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Aggregation behavior of halato-telechelic ionomers in a low-polarity solvent

1. Concentration dependence of aggregation

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Summary

The solution behavior of halato-telechelic ionomers (polybutadiene with carboxylate end groups) in a low-polarity solvent (tetrahydrofuran (THF)) was studied. It was shown that the degree of aggregation can be expressed as a function of polymer concentration by an empirical equation, $DA = 10^{\beta c}$, where DA is the degree of aggregation, c is polymer concentration, and β is a constant relating to the rate of aggregation with polymer concentration. It was also shown that the aggregation effect of the Na salt was larger than that of the Cs salt, which was reflected in the value of β.

Introduction

Ionomers are a new class of ion-containing polymers having ionic groups up to 10-15 mole% along nonionic backbone chains.[1,2] Although a wide range of studies of ionomers have been done in the solid state, studies of solution properties are few. Recently, however, the study of ionomer solutions has been active because of the realization of their unique properties.[3-13] So far, most of the solution studies of ionomers have been conducted on ionomers which have ionic groups randomly distributed along non-ionic backbone chains.

In this work, we studied the aggregation behavior of ionomers which had ionic groups only at the chain ends. This type of ionomer (halato-telechelic ionomer)[6,7] has a well characterized structure and may be used as a model for more complex ionomers.

Experimental

Carboxyl-terminated polymer, Hycar CTB (2000 X 162) was obtained from B.F. Goodrich. Hycar CTB is a low molecular weight polymer whose backbone chain is polybutadiene with carboxylic acid at both chain ends. The number-average molecular weight used was 4,200 and the functionality was 1.9. The sodium and cesium salts were prepared by neutralizing the acid with NaOH and CsOH respectively in Benzene/Methanol (90/10), freeze drying, and drying at room temperature for one week. The solutions were prepared by dissolving the polymer in THF and stirring overnight at room temperature to make a stock solution. The general procedure of ionomer sample preparation was described elsewhere.[10] The viscosity was measured with a modified Ubbelohde viscometer at 25 ± 0.1°C in a constant temperature bath. The viscometer had caps to prevent evaporation of solvent and exposure to air. Measurements at each concentration were repeated until the relative error of three successive measurements became less than 0.5%. Details

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*To whom offprint requests should be sent concerning the viscosity experiments were described elsewhere.[13]

Results and Discussion

Figure 1 shows the viscosity results on sodium and cesium forms of Hycar CTB. The viscosity of the acid form was also measured for finding constants necessary for the analysis. As is typical of dilute ionomer solutions in nonpolar solvents,[4] the viscosity rises sharply with increasing polymer concentration, rather than linearly as is seen for non-ionic polymers (for example, the acid form of Hycar CTB). This is due to an increase in aggregation of ionomer molecules with increasing polymer concentration.

The viscosity data can be used to estimate the size of the aggregates if proper assumptions are made about the nature of the solution. In this paper, it is assumed that the ionomer molecules form molecular aggregates that act like a single large molecule and interact with other aggregates in the same way as the individual ionomer molecules do. As the polymer concentration increases, the size of the aggregate increases, as well as the interaction between aggregates. The viscosity has two contributions; one from the formation of aggregates causing an increase in apparent molecular weight, and the second from the interaction between aggregates.

It is well known that the viscosity behavior of neutral polymer solution is expressed by the Huggins equation,[14]

$$\frac{\eta_{sp}}{c} = [\eta]+k'[\eta]^2c \qquad (1)$$

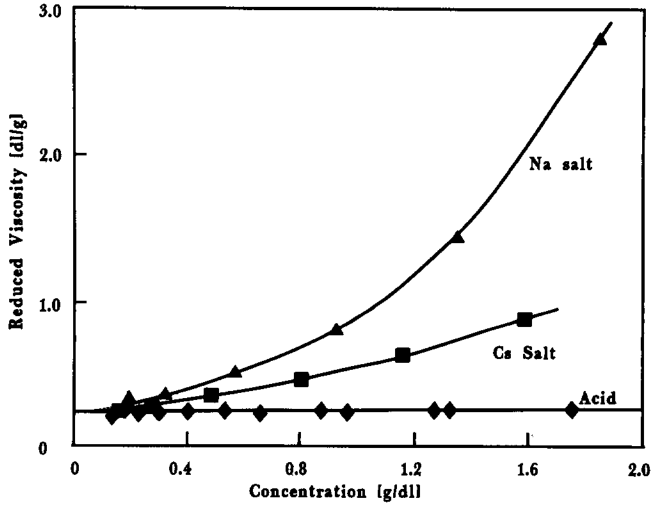

Fig. 1. Reduced viscosity, η_{sp}/c, against polymer concentration for sodium and cesium salts as well as acid of Hycar CTB in THF.

where η_{sp} is the specific viscosity, $[\eta]$ is the intrinsic viscosity, c is the polymer concentration, and k' is the Huggins constant.

As is shown in Fig. 1, the degree of aggregation increases with increasing polymer concentration. To estimate the degree of aggregation as a function of polymer concentration, we used Eq. (1). First, the apparent intrinsic viscosity of the aggregates, $[\eta]_{agg}$, which is related to the size of the aggregates at concentration c, is obtained by using Eq. (1) with experimental values of η_{sp} and c. The procedure is schematically illustrated in Fig. 2. This procedure implies that, along the line following the Huggins relation, the molecular aggregates formed at concentration c persist down to infinite dilution. Using a least squares fit, $[\eta] = 0.23$ and $k' = 0.25$ were obtained for the acid sample. The k' value obtained is reasonable compared with reported values for various polymer systems,[15] including the value for polybutadiene in toluene (0.33).[16] This k' value is used to obtain $[\eta]_{agg}$ by using Eq. (1).

