric study of low density polyethylene (LDPE) and zinc maleate low density polyethylene graft ionomer (LDPE-*g*-MAZn) samples in the mixed solution at different temperatures is presented in Figures 3 and 4. As shown in these figures, two rather abrupt changes in the slope of the straight lines representing the variation of the reduced viscosity as a function of the concentration were observed for LDPE-*g*-MAZn samples, although it was still a straight line for LDPE samples. We also noticed that the deviation from the straight line for LDPE samples changed with G of the ionomers and became obvious as G increased. For high G , more and more ion pairs aggregated, and the interactions between them also increased, thus resulting in more deviation from the mother polymer curve.

The reduced viscosity increased with the ionomer concentration. However, with different C and different G , the relation $\eta_{sp}/C-C$ showed two patterns. In the very dilute concentration region, the reduced viscosity of ionomers with low G was lower than that of pure polyethylene. The viscos-

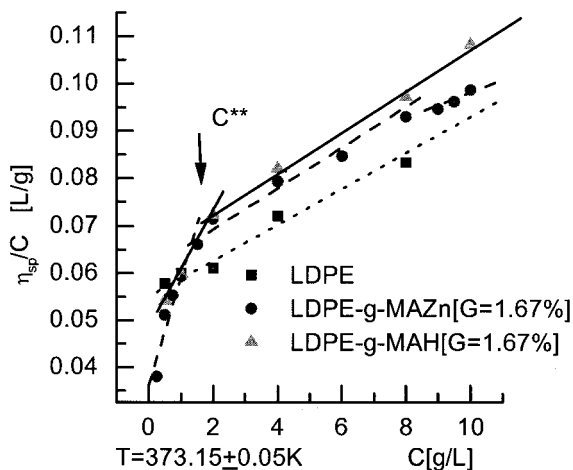


Figure 3 Variation of reduced viscosity as a function of concentration for LDPE, LDPE-g-MAH, and LDPE-g-MAZn ($T = 373.15 \pm 0.05$ K, $G = 1.67\%$).

ity of the polymer solution is basically related to the volume concentration of the polymer particles. In the low-concentration region, the interactions between the ion pairs in the coil of ionomers make the coil shrink. Although the existence of ion groups increases the volume of the coil, the increase is not obvious because of low G . Thus, the total effect was that the coil shrank and the volume of the coil was relatively smaller than that of polyethylene coils. Therefore, the viscosity was relatively low. However, the reduced viscosity of those ionomers with high G was higher than that of polyethylene. The size of the coil may have

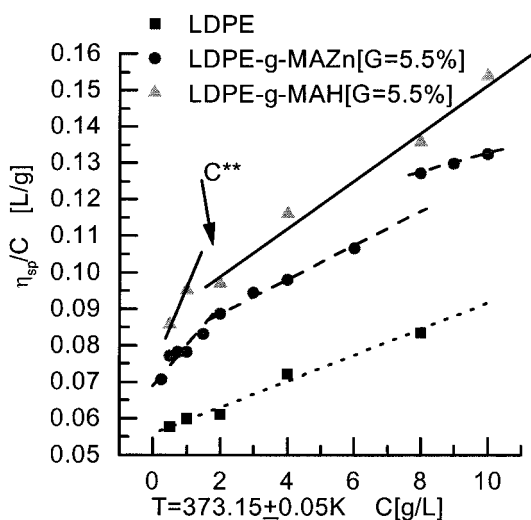


Figure 4 Variation of reduced viscosity as a function of concentration for LDPE, LDPE-g-MAH, and LDPE-g-MAZn ($T = 373.15 \pm 0.05$ K, $G = 5.5\%$).

