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Solution properties of hexamethylene diisocyanate based polyurethane cationomers

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SUMMARY

Viscosity measurements of hexamethylene diisocyanate based cationomer in various polarity solvents and in water/solvent were performed. For the un-ionized sample in pure MEK and DMF, the reduced viscosities of both solutions follow the Huggins relation. For ionized samples in pure MEK and DMF, aggregation of the ionized hard segments still exist in the MEK and DMF solution in the high polymer concentration range, whereas chain expansion occurs in the DMF solution in the low polymer concentration range. For ionized samples in water/solvent mixtures, at a mixing ratio (by weight) of 0.12, the reduced viscosity indicates an aggregation behavior in MEK/water and a polyelectrolyte behavior in DMF/water. At a mixing ratio (by weight) between 0.24 and 4.44, the reduced viscosity indicates a polyelectrolyte behavior. The polymer particles change from a clear elastic gel to microspheres. For emulsions of the ionized samples, the reduced viscosity exhibits polyelectrolyte behavior.

INTRODUCTION

The solution properties of ionomers have been extensively studied because of their unique properties(1-15). It has been well established that dilute ionomer solutions show two types of behavior depending on the polarity of solvents used (3), namely 1) aggregation due to dipolar attraction between chain segments in non-polar or low-polarity solvents, and 2) polyelectrolytic behavior due to Coulomb interaction in high-polarity solvents. In non-polar or low-polarity solvents, ionomers tend to form aggregates due to attractions between ion pairs. Lundberg and Phillips (3) showed that, for the sodium salt of lightly sulfonated polystyrene at low polymer concentration, the reduced viscosity is lower than that of the ionomer precursor, owing to the domination of intramolecular association of ion pairs. On the other hand, the reduced viscosity at high polymer concentration is higher than that of the precursor, owing to the domination of intermolecular association of ion pairs. In high-polarity solvents, ionomers show polyelectrolyte behavior. The reduced viscosity of ionomers increases markedly with decreasing polymer concentration. This polyelectrolyte behavior of ionomers can be suppressed by adding a small amount of salts such as LiCl.

For polyelectrolytes in solution, the reduced viscosity undergoes a marked increase with dilution; at very high dilutions, it reaches values that are many times higher than the intrinsic viscosity that would be expected for the polymer in the absence of charge. Flory (16) proposed that, "as the solution is diluted, the polymer molecules no longer fill all of the space and intervening regions extract some of

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the mobile ions. Net charges develop in the domain of the polymer molecules causing them to expand. As this process continued with further dilution, the expansive force increases. At very high dilutions, the polymer molecule will have lost many of its mobile ions to extend it virtually to its maximum length."

Polyurethane (PU) ionomer is a particular class of ionomers, in which each chain involves alternative ionic hard segments and non-ionic soft segments. It can be prepared by incorporation of a chain extender containing an amine group with NCO-terminated PU prepolymer and subsequent modification with an ionizable component (17). There are three types of PU ionomers, namely cationomer, anionomer and zwitterionomer. Studies on the dilute solution behavior of this kind of ionomer do not appear in the literature.

In our preceding work (18-20), we studied the phase inversion mechanism of PU cationomer during emulsification at various dispersion temperatures and the morphologies of films cast from solutions and emulsions. It was found that the phase inversion mechanism can be divided into three stages, involving separation of hard segment aggregates due to adsorption of water on their surface, water entering into disordered and then ordered hard domains, and finally a rearrangement of agglomerates to form microspheres. The films cast from solutions have a morphology with soft domains as a continuous phase and hard domains as a fibrillar network dispersed in the continuous phase. After dispersion, the hard segments originally distributed in the dispersed phase can be inverted to become a hard domain network or a continuous phase. Thus studies of chain conformations in solvents of different polarity and in water/solvent mixtures can provide a better understanding on the emulsification process.

In this article, the chain conformations of a hexamethylene diisocyanate based PU cationomer in a low-polarity solvent, methyl ethyl ketone (MEK), and a high-polarity solvent, N,N′-dimethylformamide (DMF), and in water/MEK and water/DMF mixtures are studied by use of viscosity measurements.

