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(47) Equation 47 should be compared with the counterion pressure $\pi_i \simeq k_BTcAQ^{-1}$. See also ref 11.
(48) Two extra critical concentrations can be introduced: (i) c_4 which defines the onset of polymer behavior which a polyelectrolyte inevitably shows at high concentrations; and (ii) $C_G^* \simeq A^{-2}l^{-2}$, the overlap concentration defined by De Gennes et al. in ref 11. We have not discussed regions A and E explicitly, but their presence follows from simple arguments.

Imposed Polyelectrolyte Behavior of Poly(*m*-phenyleneisophthalamide) in LiCl/Dimethylacetamide

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Received September 15, 1978

ABSTRACT: The dilute solution viscometric behavior of poly(*m*-phenyleneisophthalamide) dissolved in LiCl/dimethylacetamide was studied. Important aspects of this investigation included interactions between dimethylacetamide and LiCl and the capability of poly(*m*-phenyleneisophthalamide) to become a polyion when dissolved in LiCl/dimethylacetamide. Counterion interaction with the polyion and the ability to control the ion concentration gave rise to interesting variations in the hydrodynamic volume of poly(*m*-phenyleneisophthalamide) leading to a maximum in its intrinsic viscosity as a function of LiCl concentration.

A polymer molecule changing its dilute solution viscometric character from typical random coil to polyelectrolyte behavior as salt is added to the solution is contrary to the usual case. Ordinarily a polymer ionizes in a single component solvent and produces a polyelectrolyte. The sodium salt of poly(acrylic acid) dissolved in water is a representative example of the latter case. Such cases show increasing values of η_{sp}/C as C is decreased. However, all of this can be forced to revert to the usual viscometric behavior by the addition of uni-univalent salt.[1]

The present study considers the conversion of a polymer to a polyelectrolyte by dissolving it in an ionized solvent. The dilute solution viscometric behavior of poly(*m*-phenyleneisophthalamide) dissolved in the solvents DMA (dimethylacetamide) and DMA/variable LiCl was investigated. To properly discuss the findings of this investigation, some important earlier research on DMA/LiCl interactions and experimental behavior and theory of polyelectrolytes must be recalled.

Amide–LiCl Interactions. Pertinent studies[2-5] of amide salt solutions reported that in a LiCl/DMF (dimethylformamide) or LiCl/NMA (*N*-methylacetamide) solution it was possible to isolate solid adducts of the salt complexed with the amide. From X-ray and/or titration studies on these adducts, the ratio of LiCl to NMA or DMF was found to be 1 to 4. Viscosity, heats of interaction, and infrared spectroscopy experiments strongly suggest that similar salt–amide complexes are formed in DMA/LiCl solutions. Thus the solvent system LiCl/DMA is significant to the viscometric behavior of polymers manifesting the "polyelectrolyte effect" when dissolved in electrolytic solvents.

Behavior of Polyelectrolytes. Theoretical treatments and experimental techniques dealing with the behavior of polyelectrolytes in dilute solution have been extensively studied and presented in several books.[6-10] The typical behavior of a linear flexible polyelectrolyte in dilute solution is explained by electrostatic repulsion of the charges along the polyelectrolyte chain causing the macroion to expand to achieve greater separation of the like charges. Macroion expansion will increase as the polymer concentration is decreased until finally in very dilute solutions the macroion may be fully extended and behave as a rigid rod.[11-13]

Also the behavior of polyelectrolytes as measured by their $[\eta]$'s in solutions with various levels of added salt is of interest. It has been found experimentally that $[\eta]$ is proportional to $C_s^{-1/2}$ (C_s is the molar concentration of uni-univalent salt, in the present case LiCl) for a number of polyelectrolytes.[14-16,22] A number of theories exist which deal with the behavior of polyelectrolytes in dilute solutions with added salt.[1,17-22] Of these theories, those of Fixman, as well as those of Isihara, predict that $[\eta]$, the intrinsic viscosity, will be proportional to $C_s^{-1/2}$.