As a second step to estimate the degree of aggregation for the system, the relation between $[\eta]$ and molecular weight is used. According to Flory,[15] the intrinsic viscosity, $[\eta]$, is expressed by

$$[\eta] = K\, M^{1/2}\, \alpha^3 \qquad (2)$$

Here, K is the constant, α is the (viscosity) expansion coefficient. We define the degree of aggregation, DA, by

$$DA = \frac{M_{agg}}{M_o} \qquad (3)$$

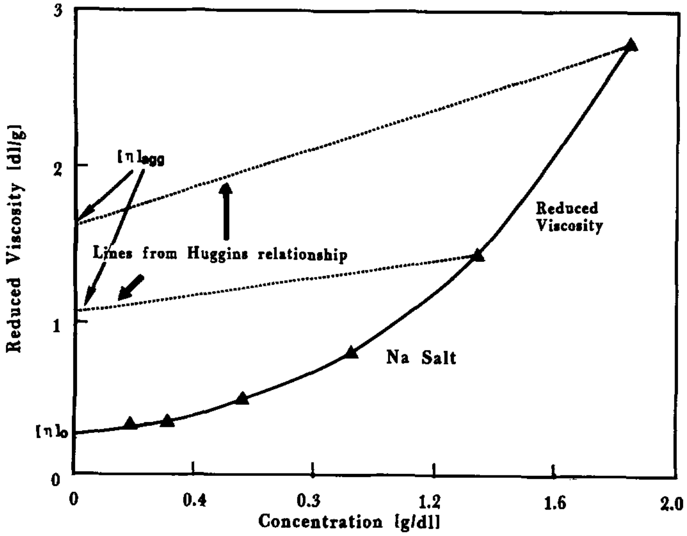

Fig. 2. Schematic illustration of the method of obtaining the apparent intrinsic viscosity of aggregates, $[\eta]_{agg}$, by use of the Huggins equation.

where M_{agg} and M_o are the average molecular weights of aggregates and of single ionomer molecule, respectively.

By using Eq. (2) and (3),

$$DA = \frac{[\eta]^2_{agg}}{[\eta]^2_o} \qquad (4)$$

Here, $[\eta]_o$ represents the intrinsic viscosity of single ionomer molecule. In this derivation, K and α are assumed to be the same for both the aggregates and the single molecule. Recently, Lantman et al.[17] showed by using small-angle neutron scattering that the size of individual ionomer molecules incorporated into molecular aggregates was almost constant over a wide range of concentration except at the very dilute solution level, where chain shrinkage was expected. Although their results were obtained for random ionomers, similar behavior is expected for halato-telechelic ionomers. Therefore, the assumption we made appears reasonable.

Table I shows the degree of aggregation as a function of polymer concentration. The degree of aggregation increases with increasing polymer concentration; for example, DA increases from ca. one at very dilute concentration to ca. 9 at 1.6 g/dl for the cesium salt. Also, it is seen that the degree of aggregation of the Na salt is larger than that of the Cs salt. This order is consistent with the results obtained for random carboxylate ionomers.[10]

Table I. Degree of Aggregation vs. Polymer Concentration

	Concentration (g/dl)	Degree of Aggregation
Na salt	1.844	45.1
	1.341	19.9
	0.9220	8.53
	0.5674	3.93
	0.3207	2.11
	0.1941	1.97
Cs salt	1.592	8.67
	1.158	5.21
	0.7961	3.22
	0.4899	1.98
	0.2769	1.32
	0.1676	1.01

To obtain the relationship between DA and c, the data are plotted on a semilog scale (Fig. 3). Straight lines are obtained for both Na and Cs systems in the concentration range studied. Lines are drawn in such a way that each line passes the point of $DA=1$ at $c=0$, which assumes implicitly that there is no aggregation at infinite dilution. An empirical relationship obtained to describe the aggregation behavior is

$$DA = 10^{\beta c} \qquad (5)$$

The constants obtained are $\beta=0.94$ for the sodium salt; and $\beta=0.60$ for the cesium salt. It is understood that β is related to the rate of aggregation with polymer concentration. We do not attempt to create a model to correlate the constant β with the physical process of aggregation at this time. This will be the subject of future studies.

Conclusion

The aggregation behavior of Hycar CTB ionomers in a low-polarity solvent was studied. An empirical relationship ($DA=10^{\beta c}$) between the degree of aggregation (DA) and the polymer concentration (c) was proposed. A model to explain the empirical relationship will be discussed in a future paper.

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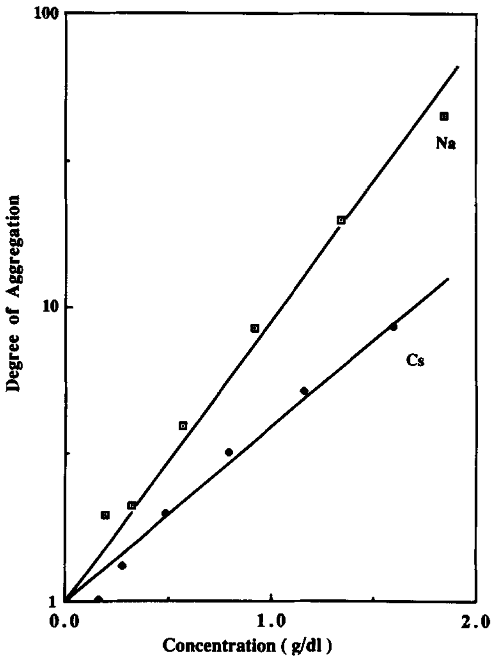

Fig. 3. Degree of aggregation against polymer concentration for sodium and cedium salts of Hycar CTB in THF.

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