

Solution and Rheological Properties of Poly(*m*-phenyleneisophthalamide) in Dimethylacetamide/LiCl

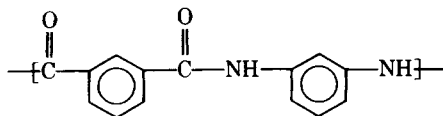
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Synopsis

An experimental study of the solution properties of poly(*m*-phenyleneisophthalamide) (MPD-I) in dimethylacetamide (DMA)/LiCl solutions is presented. Differential refractometry, light scattering photometry, dilute and concentrated solution viscometry, and normal stress experiments are reported and interpreted. This polymer in the concentration range investigated does not exhibit mesophase behavior in contrast to its *para*-linked analog. Generally, it behaves as a flexible polymer molecule; however, its capacity to become a polyelectrolyte strongly influences its behavior in the presence of LiCl. MPD-I is self-associated when dissolved in pure DMA but dissociates in DMA/LiCl solvent systems. The Zimm plots of MPD-I in DMA/LiCl solutions show distortion, probably due to polymer-salt interactions.

INTRODUCTION

Aromatic polyamides have become technologically significant during the past decade because of their importance as high-temperature, high-modulus, and high tensile-strength fibers. One of the more important of these aromatic polyamides is poly(*m*-phenyleneisophthalamide) (MPD-I), speculated to be the basic



polymer of the du Pont Nomex fiber. It is the purpose of this paper to investigate the dilute and concentrated solution properties of this polymer.

Studies of MPD-I in the open literature appear limited. The synthesis of this polymer is described in the patent literature together with some discussion of physical properties.^{1,2} More recently, Gan and his co-workers³ have described nuclear magnetic resonance (NMR), infrared (IR) spectra and the results of differential scanning calorimetry experiments. The character of solutions of MPD-I in dimethylacetamide (DMA) were discussed by Gan et al. and by Klenin and his co-workers.⁴ The latter authors argue that there are association effects leading to supermolecular aggregates in these solutions. The solution spinning of fibers of MPD-I from DMA solutions has been reported by various investigators.^{1,5}

This paper represents a continuation of studies from our group on aromatic polyamides.⁵⁻⁹ In one study mentioned above,⁵ fibers were wet spun and eval-

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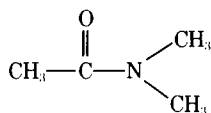
uated. In two other papers,^{6,7} block copolymers of MPD-I were synthesized and characterized. In this paper we consider the solution properties of this polymer in DMA/LiCl solvents. Special attention is given to the influence of the LiCl level in the system.

EXPERIMENTAL

Materials

Several polymers were studied, including some polymerized in this laboratory using low-temperature solution polycondensation methods. The procedures are in essence those of Morgan and Kwolek and the du Pont group^{1,2,10} and are described in earlier papers by our group.⁶⁻⁹ In addition, Nomex fiber, Type 430 T, was used. The polymers used in this study are summarized in Table I.

The solvent system utilized in this investigation is dimethylacetamide (DMA),



and lithium chloride (LiCl). The dimethylacetamide was obtained from the Aldrich Chemical Company and the LiCl, from the Mallinckrodt Chemical Company as reagent-grade materials.

Refractive Index

The refractive index increment, or difference, Δn , of MPD-I/DMA/LiCl solutions was determined using a Brice-Phoenix Model BP-2000-V differential refractometer using light of 546-nm wavelength, operated at room temperature. The dependence of Δn upon both polymer and LiCl concentrations was considered.

Light Scattering in Dilute Solutions

Light scattering measurements were carried out with a Brice-Phoenix light scattering photometer, Series 2000, employing light of 546-nm wavelength. The data were obtained at room temperature. The instrument characteristics and

TABLE I
Poly(*m*-phenyleneisophthalamide) (MPD-I) Polymers Investigated

Polymer	$[\eta]$, dl/g ^a	$M_w \times 10^{-3}$ ^a	k'	k''
P1	1.05	50.5	0.17	0.29
P2	1.13	64.5	0.31	0.18
P3	1.26	7.58	0.14	0.29
P4	1.20	—	0.36	0.15
P5	2.01	—	0.29	0.18
P6	2.22	133	0.14	0.28
Nomex fiber, Type 430 T	2.52	—	0.23	0.29

^a Determined in DMA/5% LiCl at 25°C.