Experimental Section

Materials. Two different samples of MPD-I (poly(*m*-phenyleneisophthalamide)) were synthesized in this laboratory using low-temperature solution polycondensation methods. The procedures are in essence those of Morgan and Kwolek and the DuPont group[23] and are described in an earlier paper by our group.[24]

The solvent system utilized in this investigation was DMA and

$$CH_3C(O)N(CH_3)_2 \tag{1}$$

LiCl. The DMA was obtained from the Aldrich Chemical Co. and the LiCl from the Mallinckrodt Chemical Co. as reagent grade materials.

Dilute Solution Viscosity. Dilute solution viscosities were determined using an Ubbeholde viscometer at 25 ± 0.1 °C where the flow time of the solvent exceeded 100 s. Data obtained using a number of concentrations were converted to specific and relative viscosities which were converted to intrinsic viscosity $[\eta]$ (when feasible) by extrapolation to infinite dilution. In particular[25,26]

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C + 0(C^2) \tag{2}$$

and

$$\ln(\eta_{rel}/C) = [\eta] + k''[\eta]^2C + 0(C^2) \tag{3}$$

where k' is the Huggins constant, k'' is the Kraemer constant, and

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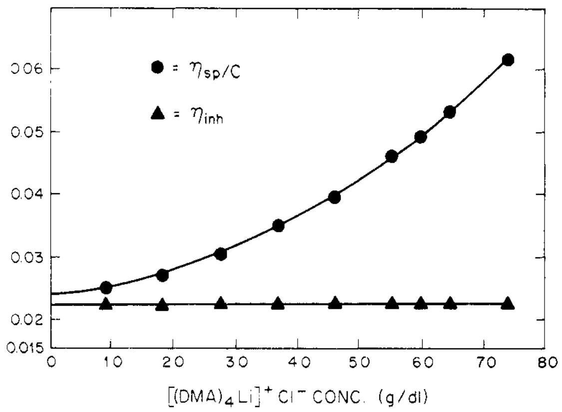

Figure 1. Reduced specific and inherent viscosities plotted against [(DMA)$_4$Li]$^+$Cl$^-$ concentration at 25 °C to test the Einstein model for a LiCl complex.

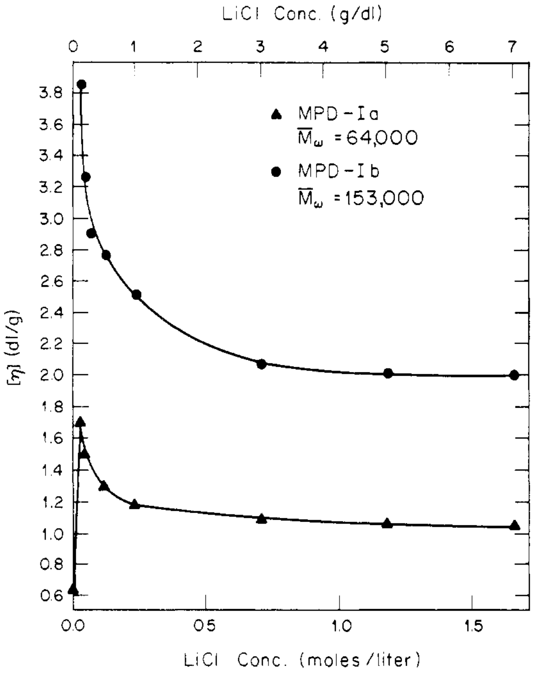

Figure 2. Intrinsic viscosity vs. LiCl concentration for MPD-I in DMA/LiCl at 25 °C. Molecular weights were determined by light scattering as described elsewhere.[27]

ln (η_{rel}/C) is the inherent viscosity.

Results

All the data produced in this study come from flow time measurements obtained with an Ubbeholde viscometer. The results are presented in Figures 1 through 6. Important trends to note are the variations in viscometric properties as the LiCl concentration changes. Since the LiCl concentration plays a role in the viscometric behavior of the system studied, it is important to know if it interacts with both the DMA and MPD-I or just one of them. In this study, it was noticed that rather significant increases in flow times occurred as LiCl was added to DMA. If one treats these flow times relative to pure DMA, an intrinsic viscosity of 0.2 dL/g is obtained for LiCl dissolved in DMA at 25 °C.[27] A modified version of the LiCl–DMA intrinsic viscosity plot is given in Figure 1. Here the concentration axis is in terms of [(DMA)$_4$Li]Cl, yielding an intercept intrinsic viscosity value of 0.024 dL/g. The reasoning for such a treatment is given in the Discussion section.