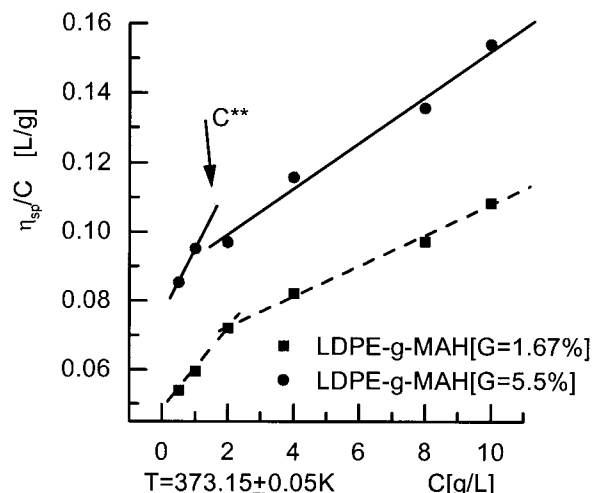


Figure 5 Variation of reduced viscosity as a function of concentration for LDPE-g-MAH ($T = 373.15 \pm 0.05$ K).

been greatly increased by the charge if the concentration of the ions was high enough. This obvious change in the coil sizes led to the increase in the viscosity. In the high-concentration region, the reduced viscosity of ionomers was higher than that of polyethylene solutions. Because the distance between the polymer chains decreased as the concentration increased, the interaction of ions between different polymer chains occurred. There may have existed three kinds of interactions: the association of ion groups, the crosslinking of polymer chains, and the coordination effects. All of these effects made the apparent molecular weight of ionomers higher. As described by the Mark-Houwink equation, the intrinsic viscosity increases with M , so the viscosity of ionomers with high G was higher than that of its mother polymer LDPE.

Compared with LDPE-g-MAH

As shown in Figures 5 and 6, the reduced viscosity-concentration curve displays different patterns for low-density polyethylene-g-maleic anhydride (LDPE-g-MAH) with different G at different temperatures. In these figures, the slope of the η_{sp}/C - C curve of LDPE-g-MAH with low G is small; that is, its η_{sp}/C increases slowly with C . This may be caused by the nonpolar solvent systems we chose. The solvent we used was low polar. According to the principle of polar similarity, this solvent system is a good solvent for low- G ionomers because there are few polar groups on the chain of ionomers with low G . Although more

polar groups graft onto polyethylene, the polarity of the ionomers increases, and the solvent will become bad for high- G ionomers.

As shown in Figures 1 and 2, for LDPE- g -MAZn curves the tendency is the same as that for LDPE- g -MAH; that is, η_{sp}/C increases slowly with C in the low-concentration region and quickly in the high-concentration region.

Near the critical concentration, the influence of G on η_{sp}/C was small. We think that G influenced η_{sp}/C in two aspects: (1) with more polar groups, the coil volume increased, and so η_{sp}/C also increased, and (2) the polar groups may have aggregated, and if this occurred in the coil, it would lead η_{sp}/C to decrease. If it occurred between the coils, the apparent molecular weight increased, and η_{sp}/C increased. In the very dilute concentration region, macromolecular chains were more independent, and the aggregates in the single coil were predominant. However, with G increasing, more ions were present in the coil, so the volume of the coil also increased, thus causing η_{sp}/C to increase. So near the critical concentration, these two effects of G reached equilibrium, explaining why the influence of G on η_{sp}/C was small.

In the high-concentration region, the coils touched one another or even overlapped. Then, the effect of aggregation between coils became predominant. High G means more polar groups, and this provided better conditions for the interaction between the coils. Therefore, the reduced viscosity increased sharply.

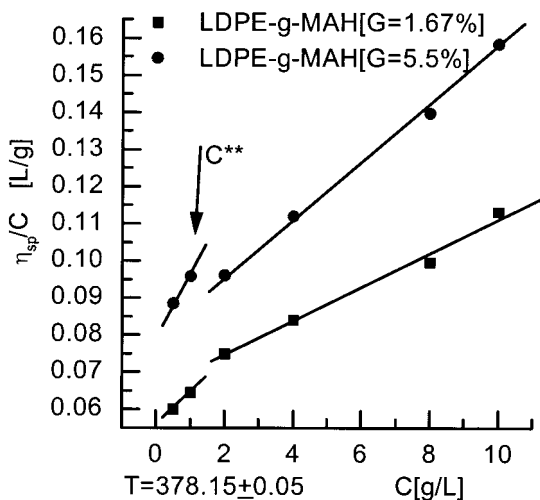


Figure 6 Variation of reduced viscosity as a function of concentration for LDPE- g -MAH ($T = 378.15 \pm 0.05$ K).

