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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 12 June 1999

To cite this Article Kim, Jin-Woong and Suh, Kyung-Do(1999) 'MOLECULAR INTERACTIONS OF CARBOXYLATED URETHANE ACRYLATE IONOMERS IN LOW-POLARITY AND POLAR SOLVENTS', Journal of Macromolecular Science, Part A, 36: 12, 1967 – 1979

To link to this Article: DOI: 10.1081/MA-100101637

URL: <http://dx.doi.org/10.1081/MA-100101637>

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MOLECULAR INTERACTIONS OF CARBOXYLATED URETHANE ACRYLATE IONOMERS IN LOW-POLARITY AND POLAR SOLVENTS

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Key Words: Carboxylated Urethane Acrylate Ionomers, Low-Polarity and Polar Solvents, Intermolecular Interaction, Polyelectrolyte Behavior, Hydrogen Bond

ABSTRACT

Carboxylated urethane acrylate ionomers that have a small number of ionic groups per chain were synthesized with varying the molecular weight of soft segment, the degree of ionization, and the sort of diisocyanate. The effect of intra- and intermolecular interactions on solution properties was studied by viscosity measurements in low-polarity and polar solvents. In a low-polarity solvent (1,4-dioxane), ionomers showed almost no intramolecular interaction at dilute concentration and a small degree of intermolecular interaction at high concentrations, resulting from a small number of ionic groups per chain. In a polar solvent (dimethylacetamide, DMAc), ionomers showed typical polyelectrolyte behavior, even though ionomers have a small number of ionic groups per chain. Intermolecular interaction caused by polyether soft segment, phenyl group, and hydrogen bond

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between urethane acrylate ionomer chains contributed to the increase of reduced viscosity at low concentration.

INTRODUCTION

Ionomers have shown marked contrast with polyelectrolytes in the solution properties: aggregation behaviors and polyelectrolyte behaviors [1-10]. Solution properties of ionomers have received considerable attention, because of these unique behaviors in solutions. Related to the solution properties of ionomers, it is known that the balance between the intramolecular interaction and intermolecular interaction is one of the important factors in controlling the solution properties of ionomers [11].

Generally, aggregation behaviors have been observed in nonpolar solvents due to dipolar attraction in the medium of low dielectric constant. Lundberg *et al.* [2, 3] showed that at low polymer concentration, the solution properties of ionomers were dominated by the intramolecular association of ion pairs, while at high polymer concentration, the solution properties of ionomers were dominated by intermolecular interaction of ion pairs. Different from aggregation behaviors, polyelectrolyte behaviors have been observed in water or polar solvent due to Coulombic interaction. Lundberg *et al.* [3] showed that the reduced viscosity of ionomers increased remarkably with decreasing polymer concentration, which was interpreted with the intramolecular repulsion between fixed ions in the polymer chain. However, Hara *et al.* [10] suggested that the intermolecular interaction played a major role in the viscosity behavior of salt-free polyelectrolytes, even in dilute concentration.

Recently, intense studies have been performed on the behaviors of polyurethane ionomers and their derivatives in water and polar organic solvent [12-17]. However, there have been many difficulties in understanding exactly the characteristics of these ionomer solutions, because they had many interaction factors such as ion content, hydrophobic interaction, and hydrogen bonding.

In this study, as a model system, we designed carboxylated urethane acrylate ionomer containing above mentioned interaction factors. The role of molecular interactions on the behavior of ionomers in low polarity and polar solvent was investigated with changing the ion content, molecular weight of soft segment, and diisocyanate in order to understand the characteristics of polyurethane ionomers and their derivatives in various solvents.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co.), toluene diisocyanate (TDI, Tokyo Chemical Industry Co., Ltd.), and 4,4'-diphenylmethane diisocyanate (MDI, Tokyo Chemical Industry Co., Ltd.) were vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w = 1.0 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$ and $2.0 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$, Hyosung BASF), dimethylolpropionic acid (DMPA, Aldrich Chemical Co.), and 2-hydroxyethyl methacrylate (HEMA, Junsei Chemical Co.) were used as received. Dimethylacetamid (DMAc, Junsei Chemical Co.) and 1,4-dioxane (Junsei Chemical Co.) of reagent grade were used.