EXPERIMENTAL

Descriptions of the chemicals used and procedures for the preparation and emulsification of PU cationomers with poly(tetramethylene oxide) (PTMO) of molecule weight 2000 as soft segment, N-methyl-diethanolamine (MDEA) as chain extender, glycolic acid as quaternization agent and hexamethylene diisocyanate (HDI) as diisocyanate were given in our preceding work (18-20). The polymer solutions were prepared from methyl ethyl ketone (MEK) and N,N′-dimethylforamide (DMF) and the emulsions were prepared by dispersing a solution in water at a temperature of 40^{o}C and then removing the solvent by vacuum.

Samples were designated so that, for example, H-1.0 means 1.0 mole ratio of glycolic acid to MDEA and the initial letter "H" refers to HDI.

The molecular-weight distribution of the polymer so prepared was measured by a model 201 gel permeation chromatograph from Waters Associates at room temperature.

The flow rate of carrier solvent, tetrahydrofuran (THF), was 0.5 ml/min; and the polymer sample for the measurement was 0.5% (by weight) solution in THF. The measured weight- and number-average molecular weights of the un-ionized sample (H-0.0) are: $\bar{M}_w=1.0x10^5$ and $\bar{M}_n=8.3x10^4$.

Reduced viscosities of solutions and emulsions were measured at 40 ± 0.05°C using a Schott Gerate (Germany) AVS 400 viscosity measuring system with a flow time autodetector having a sensitivity of 0.01 sec. The capillary tube used is of Ubbelohde type. The solutions and emulsions before testing were immersed in a thermostatic bath at 40 ± 0.05°C for 30 minutes to allow the temperature to reach equilibrium. Measurements at each concentration were carried out until the variations of flow time of three successive measurements are less than 0.5%.

RESULTS AND DISCUSSION

1.Reduced viscosity of polymers in MEK and DMF

The reduced viscosities of un-ionized (H-0.0) and ionized (H-0.7 and H-1.0) samples in MEK and DMF (Fig. 1) show that the relationship between reduced viscosity and polymer concentration of the un-ionized sample in both solvents is linear. By use of the Huggins equation: $\eta_{red} = [\eta]+[\eta]^2K'C$, the Huggins constant K' and intrinsic viscosity $[\eta]$ of both solvents were determined. For the MEK solution, K'=2.55 and $[\eta]=0.147$ dl/g; and for the DMF solution, K'= 1.31 and $[\eta]=0.453$ dl/g. The $[\eta]$ value of the DMF solution is 3.08 times that of the MEK solution. This result shows that the chain excluded volume of the un-ionized sample (H-0.0) in DMF is higher than that in MEK, and thus DMF has a higher solvent power than MEK.

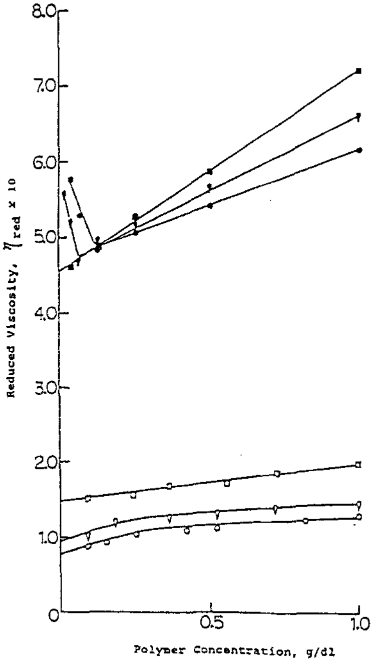

Fig. 1. The reduced viscosity curves of the polymers with various ionic content in MEK and DMF: (□ , ■) H-0.0, (○̩ , ●̩) H-0.7, (○ , ●) H-1.0. The open symbols are for MEK and the full symbols are for DMF.

Dieterich et al. (17) proposed that the ionized segments (hard segments) of PU ionomer could be bridged by counterions through Coulomb interactions to form a sort of "micro-ionic lattice" in an organic medium (such as MEK or acetone). As the association of ionic centres occurs in each macromolecule, it leads to the formation of aggregates. The reduced viscosity of the un-ionized sample in MEK is larger than that of the ionized samples by about 1.6 times at a polymer concentration of 1.0 g/dl (Fig. 1), owing to aggregation of the ionized hard segments. At this concentration, the reduced viscosity of sample H-0.7 is higher than that of sample H-1.0, because the extent of aggregation of the ionized hard segments increases with increasing ionic content.

As the solution is diluted, the reduced viscosity curves of the ionized samples are concave downwards. The reduced viscosities decrease due to the dilution effect at a polymer concentration higher than 0.25 g/dl, and drop sharply owing to aggregation of the ionized hard segment dominantly at a polymer concentration less than 0.25 g/dl.