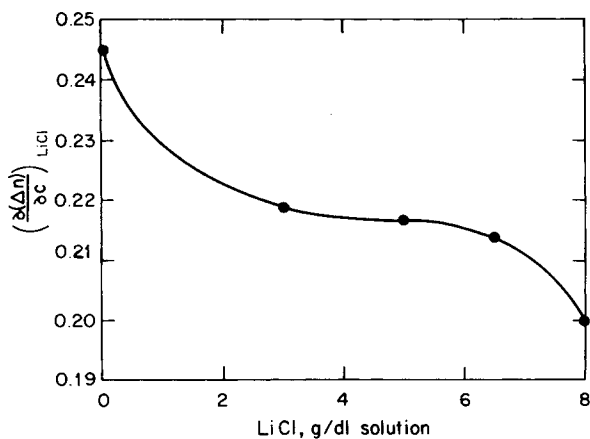


Fig. 1. Plot of $[\partial(\Delta n)/\partial c]_{LiCl}$ vs LiCl concentration.

performance were determined by using a standard polystyrene dissolved in benzene.

We have interpreted the experimental data using a Zimm plot.¹¹⁻¹⁴ Kc/R_θ was plotted as a function of $50c + \sin^2(\theta/2)$. Here,

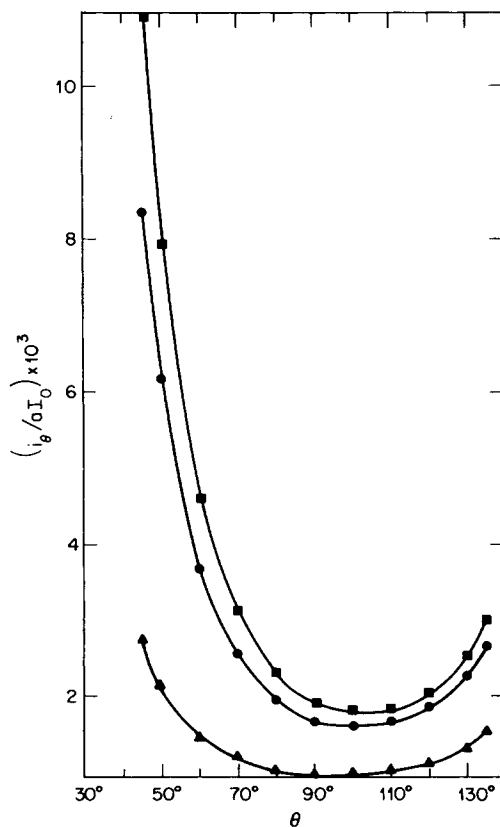
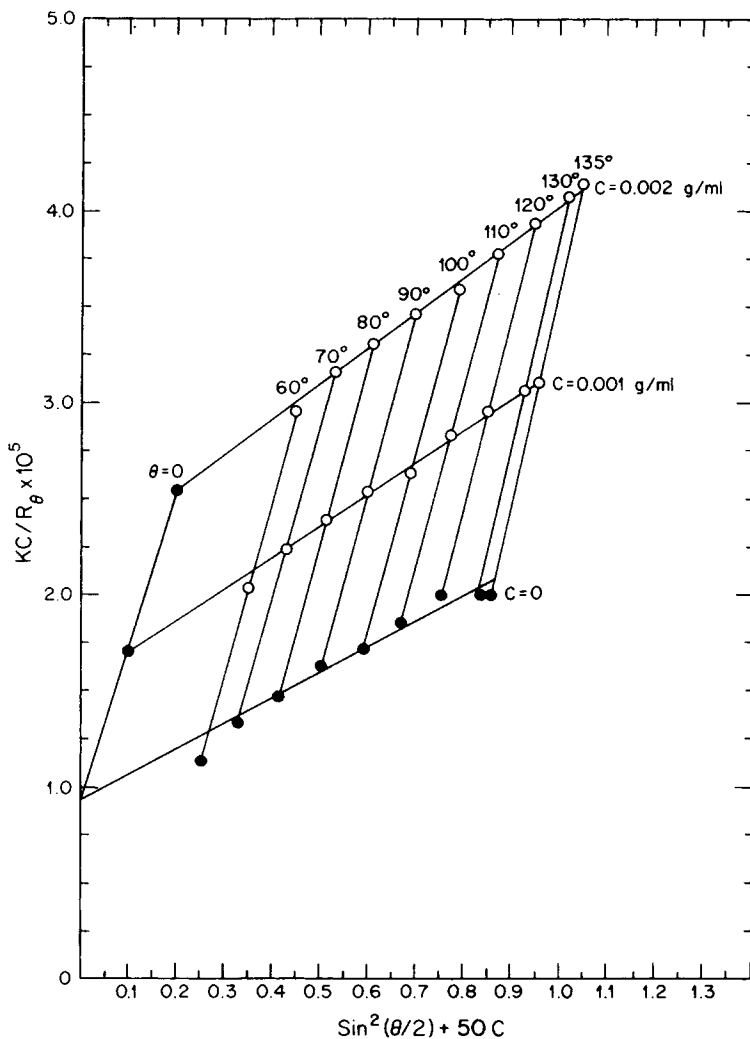