Synthesis of Carboxylated Urethane Acrylate Ionomer [15-18]

The composition for the synthesis of carboxylated urethane acrylate ionomers is listed in Table 1. The reaction procedure and molecular structure designed are shown in Scheme 1. Here, ID, TD, and MD are IPDI-, TDI-, and MDI-based urethane acrylate ionomers, respectively. The numbers, 1 and 2, correspond to the molecular weight of PTMG, $1.0 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$ and $2.0 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$. All samples were synthesized by a three-step process. All reactions were carried out in a 4-neck glass reactor equipped with stirrer, thermometer, reflux condenser, and inlet system for N₂ gas. In the first step, diisocyanate was poured into the glass reactor and nitrogen gas was inlet for 10 minutes to eliminate the residual moisture. After dissolving 1 wt% of dibutyltindilaurate, DMPA dissolved in DMAc was dropped into the reactor slowly at room temperature. The reaction temperature was raised to 80°C so that 2 mole of IPDI reacted with the 1 mole of DMPA, resulting in the molecular structure having carboxylic acid group in the middle and isocyanates on end sides. In this stage, care must be taken of controlling the molar ratio of reaction, so as not to increase the molecular weight. This temperature was maintained for 4 hours to retain an acceptable rate of reaction. The change of NCO value during reaction was determined using the dibutylamine back titration method to find the reaction end point [19].

In the second step, 0.5 mole of PTMG was added slowly into the reactor to incorporate the soft segment into the molecular backbone with the same method of the first step. Continuous reaction was carried out for 4 hours at 80°C. In the last step, after dissolving 1 wt% dibutyltindilaurate into the reactor, 2 mole of HEMA was reacted to the residual NCO group at 45°C for 12 hours, which introduced the reactive vinyl group in the molecular ends. The reaction end point

TABLE 1. The Composition for the Synthesis of the Carboxylated Urethane Acrylate Ionomers^a

Symbol	IPDI	TDI	MDI	DMPA	PTMG		HEMA	TEA ^{e)}
					1.0×10 ³ ^{b)}	2.0×10 ³ ^{b)}		
ID1-R ^{d)}	20	-	-	6.03	22.49	-	5.85	-
ID1-100 ^{e)}	20	-	-	6.03	22.49	-	5.85	4.54
ID1-75 ^{e)}	20	-	-	6.03	22.49	-	5.85	3.41
ID1-50 ^{e)}	20	-	-	6.03	22.49	-	5.85	2.27
ID2-R	20	-	-	6.03	-	44.98	5.85	-
ID2-100	20	-	-	6.03	-	44.98	5.85	4.45
ID2-75	20	-	-	6.03	-	44.98	5.85	3.41
ID2-50	20	-	-	6.03	-	44.98	5.85	2.27
TD1-100	-	20	-	7.70	-	-	7.47	5.80
MD1-100	-	-	20	5.36	-	-	5.20	4.04

^{a)} All units are in gram

^{b)} Molecular weight of polytetramethylene glycol (PTMG)

^{c)} Ion content can be controlled with the amount of triethylamine (TEA)

^{d)} Raw urethane acrylate ionomer

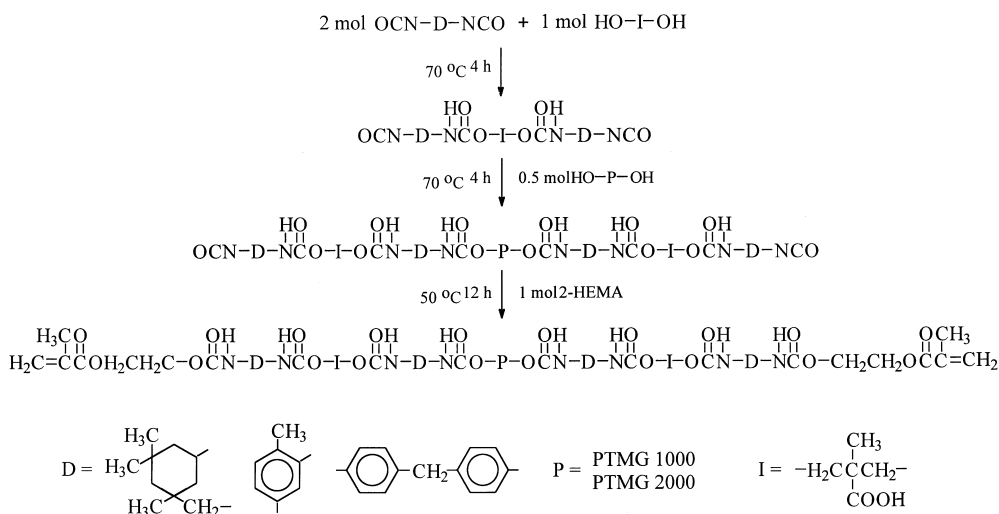
^{e)} Each number is the ionization percentage of carboxylic acid of DMPA

was determined by the disappearance of NCO stretching peak (2270 cm⁻¹) through IR spectroscopy.