As the solution is diluted, the reduced viscosity of the ionized samples in DMF first decrease due to the dilution effect, then increase to a level approximately equal to that of the un-ionized sample, and finally become higher than that of the un-ionized sample as the polymer concentration decrease to less than 0.125 g/dl (Fig. 1). This can be attributed to dissociation of the aggregated hard segments and chain expansion resulting from repulsion of the ionized hard segments (16) as the solution is diluted. As the solution is further diluted, the higher extent of dissociation and expansion of the chains cause the reduced viscosities to increase to a level approximately equal to that of the un-ionized sample. Hence, at very high dilution (polymer concentration smaller than 0.125 g/dl), the reduced viscosities of the ionized samples are higher than that of the un-ionized sample. The variation of reduced viscosity with dilution of ionized sample at high polymer concentration is the same as that of the un-ionized sample. These results show that aggregation exists and the dilution effect only appears in the high polymer concentration range; dissociation of the aggregates and chain expansion resulting from dissociation of the ionized hard segments become dominant in the low polymer concentration range.

The reduced viscosity behavior of this PU ionomer system in the low polarity solvent (MEK) is opposite to that of lightly sulfonated polystyrene ionomers in THF (also a low polarity solvent) reported by Lundberg et al. (3) and Hara et al. (14). In the present system, the reduced viscosity of the PU ionomers is lower than that of its precursor in the polymer concentration range investigated. This result can be attributed to the lower ionic content in the lightly sulfonated polystyrene system (8 mole% of repeated units) than that in the present system (70 and 100 mole% of soft-hard repeated units). So the PU ionomer could have a higher extent of aggregation, causing the existence of aggregates in the polymer concentration range investigated. For the PU ionomers in high-polarity solvent (DMF), the reduced viscosity behavior is the same as that of a typical polyelectrolyte such as the lightly sulfonated polystyrene system. But the reduced viscosity, which decreases on increasing the ionic content, is opposite to that of the lightly sulfonated polystyrene system and is the same as that of the 2,4′-dibenzyldiisocyanate cationic PU system (21), in which the ionic content is 67 mole%, close to those of the present system. This result supports the conclusion that aggregates still exist in the test polymer concentrations owing to the presence of a higher content of ionic groups in the PU polymer chains.

2. Reduced Viscosity of Ionomers in Mixed Solvents

The variations in solution viscosities of the ionized samples during the addition of water to solutions in MEK, causing emulsification, at 40°C were observed in our preceding works (20) (insert in Fig. 2).

In order to understand the changes of chain conformation during emulsification, we prepared five solutions with the mixing ratios of water/MEK of 0.12, 0.28, 0.74, 1.67 and 4.44 by weight, which correspond to the polymer contents of 9%, 8%, 6%, 4% and 2% by weight during emulsification respectively. These five solutions are subjected to determination of reduced viscosities during dilution. The reduced viscosities of these five solutions are shown in Figs. 2 and 3.

At a water/MEK mixing ratio of 0.12, the reduced viscosity curves of the ionized samples (H-0.7 and H-1.0) are concave downward (Fig. 2(a) and 3(a)). The reduced viscosities of the ionized samples in water/MEK mixture are larger than those in the pure solvents when the polymer concentration is greater than 0.25 g/dl, owing to the increased dissociation of the aggregates as the water content in the solutions increases. As the solution is diluted, the reduced viscosities of ionized samples decrease due to the dilution effect. At very high dilution, the polyether segments (soft segments) lose their solvation sheath and tend to coiling up and interweave with the hard segment situated on the polymer particle. So the reduced viscosity drops sharply and is smaller than that of the solution in pure solvent at a polymer concentration less than 0.25 g/dl. As the MEK in the mixture is replaced by the same amount of DMF, the reduced viscosities of the ionized samples (H-0.7 and H-1.0) increase with dilution and are higher than those of the ionized samples in MEK (Fig. 4). The result can be attributed to the fact that the highly polar solvent DMF can lead to a higher extent of dissociation of aggregated hard segments, causing a higher extent of chain expansion during dilution.