Fig. 2. Plot of (i_θ/aI_0a) vs angle θ at 0%, 4%, and 8% LiCl in DMA, where a is a factor due to the presence of a filter in the light path at zero angle: (■) 8 g/dl LiCl in DMA; (●) 4 g/dl LiCl in DMA; (▲) DMA.

Fig. 3. Zimm plot of polymer P₂ in DMA.

$$K = \frac{2\pi n^2 \left(\frac{\partial(\Delta n)}{\partial c} \right)_{\text{LiCl}}}{\lambda^4 N} \quad (1a)$$

$$R_\theta = \frac{r^2 i_\theta}{I_0 (1 + \cos^2 \theta)} \quad (1b)$$

where λ is the wavelength of light, I_0 is the incident beam intensity, i_θ is the scattered light intensity at angle θ , and c is the polymer concentration. The weight-average molecular weights \bar{M}_w were determined from the expression

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w} + Bc \quad (2)$$

TABLE II
Refractive Index Increment Data for MPD-I In DMA and DMA/LiCl Systems

Solvent	$\partial(\Delta n)/\partial c, (\text{g/ml})^{-1}$
DMA	0.245
DMA/3% LiCl	0.219
DMA/5% LiCl	0.217
DMA/6.5% LiCl	0.214
DMA/8% LiCl	0.200

extrapolated to zero polymer concentration and where B is a virial coefficient representing the sum of all interactions.

Certain corrections of the light scattering data are also required. Corrections for scattering by the solvent must be made. When the solvent is DMA/LiCl, the

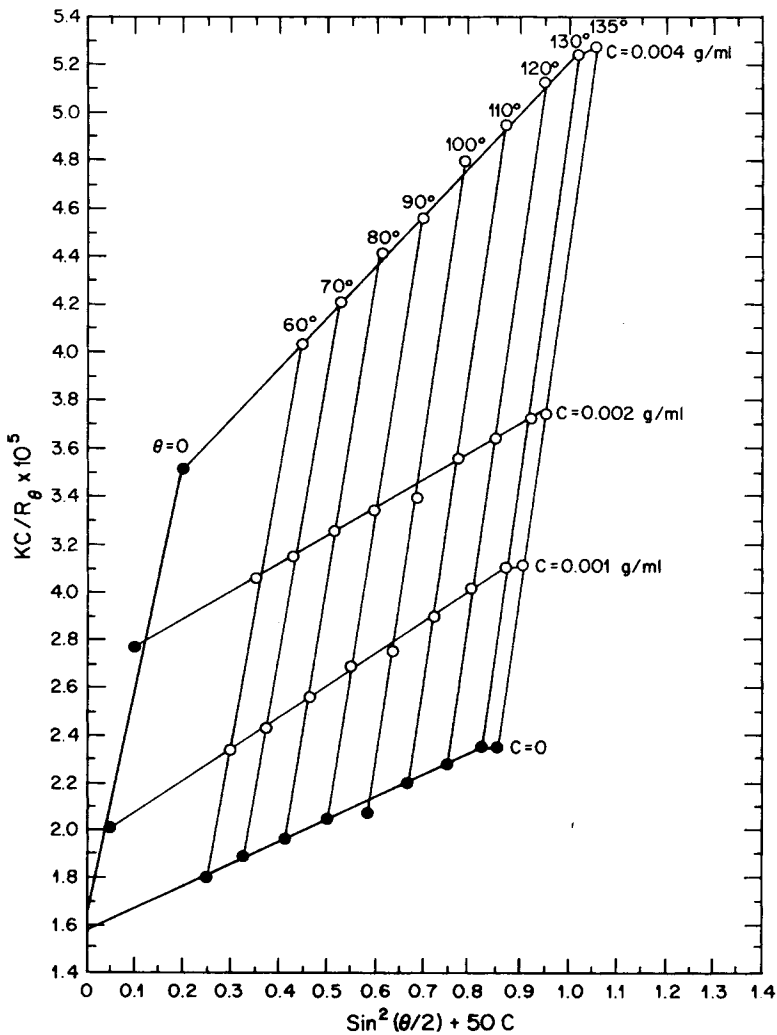


Fig. 4. Zimm plot of polymer P_2 in DMA/4% LiCl.

