Molecular Weight Determination and Establishment of a Rodlike Structure for Organonickel Polymers $-[Ni(PR_3)_2Ar^F]_n-$

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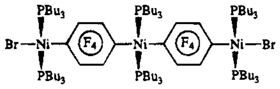
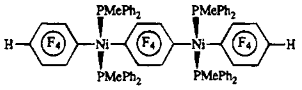
ABSTRACT: Molecular weights ($\bar{M}$) of organonickel polymers $-[Ni(PMePh_2)_2-1,4\text{-}C_6F_4-Ni(PBu_3)_2]-1,4\text{-}C_6F_4]_n-$ and $-[Ni(PMePh_2)_2-4,4'\text{-}C_{12}F_8]_n-$ have been obtained from GPC traces using both a direct calibration (relative to polystyrene standards) and a "universal" calibration (independent of the standards' nature). The universal method, requiring intrinsic viscosity data, produced $\bar{M}$ values consistent with light scattering measurements, while the direct method produced $\bar{M}$ values substantially too low. Using $[\eta] = K\bar{M}^{\alpha}$ and an iterative data-fitting procedure gave $\alpha = 1.5$ for both polymers, and dilute-solution viscosity measurements revealed $[\eta]$ to be independent of the solvent nature; both observations indicate that these polymers possess a rodlike structure. The GPC behavior of 13 related organonickel oligomeric species ($X-[Ni(PR_3)_2Ar^F]_n-H$, where $n = 1-4$, $X = Ar^FH$ or Br, $Ar^F = 1,4\text{-}C_6F_4$ or $4,4'\text{-}C_{12}F_8$, and R = Me, *n*-Bu, or Ph) was consistent with the polymer performance, in that all oligomers eluted at a given retention time possessed higher MW than did polystyrene eluted at the same time. This is due to the high repeating unit mass which counteracts the expected effect of their rigid-rod shapes. While differences in the fluoroaryl bridging units were found to have no effect on the retention times of the oligomers, separate curves were defined when ancillary PR_3 ligands were uniformly different (i.e., $PMePh_2$ vs PBu_3). Oligomers having mixed PR_3 ligands belonged to one of those two GPC curves which is always the one corresponding to the PR_3 at the terminal nickel atoms.

Introduction

Interest in transition-metal-based macromolecules has been growing over the last decade. Examples include organometallic polymers of Mo, W, Ni, Pt, Rh, etc.[1–4] Recently, our group reported the syntheses of a series of organonickel oligomeric species which were characterized by NMR and elemental analysis and, in some cases, by X-ray crystallography.[3,4] Typical examples, whose structures are illustrated below, are oligomers **1** and **2**:

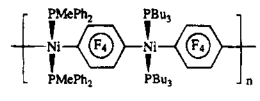


oligomer 1

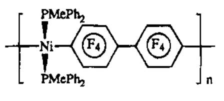


oligomer 2

One of their distinct properties is that they have a rigid-rod structure in the solid state. Evidence from NMR studies also suggests a rodlike configuration for all these oligomeric species in solution. However, a heretofore unanswered question is whether the organonickel polymeric homologues that we recently prepared,[3,4] i.e., polymers **I** and **II**,



polymer I



polymer II

also possess a rodlike structure. If they do, then the values for their molecular weight (MW) obtained directly from gel permeation chromatography (GPC) as calibrated with polystyrene standards would be significantly different from their real values, since polystyrene is a typical random-coil polymer. It is therefore necessary to ascertain the absolute molecular weight values of our organonickel polymers by different calibration methods. One convenient way to do this is to employ a method of "universal calibration", determining the molecular weights through a combination of GPC traces and viscosity measurements according to an iterative method established by several workers.[5]

Establishing methods for determining the molecular weight distribution (MWD) and associated average values ($\bar{M}$) for rigid-rod organometallic polymers is particularly significant because of the growing importance of these materials in electronics, photonics, and other advanced materials applications.[6] In the only such report known to us, Takahashi et al.[7] prepared Pt-containing rigid-rod polymers and examined their behavior. No effort has been made so far to explore the performance of organonickel-backbone polymers.[8] In this paper, we report the results of such an investigation and provide additional viscometric evidence of a rodlike structure for the organonickel polymers.