To purify DMAc, unreacted 2-HEMA, and DMPA, the reaction mixture was precipitated from the water and filtered several times to give a crude product. The crude product was dried *in vacuo*. So, we could obtain the carboxylated urethane acrylate ionomers.

Preparation of Ionomer Solution

Carboxylic acid groups in the molecular backbone of the urethane acrylate ionomers were ionized with an appropriate amount of triethylamine (TEA)



Scheme 1. The reaction procedure and molecular structure of carboxylated urethane acrylate ionomer with varying the sort of diisocyanate and molecular weight of soft segment.

at room temperature for 1 hour. The ionization percentage was controlled by ionizing the carboxylic acid groups into the carboxylated groups with TEA. Ionomer solutions were prepared by dissolving the ionomers in a proper solvent (DMAc or dioxane) under stirring for a day at room temperature.

Measurements

Molecular weight distribution of carboxylated urethane acrylate ionomers was measured by a model 410 GPC equipped with styragel HR 1-4 columns from Waters Associates at 25°C. The flow rate of the carrier solvent, THF, was 0.5 ml·min⁻¹. The average molecular weights and polydispersity (PDI) values calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standards were $M_w = 8.3 \times 10^3 \sim 1.4 \times 10^4$ g·mol⁻¹ and PDI = 1.32 ~ 2.29.

Before measuring the viscosity, the ionomer solution was passed through a sintered-glass filter to remove dust in the solution. The reduced viscosity was measured with an Ubbelohde viscometer equipped with a flow time-detecting

device at $25 \pm 0.05^\circ\text{C}$ in a thermostated bath. Considerable care was taken in each measurement, because the molecular weights of the samples were low, compared with those of the conventional ionomers. The measurement was continued until reproducible data could be obtained.

RESULTS AND DISCUSSION

Aggregation Behaviors of Carboxylated Urethane Acrylate Ionomers

Figures 1 and 2 show the reduced viscosity as a function of ionomer concentration for ID1 and ID2 samples at various ion contents in dioxane at room temperature. We selected dioxane as a low-polarity solvent [3]. The reduced viscosity of the raw urethane acrylates showed linear dependence on the concentration in dioxane. On the contrary, it was observed in Figure 1 and 2 that the reduced viscosity at high ionomer concentration increased gradually with the ion content. This result explained that although the degree of aggregation was small, there existed the intermolecular interaction.

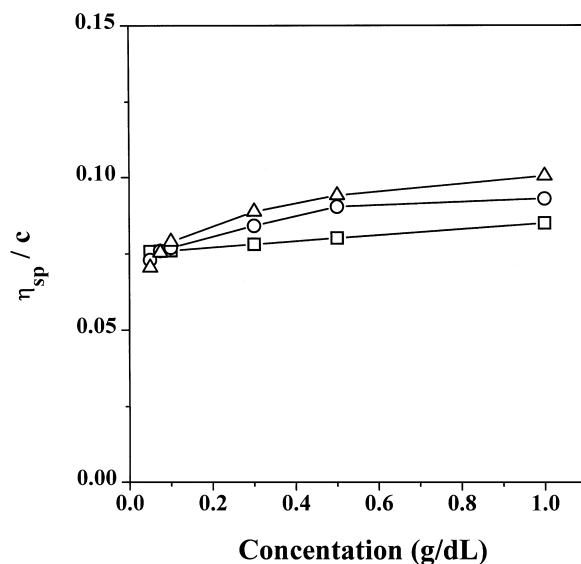


Figure 1. Reduced viscosity as a function of ionomer concentration for ID1 samples with varying ion content: ID1-R (-□-), ID1-75 (-○-), and ID1-100 (-△-) in dioxane.