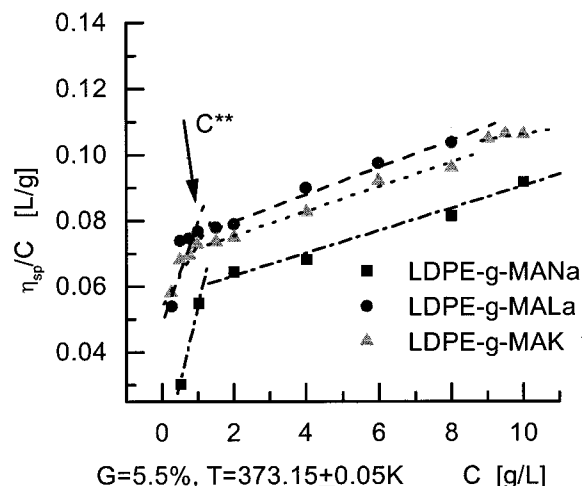


Figure 7 Variation of reduced viscosity as a function of concentration for LDPE- g -MAME (Na, K, La; $G = 5.5\%$, $T = 373.15 \pm 0.05$ K).

η_{sp}/C - C of LDPE- g -MAME (Na, K, La)

A substantial amount of work on the intrinsic viscosity of polyelectrolyte solutions has been reported previously. These studies have shown that the reduced viscosity increases sharply on dilution. However, there have been some recent reports that the reduced viscosity reaches a maximum on dilution, followed by a rapid decrease on further dilution of the polymer solutions. Such behavior has been attributed to long-range coulombic interactions, the formation of relatively large solvated clusters, or ordered quasicrystalline structures. However, when polyelectrolyte is dissolved in the nonpolar solvent, the intrinsic viscosity behaves in a classical manner and obeys the Huggins and Kraemer relations.

At moderate to high polymer concentrations, the solution thickens by an associative mechanism (intramolecular or intermolecular). The building of the network commences when the ions attached to its polymer backbone begin to aggregate to produce a network structure of polymer molecular chains. Such structural formations are commonly called intermolecular and intramolecular associations. In dilute solution, the intramolecular associations are dominant compared with the intermolecular associations. As a result of ionic interactions in ionomers, the solution exhibits some unique rheological properties with respect to common polyelectrolyte solutions.

As shown in Figure 7, for all the ionomer solutions, an obvious change in the slope was observed. As defined previously, this crossover point

is called the critical concentration. We also noticed that the La ionomer curve was different from the K ionomer curve. In the low-concentration region, η_{sp}/C of the La ionomer was smaller than that of the K ionomer, and in the high-concentration region, the La ionomer η_{sp}/C was higher than that of the K ionomer. These quite different characteristics must have been caused by a different formation mechanism that is based on the differences of the atomic structure between the rare-earth metals and group I metals. It is thought that the valence bond theory can be applied to the polymer formation mechanism, whereby these phenomena can be interpreted.¹¹ From the valence bond point of view, the formation of a coordination complex is a reaction between a Lewis acid (metal or metal ion) and a Lewis base (ligand) with the formation of a coordinate covalent valence between the ligand and the metal. La is a rare-earth element, and it has f orbitals, which can be coordinated. Therefore, there exist coordination effects in La ionomers. In the very dilute concentration solution, the coordination effects mainly occurred in the coil and then made the coil shrink, and the reduced viscosity was small. In the high-concentration solution, the coordination effects may have existed between the coils. Because of these effects, the apparent molecular weight seems to have increased, and the reduced viscosity of the solution increased as well.

CONCLUSIONS

On the basis of the investigation and analysis of the viscosity–concentration relations of different ionomers, it is concluded that

1. The variation of the reduced viscosity of the ionomers shows two crossover points corresponding to the two critical concentrations of the polymers: C^{**} and C^* .
2. There are two mechanisms and models for the ionomers. The cluster model is suitable for group I and group II metal ionomers. The coordination complex model is suitable for the transition-metal and rare-earth-metal ionomers.
3. G influences η_{sp}/C in two ways: (1) with more polar groups, the coil volume increases, so η_{sp}/C also increases, and (2) the polar groups may aggregate in the coil or between the coils and have different effects on η_{sp}/C .

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