One way to examine the influence of LiCl on the dilute solution viscosity of MPD-I is to determine intrinsic viscosities at various LiCl concentrations. The results of such an experiment are plotted in Figure 2. The higher molecular weight MPD-I shows a monotonic increase in [η] as LiCl concentration is decreased, with this MPD-I being insoluble in pure DMA. The lower molecular weight MPD-I is soluble in pure DMA and gives the lowest [η] here with a maximum observed at low LiCl concentrations.

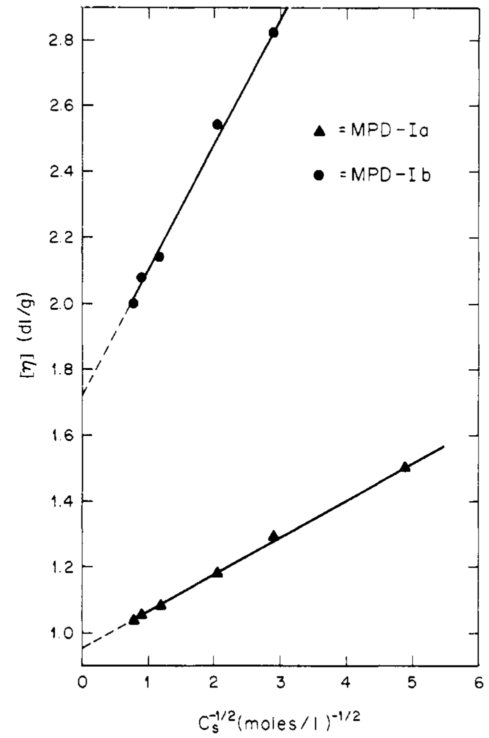

Figure 3. Intrinsic viscosity plotted against the reciprocal square root of the LiCl concentration to demonstrate the existence of polyelectrolyte behavior.

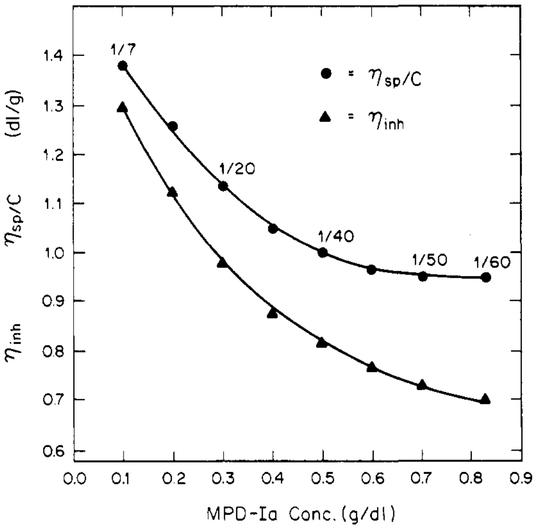

Figure 4. Reduced specific and inherent viscosities plotted against MPD-Ia concentration in DMA at 25 °C: [LiCl] = 1.18 × 10^{-3}M; ratios are C_s/C_{pa}.

A further examination of the significance of added salt to a dilute polymer solution is available. For systems known to display the polyelectrolyte effect, a straight line is obtained when [η] is plotted against the inverse square root of the salt concentration. Such a treatment is presented in Figure 3.

An alternative way to view the behavior of the DMA/LiCl/MPD-I ternary system is to argue it is more pertinent to consider the ratio C_s/C_{pa} (ratio of the molar concentrations of LiCl to the polymer amide groups) rather than