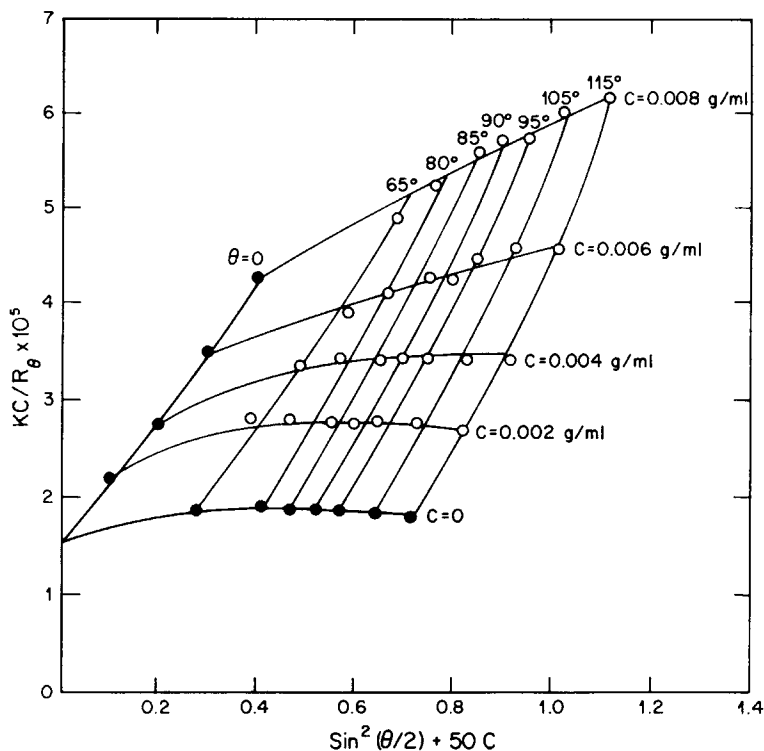


Fig. 5. Zimm plot of polymer P₂ in DMA/5% LiCl.

lower-angle solvent scattering is very pronounced. Furthermore, it is appropriate to correct for depolarization and fluorescence in these solutions. It was found that fluorescence occurred in polymer/DMA solutions but not in polymer/DMA/LiCl solutions. Depolarization occurred to a significant extent in polymer/DMA and polymer/DMA/4% LiCl. At 8% LiCl, depolarization was not significant.

Dilute Solution Viscosity

Dilute solution viscosities were determined using an Ubbelohde viscometer at $(25 \pm 0.1)^\circ\text{C}$. Data obtained using four to eight concentrations were converted to specific and relative viscosities which were converted to intrinsic viscosity $[\eta]$ by extrapolation to infinite dilution. In particular,¹²

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c + o(c^2) \quad (3a)$$

$$\ln \frac{\eta_{rel}}{C} = [\eta] + k''[\eta]^2c + o(c^2) \quad (3b)$$

where k' and k'' are the Huggins-Kraemer constants.

Optical Anisotropy in Concentrated Solutions

Some aromatic polyamides exhibit liquid crystalline or mesophase behavior.¹⁵ To test for such characteristics, Kwolek's DDA test¹⁵ was carried out on the solutions using a Leitz-Ortholux polarized light microscope.

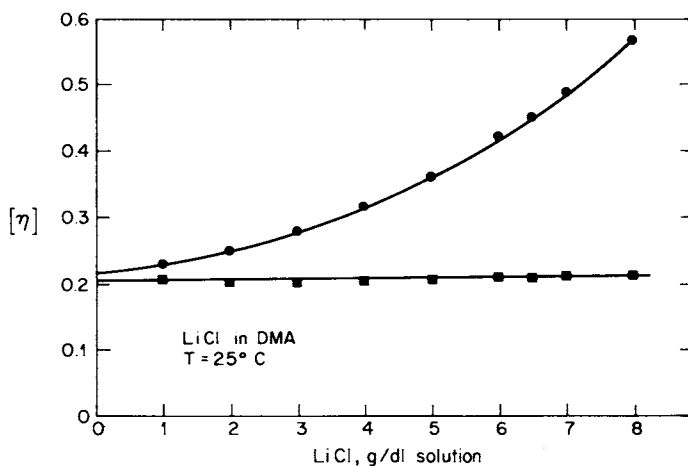


Fig. 6. Dilute solution viscosity of DMA/LiCl as function of LiCl level: (●) η_{sp}/c ; (■) η_{inh} .