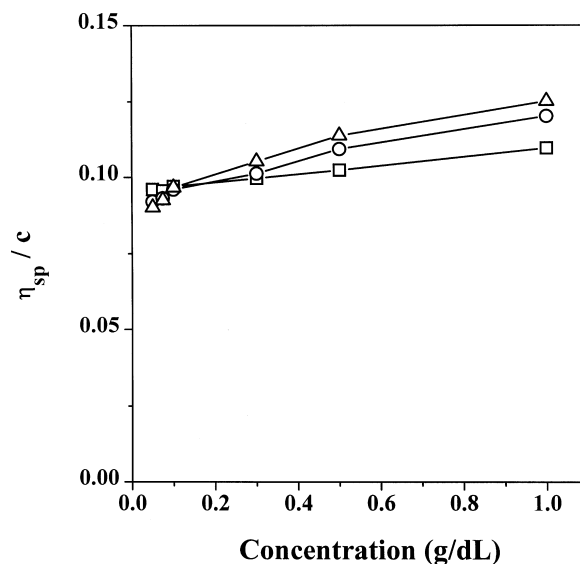


Figure 2. Reduced viscosity as a function of ionomer concentration for ID2 samples with varying ion content: ID2-R (□), ID2-75 (○), and ID2-100 (△) in dioxane.

Basically, ionomers have been shown that at low polymer concentration, the viscosity of ionomer solution is lower than that of the precursor polymer solution. This is due to the dominant intramolecular association between the ion pairs, while at high polymer concentration, the viscosity is higher than that of the precursor polymer solution because of the intermolecular association between ion pairs, and the curve is concave up, which is attributed to the increasing aggregation with the ionomer concentration [3, 4, 6, 10]. However, differing from the general concept, the reduced viscosity for the carboxylated urethane acrylate ionomers at low ionomer concentration changed slightly, and the overall curves were concave down. These results could be explained by considering the number of ion pairs in a chain. As shown in Scheme 1, the carboxylated urethane acrylate ionomers had only several ionic groups per chain so that the intramolecular association causing the shrinkage of molecule seemed to be negligible [10]. In order to confirm this effect, the intrinsic viscosities of the carboxylated urethane acrylates was measured at room temperature and shown in Figures 3 and 4. The intrinsic viscosities of these samples decreased slightly with the ion con-

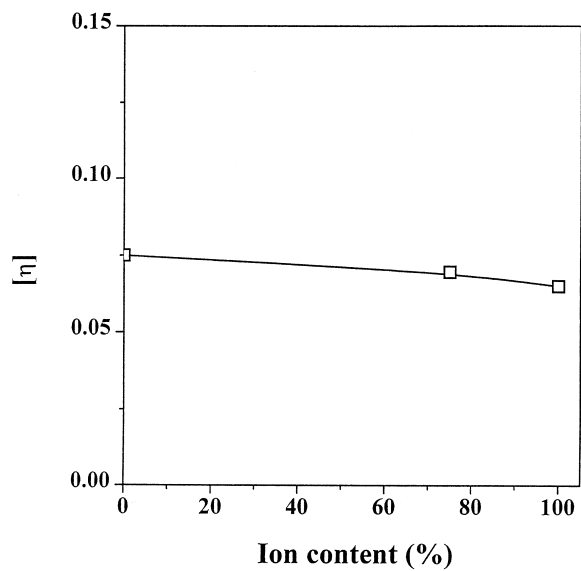


Figure 3. Intrinsic viscosity change with the ion content for ID1 samples in dioxane.

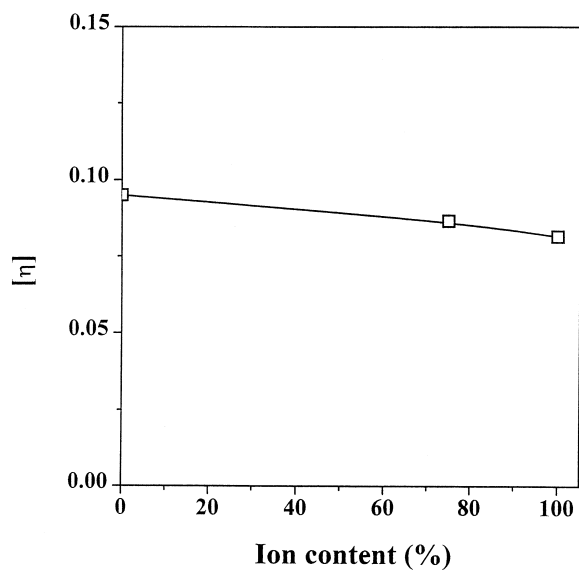


Figure 4. Intrinsic viscosity change with the ion content for ID2 samples in dioxane.

tent, meaning that the carboxylated urethane acrylate ionomers dissolved in dioxane at the given whole concentration. From this result, it was possibly confirmed that the intramolecular interaction of the carboxylated urethane acrylate ionomers was negligible, as assumed.