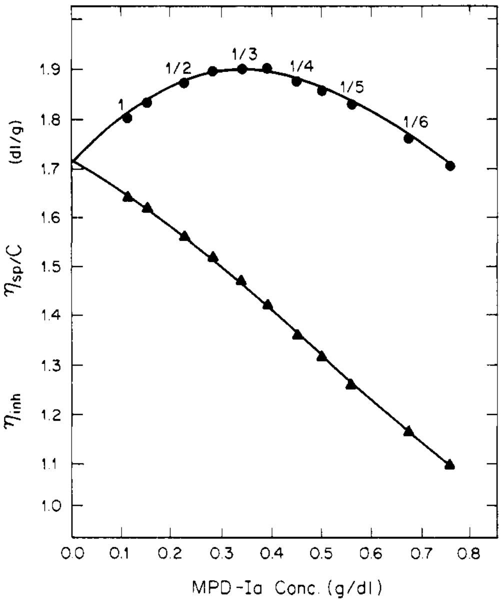

Figure 5. Reduced specific and inherent viscosities plotted against MPD-Ia concentration in DMA at 25 °C: [LiCl] = 9.44 × 10^{-3} M; ratios are C_s/C_{pa}.

the absolute value of the LiCl concentration. Figures 4 and 5 treat the data to examine the importance of a variable C_s/C_{pa} ratio as opposed to the LiCl concentration. Figure 6 considers the behavior when the ratio is set at several different constant values.

Discussion

This discussion is structured to consider several concepts involving solutions of LiCl/DMA and LiCl/DMA/MPD-I and especially to evaluate conclusions about the polyelectrolyte behavior of MPD-I. Attention is first given to the kind of interaction found in LiCl/DMA solutions, with special emphasis on their possible electrolytic character. Another concept explored is the change in the conformation of the polyamide MPD-I in LiCl/DMA solvents as the LiCl concentration is changed.

LiCl/DMA Solutions. Earlier research[2-5] has established that LiCl develops significant interaction with amide solutions. In the present studies, large increases were noted in the viscometric flow time measurements of DMA/LiCl solutions compared to DMA itself. The Einstein concept of spheres dispersed in a flowing medium was used to probe this observation. Thus starting with the usual form of the Einstein equation

$$\eta = \eta'(1 + 2.5\phi) \qquad (4)$$

it can be shown that

$$\eta_{sp}/C = 2.5/100\rho \qquad (5)$$

when η is the viscosity of the solution and η' is the viscosity of the solvent. Equation 5 shows the intrinsic viscosity should be 0.025 dL/g, for a density of 1 g/mL, which is the approximate density of the complex postulated below.

For the LiCl/DMA system studied here, if one uses the concentration of LiCl, the obtained $[\eta]$ is 0.22 dL/g. However, when the concentration is taken on the basis of $(DMA)_4(LiCl)_1$ stoichiometry, an $[\eta]$ of 0.024 dL/g is found (see Figure 1). Thus it is concluded that the coincidence between the Einstein model prediction of $[\eta]$ = 0.025 dL/g and the experimentally observed 0.024 dL/g is not circumstantial but of real significance. A further analysis of Figure 1 is informative. Calculations of the limiting slopes of the two curves as concentration approaches zero yields a difference in the Huggins–Kraemer constants very nearly equal to 0.5 as expected in dilute solution. However, at the higher LiCl concentrations near 7%, this same treatment yields a value of 0.85. Thus at the higher LiCl concentrations, there are significant second-order interactions as the coefficients for the square powered concentration terms in eq 2 and 3 can no longer be zero. Acceptance of the implications of the intercept and changing slope values for Figure 1 means that a polyamide dissolved in a LiCl/DMA solvent system will interact with a species that in all probability is electrolytic and formulistically written as $[(DMA)_4Li]^+Cl^-$.

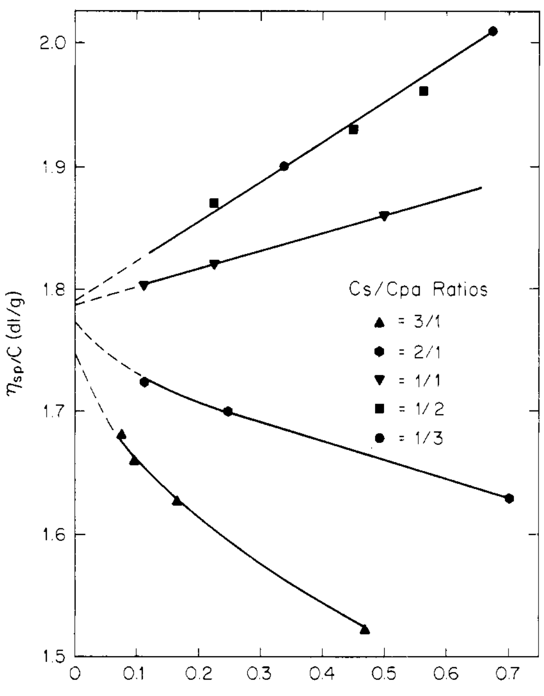

Figure 6. Reduced specific viscosities plotted against concentration in DMA at 25 °C, where C_s/C_{pa} is held constant.