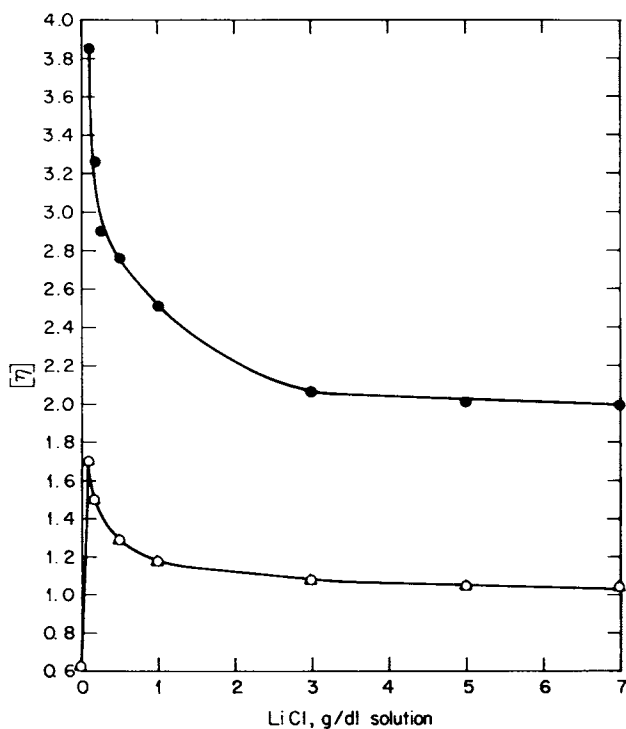


Fig. 7. Intrinsic viscosity vs LiCl concentration for polymers P_2 (○) and P_5 (●) at 25°C.

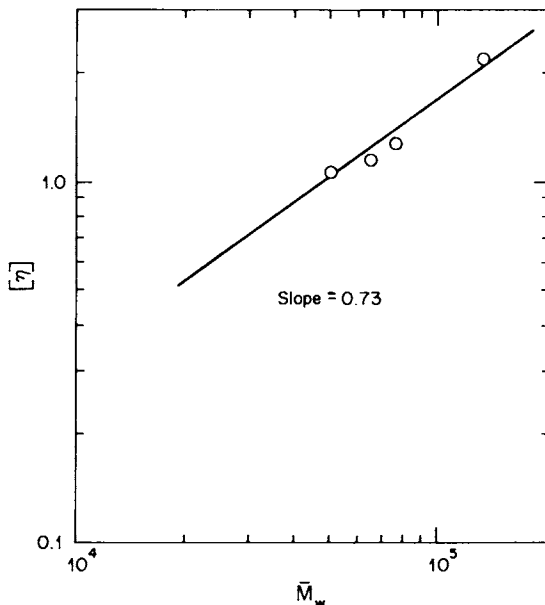


Fig. 8. Intrinsic viscosity as function of weight-average molecular weight.

Concentrated Solution Rheological Measurements

Measurements of rheological properties of solutions of dissolved Nomex fiber in DMA/5% LiCl were carried out using a Model R16 Weissenberg rheogoniometer. Studies were made in both laminar shear and oscillatory shear flow in the cone-plate attachment at room temperature.

In laminar shear flow $v_1 = \dot{\gamma}x_2$, the shear rate is determined by the rotation speed Ω of the cone and the angle α between the cone and plate through^{16,17}

$$\dot{\gamma} = \Omega/\alpha \quad (4)$$

The shear stress σ_{12} and viscosity η were determined from the torque T using the expression^{16,17}

$$\sigma_{12} = \eta\dot{\gamma} = 3T/\pi R^3 \quad (5)$$

The principal normal stress difference $N_1 = \sigma_{11} - \sigma_{22}$ and principal normal stress difference coefficient Ψ_1 were determined^{16,17} from the thrust F through

$$N_1 = \Psi_1\dot{\gamma}^2 = 2F/\pi R^2 \quad (6)$$

In the dynamic experiments, a sinusoidal shearing oscillation of form

$$\gamma(t) = \gamma_0 \sin \omega t \quad (7)$$

is imposed. The stress in response to this deformation has the form^{16,17}

$$\sigma(t) = G'(\omega)\gamma(t) + \eta'(\omega) \frac{d\gamma}{dt} \quad (8)$$

yielding two rheological functions, the dynamic storage modulus $G'(\omega)$ and the dynamic viscosity $\eta'(\omega)$.