Experimental Section

Sample Preparation. The syntheses and characterizations of the oligomeric species have been reported previously, as have the syntheses and characterizations of polymers **I** and **II**.[3,4] Samples of polymers for physical measurements were prepared by repeated fractional precipitation from dichloromethane solutions into hexanes or methanol.

Measurements. For the GPC calibrations, 23 monodisperse polystyrene standards were obtained from Showa Denko K.K. (Shodex) and from Polymer Laboratories Ltd. (Church Stretton, Shropshire, U.K.), covering the MW range between 580 and 7.1×10^6. They were used to construct the direct

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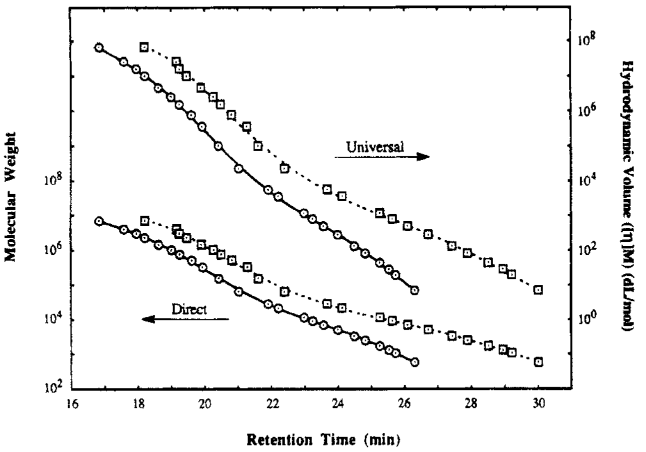

Figure 1. Direct calibration (left) and universal calibration (right) curves using monodisperse polystyrene standards: (—⊙—) three-column set; (- - -⊡- - -) four-column set. Column flow rates were 1.20 and 1.40 mL/min, respectively.

Table 1. Comparison of the GPC Molecular Weight Data[a]

polymer	calibration method	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_v$	$\bar{M}_p$[b]
I	direct	0.68	1.46	2.1	1.30	1.22
	universal	1.29	1.84	1.4	2.02	1.78
II	direct	0.46	7.86	17.1	3.56	0.52
	universal	3.15	11.07	3.5	21.07	3.12

[a] Molecular weight values are to be multiplied by 10^4. [b] Molecular weight values at the peak of the GPC traces.

calibration curve in tetrahydrofuran (THF) at 30.0 °C, given in Figure 1. From $[\eta] = KM^{\alpha}$ with values of $\alpha = 0.712$ and $K = 1.28 \times 10^{-4}$ dL/g for these polystyrene standards under the same conditions,[9] a "universal" calibration curve in terms of $[\eta(M)]M$—equivalent to hydrodynamic volume occupied by the polymer—was also established, as shown in Figure 1. To facilitate later iterative computations, a sixth-order polynomial was fitted to each calibration curve with standard deviations $R = 0.9996-0.9999$.

For GPC measurements on the organonickel polymers, the polymer (*ca.* 10 mg) was dissolved in 1 mL of THF, and a 100-μL sample of the solution was injected into a Waters Model 600E HPLC/GPC system (Waters, Division of Millipore, Mississauga, Ontario) operating at 30.0 °C with THF as the eluting solvent. A flow rate of 1.20 mL/min was used with a series of three columns (identified by Waters as 10^3 Å, 10^6 Å, and "10 μm linear" for $M = 5000-10^7$). The eluted materials were detected on Waters Model 991 photodiode array (UV-vis) and Waters Model 410 differential refractive index detectors. MW calculations for the polymers were performed using both the Maxima 820 chromatography software from Waters and a computer program developed in this laboratory,[10] and the averages of the two values (always close) are tabulated in Table 1 for both GPC methods to be discussed here. For GPC measurements on the oligomeric species, resolution was improved in the critical low-MW region by adding to the three-column assembly a fourth column (labeled 7 × 10^4 Å by Waters). This expanded the range of retention times in the working region ($M = 700-2600$) as shown in Figure 1, with the flow rate increased to 1.40 mL/min for convenience.