Polyelectrolyte Behaviors of Carboxylated Urethane Acrylate Ionomers

Figures 5 and 6 show the reduced viscosity as a function of ionomer concentration for ID1 and ID2 samples of various ion contents in DMAc at room temperature. DMAc was selected as a polarity solvent [7-10]. The fashion of the reduced viscosities, with the concentration in these figures showed the typical polyelectrolyte behavior; the reduced viscosity increased significantly as the concentration of ionomers decreased. Also, the polyelectrolyte behavior was enhanced as the ion content increased. These results illustrated that although the carboxylated urethane acrylate ionomers had a small number of ion pairs, they still had the intramolecular ionic repulsion between ion pairs, showing good agreement with those reported by Lundberg *et al.* [3].

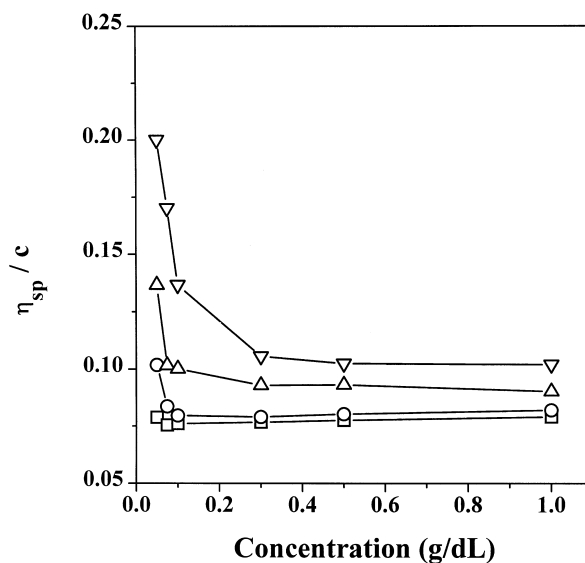


Figure 5. Reduced viscosity as a function of ionomer concentration for ID1 samples with varying ion content: ID1-R (-□-), ID1-50 (-○-), ID1-75 (-Δ-), and ID1-100 (-∇-) in DMAc.

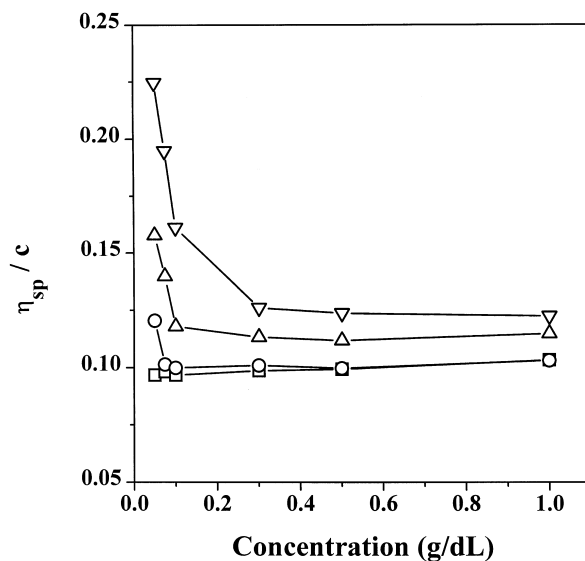


Figure 6. Reduced viscosity as a function of ionomer concentration for ID2 samples with varying ion content: ID1-R (-□-), ID1-50 (-○-), ID1-75 (-Δ-), and ID1-100 (-∇-) in DMAc.

The polyelectrolyte behavior for ID2 samples, having almost the same number of ionic group per chain as ID1 samples, appeared to be similar to that for ID1, even though the molecular weight ionomer increased (M_w of ID1 and ID2 were $8.3 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$ and $1.4 \times 10^4 \text{ g}\cdot\text{mol}$, respectively). Based on the suggestion of Hara *et al.* [10, 20, 21], this result could be explained by the intermolecular interaction caused by hydrophobic interaction between polyether soft segments [18].

Figure 7 shows the reduced viscosity as a function of the concentration for ID1, TD1, and MD1 samples in DMAc at room temperature. TD1 and MD1 also showed typical polyelectrolyte behaviors by ionic groups, however, it was notable that the polyelectrolyte effect increased slightly as the number of phenyl group of diisocyanate increased. This result indicates that the intermolecular interaction between ionomer chains increased due to the increased hydrophobic interaction by the phenyl groups [18].