RESULTS

Refractive Index

The refractive index increment data for MPD-I solutions are given in Table II. The basic data are refractive index increments as a function of MPD-I concentration. These functions are linear and the column reporting $\partial(\Delta n)/\partial c$ was evaluated by a least-squares data treatment.

In Figure 1 the refractive index increment-polymer concentration gradient $(\partial\Delta n/\partial c)_{\text{LiCl}}$ is plotted as a function of LiCl concentration. It is clear that increasing amounts of LiCl decreases the value of this gradient. This is expected since the refractive index of LiCl is greater than that of DMA. However, non-linearity of this behavior is not necessarily expected.

Light Scattering Results

Attention is drawn to the light scattering characteristics of DMA/LiCl solutions. The angular variation of light scattering is shown in Figure 2. Addition of LiCl induces increasing levels of scattering, especially at the lower angles.

Zimm plots were constructed and weight-average molecular weights were determined for various polymer samples in solvents containing different DMA/LiCl proportions. The LiCl level was found to have a very strong influence on the shape of the Zimm plot. Typical Zimm plots at various LiCl levels are shown in Figures 3 to 5. The distortion of some of these plots is obvious.

The weight-average molecular weights determined depended upon the presence or absence of LiCl. When no LiCl was present, for one sample an \bar{M}_w of

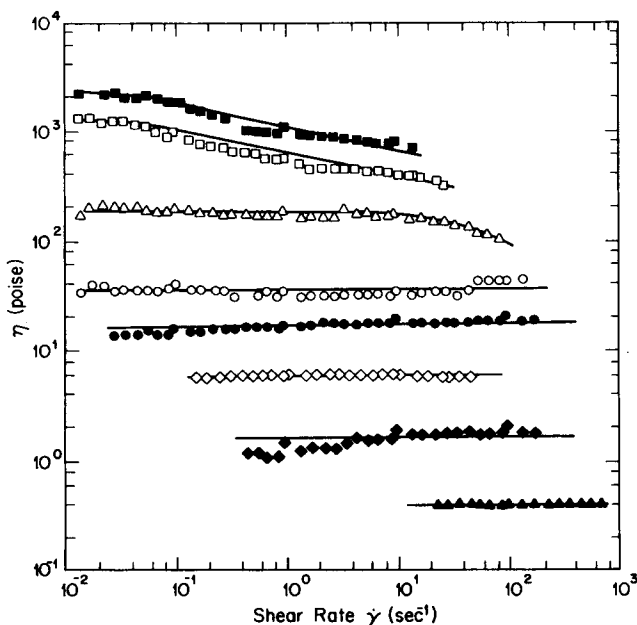


Fig. 9. Viscosity as function of shear rate for redissolved Nomex (Type 430 T) in DMA/5% LiCl for various Nomex concentrations: (■) 20%; (□) 16%; (△) 12%; (○) 10%; (●) 8%; (◇) 6%; (◆) 4%; (▲) 2%.

$(1.1 \pm 0.1) \times 10^5$ was found. At 4%, 5%, and 8% LiCl, $(6.3 \pm 0.1) \times 10^4$ was the \bar{M}_w found for the same material. The values of molecular weights obtained in a DMA/5% LiCl solution are summarized in Table I.

Dilute Solution Viscosity

We first considered the influence of LiCl on the viscosity of the DMA solvent. This is shown in Figure 6. Increasing levels of LiCl cause a monotonic increase in viscosity.

We also studied $[\eta]$ versus percent LiCl for particular polymers. In Figure 7 we show $[\eta]$ versus LiCl concentration for samples P2 and P5.

Intrinsic viscosities obtained in the 5% LiCl solutions were compared with weight-average molecular weights. The $[\eta]$ values are summarized in Table I and are plotted as a function of weight-average molecular weight (DMA/5% LiCl solutions) in Figure 8. The data may be represented in terms of a Mark-Houwink equation of form

$$[\eta] = K\bar{M}_w^a \quad (9)$$

where K has a value of 3.7×10^{-4} and a is 0.73.

Optical Anisotropy of Concentrated Solutions

The results of the studies using Kwolek's DDA tests were negative. Solutions of up to 20% Nomex in DMA/5% LiCl do not exhibit liquid crystalline behavior.