Viscosities of 0.05–0.10% polymer solutions were measured using an Ubbelohde viscometer in a water bath maintained at 30.00 ± 0.01 °C. From these data intrinsic viscosity, $[\eta]$, was calculated according to the single-point method described by Solomon and Ciuta;[11] kinetic corrections were furnished where necessary.[12] Light scattering measurements on polymer I in THF were conducted by Wyatt Technology Corp. (Santa Barbara, CA) on GPC effluent using a GPC/LS on-line DAWN F (90°) light scattering detector with a He–Ne laser operating at 633 nm. For the MW calculations, Wyatt employed a dn/dc (refractive index dependence on concentration) value of 0.145 mL/g obtained indirectly by integration over the entire refractive index trace and reported here for the first time. From these data, MW averages for polymer I were found to be $\bar{M}_w = 1.56 \times 10^4$, $\bar{M}_n = 1.25 \times 10^4$ ($\bar{M}_w/\bar{M}_n = 1.2$), and $\bar{M}_z = 1.91 \times 10^4$.

Results and Discussion

GPC Studies on the Oligomeric Species. As models for the organonickel polymers, a series of oligomeric species has been synthesized in this laboratory.[3,4] It is important to examine the GPC behavior of these species before we go to the more complex polymeric systems, as it may reveal valuable information which can be extrapolated to the polymers. Specific chemical factors which can be explored include (1) the effect of ancillary PR_3 ligands (i.e., $PMePh_2$ *vs* PBu_3 and mixed PR_3 *vs* uniform $PMePh_2$ or PBu_3) and (2) the effect of fluoroaryl bridging units (i.e., 1,4-C_6F_4 *vs* 4,4′-$C_{12}F_8$).

GPC traces of 13 samples of the oligomeric species (Table 2) were obtained using the four-column set. A plot of log (M) *vs* retention time is shown in Figure 2, along with data for the low-MW polystyrene samples for comparison. We observe that the organonickel oligomers eluted at any given retention time possess a higher MW than the corresponding polystyrene. This is largely because the elements Ni, P, and F in these species are much heavier than the C and H comprising polystyrene. This phenomenon counteracts the geometrical fact that rodlike species should be expected to have a lower MW than coil-like species at a given retention time due to the effectiveness of rodlike rotational hydrodynamic resistance, provided that they have

Table 2. GPC Data for the Oligomeric Species

oligomeric species[a,b]	no.	MW[c]	retention time (min)
$Ni(PMePh_2)_2$ Group			
$Ni(PMePh_2)_2(C_6F_4H)Br$	3	688.1	30.37
$Ni(PMePh_2)_2(C_6F_4H)_2$	4	757.3	30.11
$Ni(PMePh_2)_2(C_{12}F_8H)Br$	5	836.2	30.15
$Ni(PMePh_2)_2(C_{12}F_8H)_2$	6	1053.4	29.54
$[Ni(PMePh_2)_2]_2(\mu\text{-}C_6F_4)(C_6F_4H)_2$	2	1364.5	29.40
$[Ni(PMePh_2)_2]_3(\mu\text{-}C_6F_4)_2(C_6F_4H)_2$	7	1971.6	28.92
1,3-$[Ni(PMePh_2)_2]_2$-2-$[Ni(PBu_3)_2](\mu\text{-}C_6F_4)_2(C_6F_4H)_2$	8	1975.8	28.85
$[Ni(PMePh_2)_2]_3(\mu\text{-}C_{12}F_8)_2Br_2$	9	2129.4	28.84
$Ni(PBu_3)_2$ Group			
$Ni(PBu_3)_2(C_6F_4H)Br$	10	692.3	29.94
$Ni(PBu_3)_2(C_6F_4H)_2$	11	761.5	29.76
$[Ni(PBu_3)_2]_2(\mu\text{-}C_6F_4)(C_6F_4H)Br$	12	1303.7	29.24
1,3-$[Ni(PBu_3)_2]_2$-2-$[Ni(PMePh_2)_2](\mu\text{-}C_6F_4)_2(C_6F_4H)_2$	13	1980.0	28.64
1,4-$[Ni(PBu_3)_2]_2$-2,3-$[Ni(PMePh_2)_2]_2(\mu\text{-}C_6F_4)_3(C_6F_4H)_2$	14	2587.2	28.28