MPD-I/LiCl/DMA Solutions. Gaining an understanding of MPD-I dissolved in LiCl/DMA is difficult due to an apparently complex set of interactions. Figure 2 shows intrinsic viscosity is sensitive to the concentration of LiCl. Now the increase in the intrinsic viscosity as the LiCl concentration decreases establishes that the coil dimensions are significantly changing as the solvent character changes. A second feature of some significance is that the intrinsic viscosity of MPD-Ia at high LiCl concentration is greater than its intrinsic viscosity in pure DMA. This is in spite of the fact that MPD-I is associated in pure DMA but completely dissociated above 4% LiCl content.[27] These features indicate that MPD-I/LiCl/DMA solutions are fundamentally different from MPD-I/DMA solutions and the LiCl in some way induces considerable coil expansion.

Several papers[28-31] indicate that MPD-I could have polyelectrolyte behavior. Early research[28] showed that aliphatic polyamides can in some circumstances act as polyelectrolytes. Very recently the dilute solution viscosity of poly(*p*-phenyleneterephthalamide) in H_2SO_4 was discussed and interpreted in terms of polyelectrolyte behavior.[29] More directly, two other papers specifically consider aromatic polyamides dissolved in LiCl/DMA and the resulting polymer–solvent interactions.[30-31]

MPD-I is not an inherently ionizable polymer, and thus some kind of ionizable species would have to be formed before polyelectrolyte behavior could occur. Recognition of this led to a search of the literature for studies which might explain polyelectrolyte behavior on a molecular basis. The studies on amide salt solutions mentioned previously were helpful. They showed that in a LiCl/NMA solution the Li^+ ions are coordinated with the carbonyl oxygen of the NMA molecule. Also, the Cl^- ions are coordinated or hydrogen bonded[30] to the amide hydrogens. Using this information plus studies of their own, Gan et al.[30] and Panar and Beste[31] have shown that in an aromatic polyamide/DMA/LiCl solution the Cl^- ions will be hydrogen bonded to the amide hydrogen of the polyamide. The Li^+ ions are then associated with the carbonyl oxygens present in the system. Panar and Beste show the Li^+ coordinated with the carbonyl oxygens of DMA while Gan et al. believe the Li^+ ions can also be coordinated with the carbonyl oxygens of the MPD-I molecule. Panar and Beste developed a model for poly(1,4-benzamide) in DMA/LiCl. In this model the N–H groups of the polymer chain are fully associated with chloride ions. The resulting polyelectrolyte is solvated by a weak Li^+–amide complex; this neutral entity is then soluble in DMA.

This model should also be qualitatively correct for the MPD-I/DMA/LiCl system. However, in the system under study here we consider the Cl^- ions coordinated with the amide hydrogens as not completely neutralized by the Li^+–DMA complexes. Instead, the net charge of the Cl^- ions on the MPD-I molecule is sufficient to cause polyelectrolyte expansion of the polymer molecule.

In further discussing and presenting the dilute solution viscometric results for MPD-I, two assumptions are made. One is that in a MPD-I/DMA/LiCl system the N–H groups of the polymer molecule will be fully associated with Cl^- ions (to the extent that a sufficient number of Cl^- ions are present[31]). The Li^+/DMA complexes will then act as counterions to the negative polyelectrolyte. Assumption number two is that the cationic layer of Li^+/DMA complexes will not have a significant effect on $[\eta]$. In other words, primary electroviscous effects are considered negligible, and changes in $[\eta]$ (or irregular behavior of reduced and inherent viscosity) are taken to reflect a change in the size of the macromolecule.