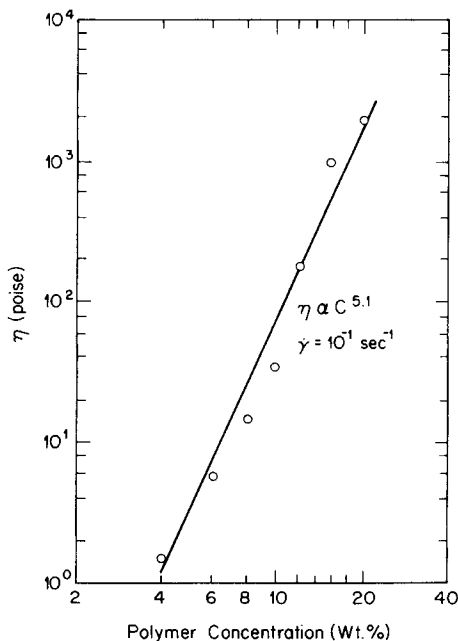


Fig. 10. Shear viscosity as a function of concentration of Nomex (Type 430 T) in DMA/5% LiCl.

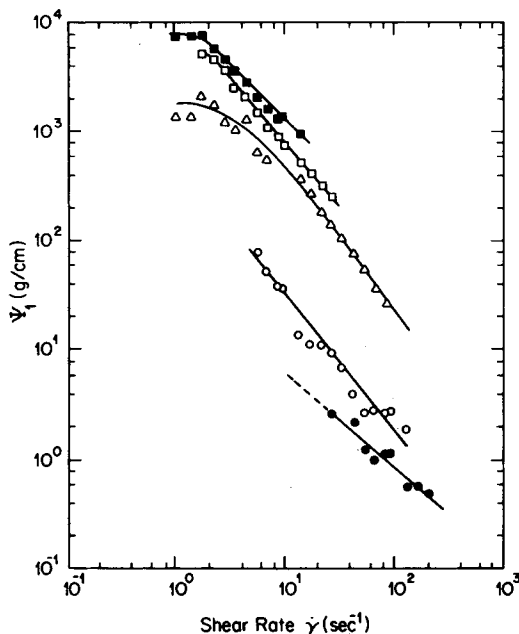


Fig. 11. Principal normal stress difference coefficient Ψ_1 as function of shear rate for various concentrations of Nomex (Type 430 T) in DMA/5% LiCl: (■) 20%; (□) 16%; (△) 12%; (○) 10%; (●) 8%.

Concentrated Solution Rheological Properties

The viscosity η is plotted as a function of shear rate at various concentrations of Nomex in 5% LiCl in DMA in Figure 9. It may be seen that viscosity generally increases with increasing concentration and is independent of shear rate over a wide range of shear rates. In Figure 10, we plot this viscosity as a function of concentration on logarithmic paper. The slope is 5.1 when $\dot{\gamma} = 10^{-1} \text{ sec}^{-1}$.

The principal normal stress difference coefficient Ψ_1 is plotted as a function of shear rate in Figure 11 for a series of concentrations. Ψ_1 is an increasing function of concentration, but a decreasing function of shear rate.

The dynamic storage modulus $G'(\omega)$ (Fig. 12) and dynamic viscosity $\eta'(\omega)$ (Fig. 13) are plotted as a function of frequency at several concentrations. Both $G'(\omega)$ and $\eta'(\omega)$ are increasing functions of concentration.

DISCUSSION

Dilute Solution Behavior

The 0.73 exponent in the Mark-Houwink equation strongly suggests that the polymer chains are flexible. In a related system with three meta links for every para link, Burke¹⁸ found a equal to 0.77. This is unlike the case for the fully paralinked polymers where values of a greater than unity are obtained^{15,19-21} and the macromolecules are considered near rigid.

We now discuss the optical character of dilute solutions of MPD-I/DMA/LiCl. First, we must realize that the solvent has two components and association with the polymer can complicate the interpretation of light scattering data.^{13,14,22,23}