[a] Unspecified phenylenes denote para linkages. [b] Separate GPC curves are defined for each group in Figure 2. [c] Values computed from the molecular structures shown in the left-hand column and confirmed by elemental analyses, ^1H and ^{19}F NMR, and in some cases X-ray crystallography.[3,21]

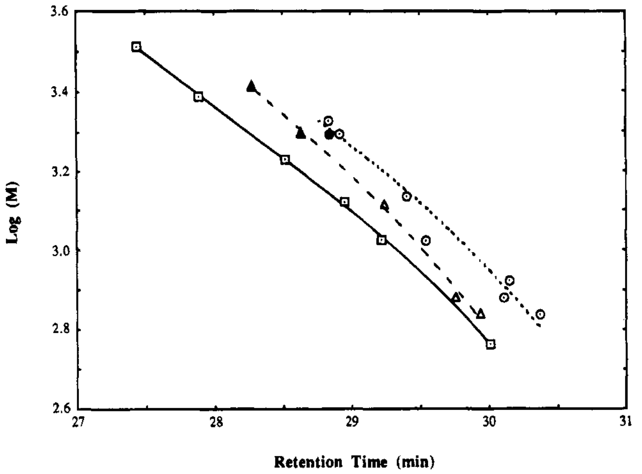

Figure 2. GPC behaviors of the organonickel oligomers compared with polystyrene plotted according to Table 2: (- - -⊙- - -) $Ni(PMePh_2)_2$ group; (– –△– –) $Ni(PBu_3)_2$ group; (—□—) polystyrene standards. Filled symbols designate oligomers with mixed PR_3 ligands, bearing at their ends the ligands characterizing the curve to which they belong.

the same chemical composition (which is not the case in our study). Since the GPC retention time of a particular species is determined by its hydrodynamic volume given by $[\eta]M$, a higher MW for the oligomers in Figure 2 also implies a lower $[\eta]$ than for polystyrene at the same retention time. The same result is thus expected for the organonickel polymers, as was confirmed by $[\eta]$ measurements for polymers **I** and **II**. By inverting the comments above, we can also expect that Ni-containing oligomeric species possessing the same MW as polystyrene will be eluted at longer retention times (due to their smaller hydrodynamic volumes), as Figure 2 confirms. This implies that a GPC direct calibration method using polystyrene standards will significantly underestimate the molecular weights of the organonickel polymers and therefore will not be adequate to characterize polymers **I** and **II**.

The ancillary PR_3 ligands have a significant effect on the GPC behaviors of their parent species. For example, species belonging to the $Ni(PBu_3)_2$ group (Table 2) are shown in Figure 2 to elute earlier than those belonging to the $Ni(PMePh_2)_2$ group, for a given MW. This may be rationalized in terms of a larger hydrodynamic volume for the $Ni(PBu_3)_2$ species, since the butyl branches are presumably much more elongated in solution. The effect on GPC behavior of the oligomeric species with mixed ancillary ligands (i.e., alternating $PMePh_2$ and PBu_3) is somewhat unexpected. One could speculate about whether data would fall onto curves between those established for the $PMePh_2$ and PBu_3 groups, but this proves not to be so. Results in Figure 2 indicate that the retention time is independent of the internal composition of these species and depends only on the nature of the ancillary PR_3 ligands carried by the terminal Ni atoms. For example, tri-Ni species **8** (Table 2) carries $PMePh_2$ at the ends, and we see that it falls onto the well-defined $PMePh_2$-group curve in Figure 2 despite the presence of PBu_3 ligands on the middle Ni atom. Analogous behavior is exhibited by the tri-Ni and tetra-Ni species **13** and **14**; they clearly belong to the PBu_3-group curve, despite carrying $PMePh_2$ ligands on the middle Ni atoms.