At a mixing ratio of water/MEK between 0.28 and 0.74, the reduced viscosities of the ionized samples (H-0.7 and H-1.0) increase with mixing ratio and dilution (Figs. 2 and 3). Since the association of ionized hard segments is found to decrease with increasing dielectric constant and polarizability of the solvent (17), and the polarity of water is higher than that of MEK, on increasing the amount of water in the water/MEk mixture, the extent of dissociation of the aggregated hard segments increases. So the reduced viscosities of the ionized samples increase with mixing ratio. During dilution, the higher extent of dissociation and chain expansion resulting from repulsion of the ionized hard segments leads to an increase of the reduced viscosity.

At a mixing ratio of water/MEK between 0.74 to 4.44, the reduced viscosities of the ionized samples (H-0.7 and H-1.0) decrease with mixing ratio and increase with dilution. In this mixing ratio range, the polyether segments lose their solvation sheath, and they come together to form hydrophobic associates, which rearrange into microspheres. So, on increasing the mixing ratio, the extent of association of polyether segments increases, which leads to a decrease of the reduced viscosity. During dilution, the increased extent

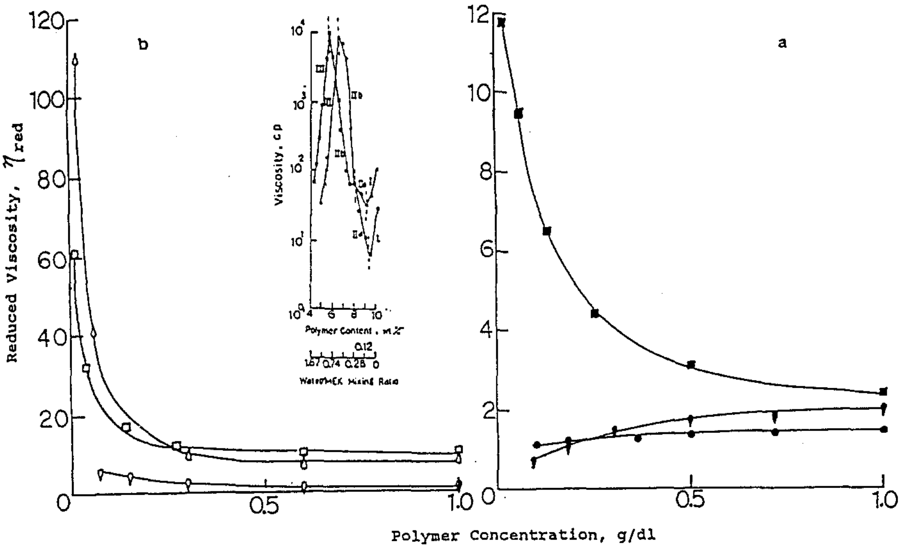

Fig. 2. The reduced viscosity curves of sample H-0.7 in water/MEK with various mixing ratios (by weight): (●) 0.0, (▼) 0.12, (▽) 0.28, (△) 0.74, (□) 1.67, (■) 4.44. The insert in Figure is taken from Ref. 20:(lower curve) H-0.7, (upper curve) H-1.0.

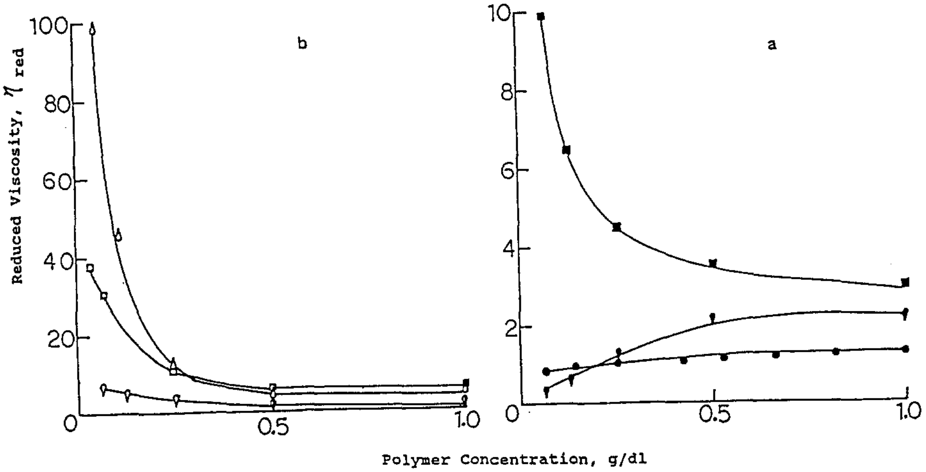

Fig. 3. The reduced viscosity curves of sample H-1.0 in water/MEK with various mixing ratios (by weight): (●) 0.0, (▼) 0.12, (▽) 0.28, (△) 0.74, (□) 1.67, (■) 4.44.