Typical Polyelectrolyte Behavior of MPD-I in DMA/LiCl. The MPD-I/LiCl/DMA system can be a typical polyelectrolyte as judged by the behavior shown in Figure 3. Also the usual behavior of coil expansion to reduce electrostatic repulsion is shown in Figure 4 and to some extent in Figure 5.

Figure 4 is a plot of η_{sp}/C and η_{inh} vs. MPD-Ia concentration in DMA with 1.18×10^{-3} M added LiCl. In this system, the LiCl concentration is always less than the concentration of polymer amide groups. Therefore, as the polymer concentration decreases, the fraction of polymer amide hydrogens coordinated with a Cl^- ion increases since C_s is constant. The result is that the polymer molecules expand due to the increasing electrostatic repulsion. This expansion gives rise to the atypical η_{sp}/C and η_{inh} curves. The value of η_{sp}/C is a function of at least three variables: (1) MPD-Ia concentration, (2) C_s/C_{pa}, and (3) the fraction of coordinated Cl^- ions which bind with a Li^+/DMA complex to effectively neutralize the site charge. The value of the fraction in (3) is unknown and is probably a complex function of C_s/C_{pa}.

Nonlinear behavior is also present in the η_{sp}/C vs. MPD-Ia concentration plot in Figure 5. Here DMA with 9.44×10^{-3} M added LiCl is the solvent. At the higher polymer concentrations, C_s/C_{pa} is less than one so that maximum electrostatic repulsion has not been reached. The macromolecule expands as C_s/C_{pa} increases until at $C_s/C_{pa} = 1/3$ a maximum in η_{sp}/C is reached. When $C_s/C_{pa} \gtrsim 1/2.5$, the value of η_{sp}/C decreases with decreasing polymer concentration indicating that any further coil expansion is relatively slight.

Atypical Polyelectrolyte Behavior of MPD-I in DMA/LiCl. The ordinate intercept of the $[\eta]$ vs. $C_s^{-1/2}$ plot for MPD-Ia (Figure 3) is 0.95 dL/g. This value of $[\eta]$ at infinite salt concentration is higher than the value of $[\eta]$ for MPD-Ia in DMA without any added LiCl. This is not the result that would be expected based on the behavior of other flexible polyelectrolytes. At high salt concentrations a typical flexible polyelectrolyte will coil up and assume the dimensions of the equivalent neutral parent polymer.[33,34] A number of other polyelectrolytes would have actually precipitated from solution at the higher salt concentrations used here.

The relatively high viscosity of MPD-Ia in DMA (at high concentrations of added LiCl) may be caused by some inability of the $Li^+(DMA)_n$ counterions to completely neutralize the polyion charge sites. By complexing with DMA, a Li^+ ion would be expected to share its charges with the amide nitrogens of the DMA molecules.[5] The counterion charge would then not be a point charge but a charge distributed throughout the $Li^+(DMA)_n$ complex. This distributed charge will not be as accessible to the Cl^- sites along the polymer chain as the charge on Li^+ would be. Further evidence that MPD-I in DMA/LiCl does not behave like a typical flexible polyelectrolyte is found in plots of η_{sp}/C vs. MPD-Ia concentration where the ratio of Li^+ ions to polymer amide groups is a constant (C_s/C_{pa} = constant). Such plots at values of $C_s/C_{pa} = 1/3$, 1/2, 1/1, 2/1, and 3/1 are presented in Figure 6. These curves were obtained from data of MPD-Ia solutions at several levels of added salt.

The systems where C_s/C_{pa} is constant at 3/1, 2/1, and 1/1 are similar to polyelectrolytes with degree of ionization equal to $^1/_3$, $^1/_2$, and 1, respectively, in solutions with no added salt. Such polyelectrolyte systems will have η_{sp}/C vs. polymer concentration curves which display an upward curvature as the polymer concentration decreases.[11,35] This upward curvature is caused by the increasing expansion of the polymer molecule. Macroion expansion results from the counterions becoming distributed throughout the solution as the polymer concentration decreases. The counterions, therefore, become less effective in neutralizing the charges on the macroion leading to increased electrostatic repulsion. As can be seen in Figure 6, none of the η_{sp}/C vs. MPD-Ia concentration plots at $C_s/C_{pa} = 1/3$, 1/2, or 1/1 exhibit an increase in η_{sp}/C with a decrease in polymer concentration. The data points instead form straight lines (at $C_s/C_{pa} = 1/3$ the straight line is arbitrary) with a slight maximum in $[\eta]$ at $C_s/C_{pa} = 1/2$. The η_{sp}/C versus MPD-Ia concentration plot at $C_s/C_{pa} = 2/1$ does increase with decreasing polymer concentration. This is reasonable in this case since there is a large decrease in the free counterion concentration with a decrease in polymer concentration. In the other cases, a number of the counterions may be bound to specific Cl^- sites on the polyion.