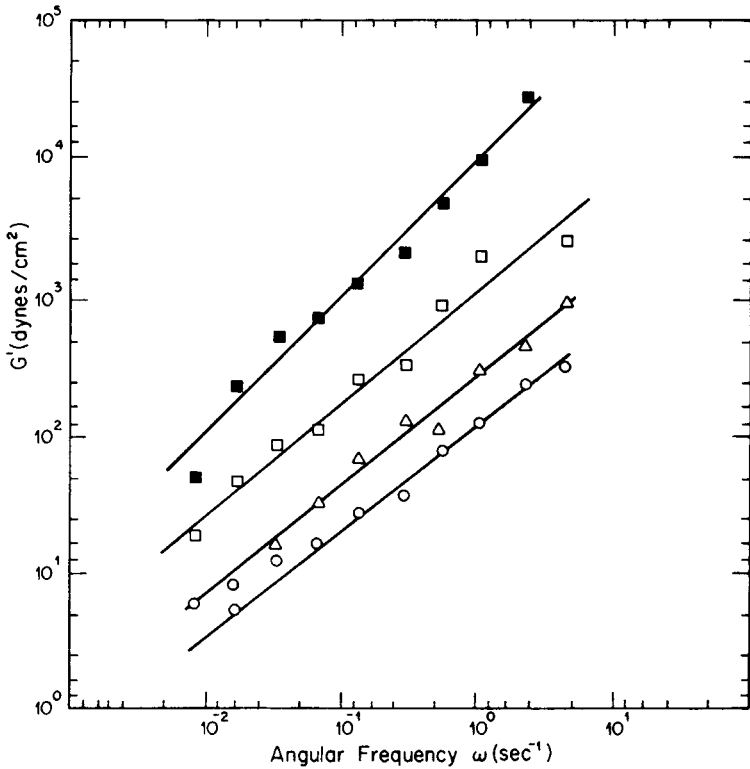


Fig. 12. Dynamic storage modulus as function of frequency for different concentrations of Nomex (Type 430 T) in DMA/5% LiCl: (■) 20%; (□) 16%; (Δ) 12%; (○) 10%.

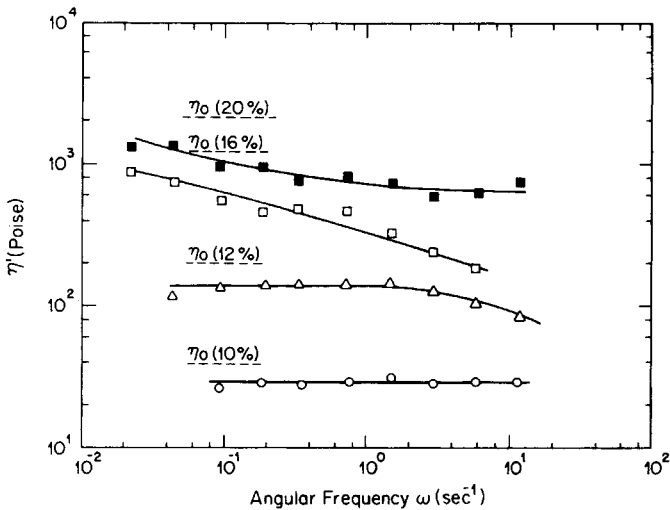


Fig. 13. Dynamic viscosity as function of frequency for different concentrations of Nomex (Type 430 T) in DMA/5% LiCl: (■) 20%; (□) 16%; (Δ) 12%; (○) 10%.

Since the refractive index increment decreases nonlinearly with increasing LiCl concentration, it is probable that the salt interacts with and collects around the polymer chains causing refractive index variations in the solvent sea.

We conclude that the presence of LiCl imposes polyelectrolyte behavior into the system MPD-I/DMA/LiCl. To support this conclusion, consider two experiments that speak directly to it. First of all, Figure 7 shows a well-known polyelectrolyte effect; the hydrodynamic volume of MPD-I depends on the amount of LiCl present. Further, the severe curvature in Figure 1 also indicates specific MPD-I/LiCl/DMA interactions.

Another important result is that MPD-I is associated in pure DMA and beyond 4% LiCl, \bar{M}_w is independent of LiCl concentration. Klenin et al.,⁴ also propose association of MPD-I in DMA and the low solubility levels of MPD-I in DMA relative to DMA/LiCl are mentioned. This subject is further developed in a later paper.²⁴

Concentrated Solution Behavior

The optically isotropic character of concentrated MPD-I is in contrast to the birefringent mesophase character of the para-linked analog.^{5,15,19,25}

The viscosity-concentration behavior of the Nomex solutions is similar to that reported on polyisobutylene²⁶ and polystyrene²⁷ solutions by earlier investigators. These are flexible molecules. The behavior is very different from that observed in solutions of para-linked aromatic polyamides such as poly-*p*-benzamide,^{15,19,28} which exhibit maxima in viscosity-concentration plots in the range studied. The latter solutions exhibit liquid crystalline behavior, and Nomex does not for the conditions studied. The viscoelastic behavior is also similar to solutions of flexible chains.

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