A weak trend for the curves of the two groups of organonickel oligomers (i.e., $Ni(PMePh_2)_2$ and $Ni(PBu_3)_2$ groups in Table 2) is that they appear to approach merging at high-MW or short retention time, seen from Figure 2. This suggests that the organonickel polymers having either of the PR_3 ligands may behave very similarly as far as GPC measurements are concerned. If so, they might be expected also to have similar $[\eta]$ behavior, meaning close values of α and K. This is indeed demonstrated by the comparison between polymers **I** and **II** described in the following discussion. Another conclusion that can be drawn from Figure 2 is that the identity of the fluoroaryl bridging units (1,4-C_6F_4, or 4,4′-$C_{12}F_8$) seems to have no effect on the GPC behavior of their parent species beyond contributing the corresponding mass units to the group curve. Thus these species were treated as being functionally identical when found in the same $Ni(PR_3)_2$ group (e.g., examine the $Ni(PMePh_2)_2$ group in Table 2). An extrapolation of this conclusion to the fluoroarene-bridged organonickel polymers means that the nature of the bridging units may have little or no effect on their α values, which is again reflected in the results of viscosity measurements for polymers **I** and **II**.

Relationship between Solution Viscosity and Molecular Weight. Experience has shown that coil-like polymers such as polystyrene, polybutadiene, and poly(vinyl chloride), whose dilute-solution viscosities are described by the Mark–Houwink equation,

$$[\eta] = K\bar{M}^{\alpha} \tag{1}$$

possess α values of 0.5–1.0,[13] while rodlike polymers show larger α values ($\alpha > 1.0$). Typical examples of the latter are poly(γ-benzyl L-glutamate)[14] and poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadynediyl][7] which have α values of 1.7.

Several workers[5] have proposed a convenient iterative method to determine the parameters α and K in eq 1 from GPC traces and $[\eta]$ measurements on polymer samples of the same type but different MW in the same solvent and temperature. Suppose one takes two samples (1 and 2) with different molecular weight distributions (MWD), measures $[\eta]_1$ and $[\eta]_2$, and uses the GPC traces to find MWD_1 and MWD_2 in terms of their respective sets of weight fractions W_{1i} and W_{2i}. Then, applying eq 1 to each fraction gives:

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\sum_i W_{1i} J_i^{\alpha/(\alpha+1)}}{\sum_i W_{2i} J_i^{\alpha/(\alpha+1)}} \tag{2}$$

where $J_i = J_i(M_i) = [\eta]_i M_i$ is the *hydrodynamic volume* of the ith fraction. If α is taken to be a constant, we will designate by α_{12} the value obtained by an iterative process on the (1 + 2) pair of samples, as shown in eq 2. Then K_{12} can be found using either $[\eta]_1$ or $[\eta]_2$ according to eq 3:

$$[\eta] = K^{1/(\alpha+1)} \sum_i W_i J_i^{(\alpha/\alpha+1)} \tag{3}$$

This analysis is facilitated by noting that J_i values for eqs 2 and 3 can be directly obtained from the universal calibration curve (Figure 1) constructed using polystyrene standards, since this curve is considered independent of the polymer architecture (coil-like, linear, branched or star, and rodlike polymers).[15]

Three samples of polymer **I** (**Ia**, **Ib**, and **Ic**) having different MWD's were chosen, and their GPC traces and intrinsic viscosities ($[\eta]$ = 0.184, 0.118, and 0.0487 dL/g for samples **Ia**, **Ib**, and **Ic**, respectively) were measured.