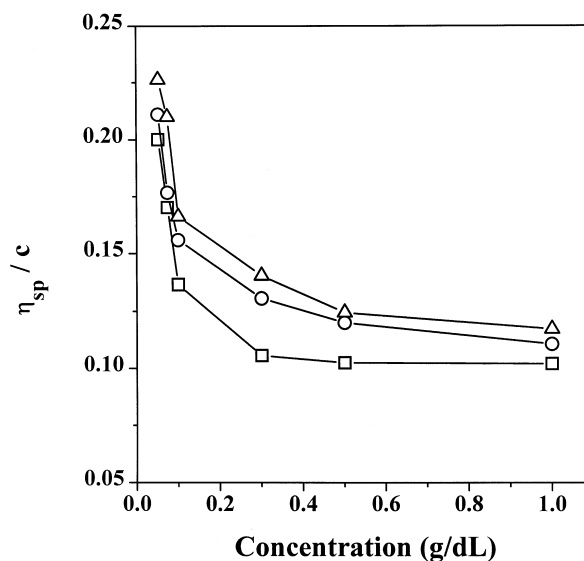


Figure 7. Reduced viscosity as a function of ionomer concentration for ID1-100 (-□-), TD1-100 (-○-), and MD1-100 (-△-) in DMAc.

Effect of Hydrogen Bond on Viscosity Behaviors

Figure 8 shows the effect of the additives (HCl and Urea) on the reduced viscosity as a function of concentration for ID1 sample in DMAc at room temperature, in order to consider the effect of the hydrogen bond on the solution properties. For the sample dissolved in HCl salt solution, the polyelectrolyte effect decreased at low concentration region, compared to salt-free solution, but still the polyelectrolyte effect could be observed. In order to verify this, we observed the reduced viscosity for this sample in DMAc containing urea which is the dehydrogen bonding agent. The polyelectrolyte effect was much more suppressed, compared to that in HCl salt solution. These results suggested that for the carboxylated urethane acrylate ionomers, the intermolecular interaction caused by the hydrogen bond between chains also enhanced the reduced viscosity at low concentration.

CONCLUSION

A series of carboxylated urethane acrylate ionomers were designed as a model system, in order to understand the molecular interaction of polyurethane

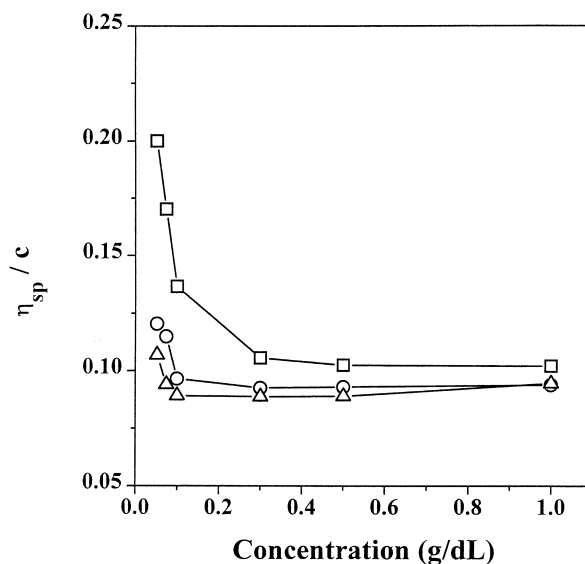


Figure 8. Reduced viscosity as a function of ionomer concentration for ID1-100 in DMAc (-□-), 0.1 N HCl salt solution (-○-), and 0.1 N Urea solution (-△-).

ionomers and their derivatives. The effect of intra- and intermolecular interaction on the carboxylated urethane acrylate ionomers was examined by viscosity measurements in low-polarity and polar solvents. In a low-polarity solvent (1,4-dioxane), the ionomers showed almost no intramolecular interaction at dilute concentration and a small degree of intermolecular interaction at high concentration, resulting from small number of ionic group per chain. In a polar solvent (dimethylacetamide, DMAc), the ionomers showed typical polyelectrolyte behavior, even though the ionomers had a small number of ionic groups per chain. However, for the carboxylated urethane acrylate ionomers, the intermolecular interaction caused by hydrophobic polyether soft segment, phenyl group and hydrogen bond between ionomer chains enhanced the reduced viscosity of ionomer solutions at dilute concentration.

ACKNOWLEDGEMENTS

This work was supported by the Korean Science and Engineering Foundation (96-0300-12-01-3). J-W Kim is grateful to the Graduate School of Advanced Materials and Chemical Engineering at the Hanyang University for a fellowship.

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Received July 10, 1998

Final revision received August 13, 1999