Conclusions

1. From both earlier and the present studies, it is concluded that LiCl interacts with amides. By considering the dilute solution viscometric behavior of LiCl in DMA via the Einstein model, the complex $[(DMA)_4Li]^+Cl^-$ is postulated.

2. The electrolytic nature of LiCl in DMA imposes polyelectrolyte behavior on dilute solutions of MPD-I in LiCl/DMA solvents.

3. The ratio of C_s/C_{pa} is important. It controls both the number of charged sites that can be formed on a polymer molecule in solution and the degree of polymer coil expansion.

Acknowledgment. This work was supported in part by the U.S. Office of Naval Research.

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Studies of Sulfonyl Radicals. 6.[1] Chain-Transfer Constants of Some Sulfonyl Chlorides in Styrene and Methyl Methacrylate Polymerizations

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ABSTRACT: Chain-transfer constants (C_{tr}) of arene- and alkanesulfonyl chlorides at 60 °C in styrene and methyl methacrylate (MMA) polymerizations have been determined using the conventional $\bar{P}_n$ (degree of polymerization)–C_{tr} relationship. Large C_{tr} values for the polystyryl radical were obtained with the sulfonyl chlorides (0.1–2.6) compared to that with CCl_4 (0.01). A Hammett plot for substituted benzenesulfonyl chlorides gave $\rho = 0.86$, which may be explained by the contribution of a charge-transferred resonance form ($ArSO_2^-$ Cl $^+CH(Ph)CH_2\sim$) in the transition state. On the other hand, C_{tr}'s for poly(MMA) radical were found to be $(5\text{–}9) \times 10^{-4}$ with arenesulfonyl chlorides.

In connection with the propagation mechanism of radical copolymerization[2] of vinyl monomers with sulfur dioxide, we have been investigating the chemistry of sulfonyl radicals. We have already reported that sulfonyl radicals have a strong electron-accepting and electrophilic nature,[3] and the elimination of SO_2 from sulfonyl radicals and the recombination rate constants for these radicals have also been investigated.[4,5] With respect to chain-transfer reactions concerned with sulfone compounds, relatively large transfer constants (C_{tr}) for polystyryl radical with azosulfones were observed in our laboratory.[6]

In this study, the chain-transfer reaction of various sulfonyl chlorides, as shown in eq 1, has been investigated.

$$\sim P\cdot(\text{polymer radical}) + RSO_2Cl \rightarrow \sim PCl + RSO_2\cdot \quad (1)$$

Although similar processes were involved in the mechanism of the adduct formation of sulfonyl chlorides with alkenes,[7] no chain-transfer constant of sulfonyl halides has been reported so far, as far as we know, and this reaction may be expected to show a strong polar effect due to the formation of electron-accepting sulfonyl radicals.

Polymerizations of styrene and methyl methacrylate (MMA) were carried out in the presence of sulfonyl chlorides at 60 °C using azobis(isobutyronitrile) (1.2×10^{-2}M) and stopped at a low conversion. Conversion was measured gravimetrically. The polymerization rates of styrene and MMA were not changed by the addition of a small quantity of sulfonyl chlorides in this experiment. Molecular weights were evaluated from the intrinsic viscosities of benzene solutions of polystyrene[8] and poly(MMA).[9]

Figure 1 shows that the plots of $1/\bar{P}_n$ vs. [S]/[M] are straight lines according to

$$1/\bar{P}_n = 1/\bar{P}_o + C_{tr}[S]/[M] \quad (2)$$

where $\bar{P}_n$ and $\bar{P}_o$ are the degrees of polymerization in the presence and the absence of sulfonyl chlorides, and [S] and

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