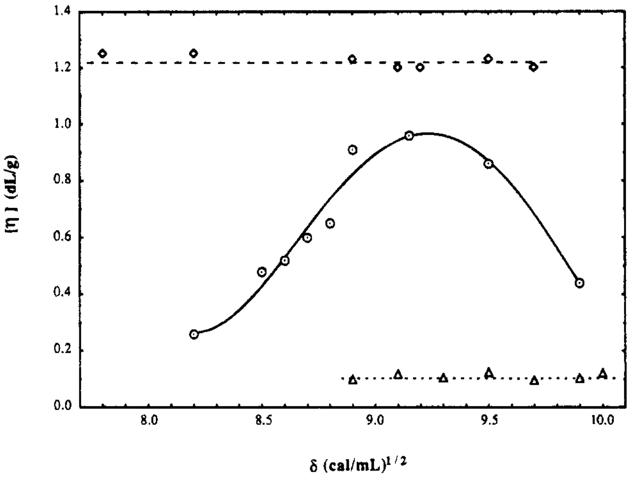

Figure 3. Intrinsic viscosity $[\eta]$ *vs* solubility parameter (δ): (—⊙—) polystyrene according to ref 18; (– –◇– –) organoplatinum rigid rod: poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadynediyl] according to ref 7; (- - -△- - -) polymer I in the following solvents (δ): toluene (8.9), THF (9.1), chloroform (9.3), chlorobenzene (9.5), dichloromethane (9.7), bromobenzene (9.9), and *o*-dichlorobenzene (10.0).

Subsequently, parameter α for polymer **I** was calculated using eq 2 for three sets of combinations of two samples (**Ia** + **Ib**, **Ia** + **Ic**, and **Ib** + **Ic**); through iteration, values $\alpha = 1.6$, 1.5, and 1.5 were obtained, respectively, and thus an average value, $\bar{\alpha}_1$, of 1.5. Parameter $\bar{K}_1$ was obtained using eq 3 and $\bar{\alpha}_1$, giving 3.0×10^{-8} dL/g. The same procedure applied to polymer **II** yielded $\bar{\alpha}_2 = 1.5$ and $\bar{K}_2 = 1.7 \times 10^{-9}$ dL/g. The value $\bar{\alpha} = 1.5$ for both polymers suggests that these organonickel structures behave as rigid rods in solution. Calculations were also made of $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_v$ for both polymers,[5] using $\bar{\alpha}$ and $\bar{K}$ values obtained above, and these are listed in Table 1 (along with $\bar{M}_p$) as the universal calibration values. For polymer **I**, they are consistent with the results from direct measurements by light scattering (see the Experimental Section).[16,17]

Dependence of Solution Viscosity on Solvents. The intrinsic viscosities of coil-like polymers are strongly dependent on the nature of the solvents. A maximum in $[\eta]$ is observed for such polymers in the best solvent and smaller values in poor solvents. For rodlike polymers, $[\eta]$ is essentially independent of the solubility parameters (δ) of the solvents.[7,18] We have therefore explored the solvent dependence of $[\eta]$ for polymer **I**. Seven solvents having δ values ranging from 8.9 to 10.0 (cal/mL)$^{1/2}$ were used to acquire the $[\eta]$'s for the polymer, with results shown in Figure 3 along with typical examples of coil-like and rodlike polymers quoted from other sources. We observe that, whereas coil-like polystyrene exhibits the expected bell-shaped curve within this δ range,[18] polymer **I** displays little change in $[\eta]$ (*ca.* 0.11 dL/g, with minor scatter). This resembles the behavior of another organometallic rodlike polymer: poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadynediyl].[7] The limited solubility of the polymer precluded attempts to explore an even wider range of solvent δ values. This independence of $[\eta]$ with respect to solvent power for polymer **I** confirms that it possesses a rodlike structure in solution. We were unable to explore a similar relationship for polymer **II** due to its very limited solubilities, but its chemical structure is sufficiently similar to that of polymer **I** that we expect it is rodlike, as is suggested by its α value derived above.