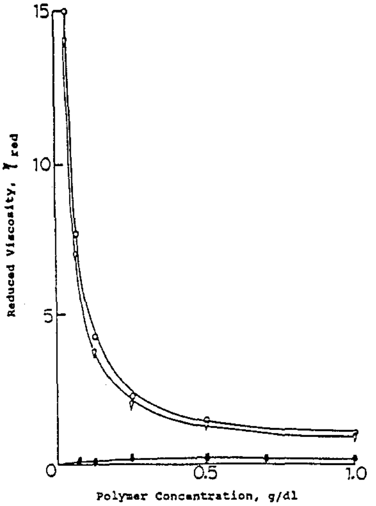

Fig. 4. The reduced viscosity curves of the ionized samples in water/MEK and water/DMF with a mixing ratio of 0.12: (○ , ●) H-0.7, (♀ , ♀) H-1.0. The full symbols are for water/MEK and the open symbols are for water/DMF.

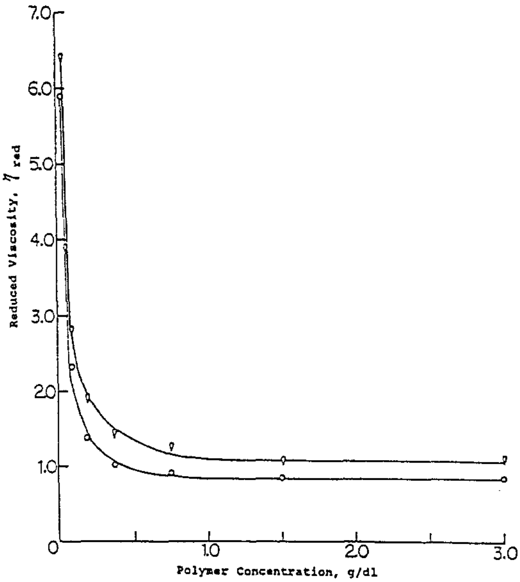

Fig. 5. The reduced viscosity curves of emulsions with pure water: (♀) H-0.7, (○) H-1.0.

of dissociation and chain expansion resulting from repulsion of the ionized hard segments leads to an increase of the reduced viscosity.

The variations of reduced viscosity of solutions with various water/MEK mixing ratios are consistent with the solution viscosity variations during emulsification reported in our preceding works (20). The variation in chain conformations resulting from the above analysis of reduced viscosity is in agreement with the change in morphology of the polymer particle during the addition of water to the solution.

3. Reduced viscosity of emulsion

The variations of reduced viscosity of emulsions are shown in Fig. 5. The reduced viscosities of emulsions are higher than those of the corresponding solutions with pure solvent (Fig. 1), and increase with dilution. In the emulsion, the hydrophobic associates (polyether segments) situated in the microspheres are not swollen with MEK and the inverted hard segment situated on the microsphere surface are swollen with water, which lead to chain expansion resulting from dissociation of the inverted hard segment. Hence, the reduced viscosities of emulsions are higher than those of the solutions with pure MEK. During dilution, a higher extent of chain expansion of the inverted hard segment leads to an increase of the reduced viscosity. The reduced viscosity of H-1.0 emulsion is smaller than those of emulsion H-0.7 because the higher ionic content cause higher extent of aggregation.

CONCLUSION

For the un-ionized sample in pure MEK and DMF, the reduced viscosities of both solutions follow the Huggins relation. For ionized samples in pure MEK and DMF, aggregation of the ionized hard segments still exists in the MEK and DMF solution in the high polymer concentration range, whereas chain expansion occurs in the low polymer concentration range. For ionized samples in water/solvent mixture, at a mixing ratio (by weight) is 0.12, the reduced viscosity indicates an aggregation behavior in MEK/water and a polyelectrolyte behavior in DMF/water. At a mixing ratio between 0.24 and 4.44, the reduced viscosities exhibit a polyelectrolyte behavior. The polymer particles change from a clear elastic gel (at a water/MEK mixing ratio less than 1.0) to microsphere (at a water/MEK mixing ratio larger than 1.0). For emulsions of the ionized samples, the reduced viscosity exhibits a polyelectrolyte behavior.

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