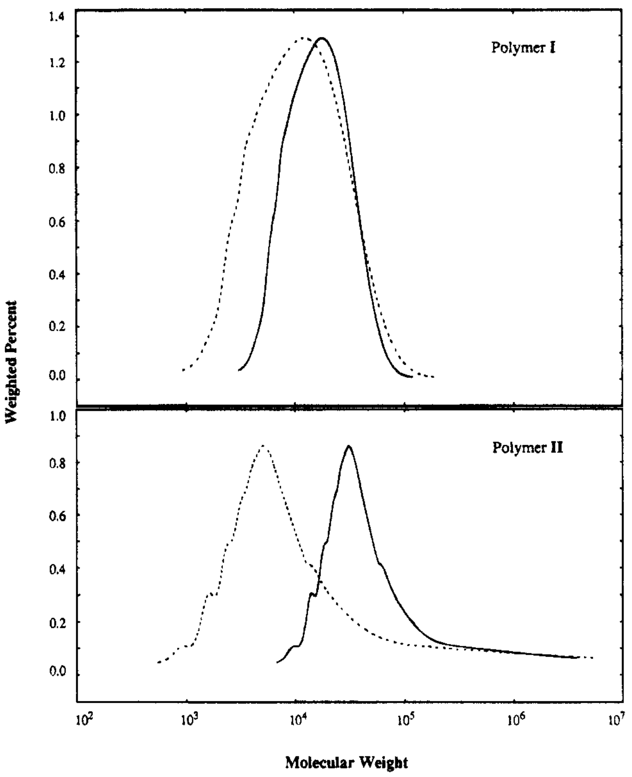

Figure 4. MWD curves of the polymers ascertained by the two calibration methods: (- - -) direct method; (—) universal method.

Comparison of Two GPC Methods For Molecular Weight Determination. $\bar{M}$ values for polymers **I** and **II** presented in Table 1 emerged from MWD curves obtained from GPC data using both the direct calibration method and the universal method. These two MWD curves are shown in Figure 4 for both polymers, demonstrating substantial differences between the two polymers as obtained from either calibration scheme. For polymer **I**, use of the more accurate universal calibration leads to a narrowing of the MWD display as the low-MW tail is shifted to higher MW and the high-MW portion is relatively unaffected. For polymer **II**, the universal method demonstrates that the whole MWD is shifted about a full order of magnitude higher than suggested by the direct method, with considerable narrowing as well. Corresponding to these method-related MWD differences, there are also significant differences between the $\bar{M}$ values calculated from them, especially for polymer **II**: much smaller values (up to one order of magnitude) are obtained through the unreliable direct method. As with the oligomers, this can be attributed primarily to the fact that polystyrene possesses a low-mass repeating unit, in contrast to organonickel polymers **I** and **II** which have high-mass units. It seems that a direct polystyrene calibration for $\bar{M}$ determination for metal-containing polymers in general is likely to suffer from similar effects.

It is worth emphasizing one important difference between the relative values of $\bar{M}_w$ and $\bar{M}_v$ for the two different classes of polymers. For coil-like polymers such as polystyrene, one finds by independent experiments that $\alpha < 1$ and that $\bar{M}_v < \bar{M}_w$. It can also be shown[19] that $\bar{M}_v < \bar{M}_w$ is a mathematical consequence of $\alpha < 1$. However, the analogous mathematical prediction when $\alpha \geq 1$ (as is established for polymers **I** and **II**) gives $\bar{M}_v > \bar{M}_w$, so any GPC calibration that fails to produce this result from GPC data is inadequate. Table 1 shows that the direct GPC calibration method fails this test and the universal method passes. In effect, the direct method produces the wrong result because its use implies that rodlike molecules behave hydrodynamically as if they were flexible coils.

Finally, values of α and K obtained by iteration for the organonickel polymers can be compared to those reported by Takahashi et al.[7] for a related organoplatinum rodlike polymer, poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadynediyl]. They obtained $\bar{\alpha} = 1.7$ and $\bar{K} = 6.5 \times 10^{-9}$ dL/g for the organoplatinum polymer by the same approach, in the same range as the values obtained for our two organonickel polymers.

In conclusion, we have examined the GPC and viscometric behavior of two organonickel polymers and have established their rodlike structure. We are extending our current study to investigate the MW dependence of the viscometric parameters for these rigid-rod polymers, and a detailed report will appear elsewhere.[20]

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