Intrinsic Viscosity and Molecular Weight Measurement of Nylon 66 Polymers

S. R. SAMANTA

Monsanto Chemical Company, Pensacola, Florida 32575

SYNOPSIS

Intrinsic viscosity of several nylon 66 polymers in the molecular weight range 25,000–105,000 was measured in hexafluoroisopropanol (HFIP). The experimentally measured viscosity was compared with the data obtained by least-squares fit of the classical equations of Huggins and Kraemer. The utility of the single-point viscosity measurement is also discussed and compared with the measured data. The apparent hydrodynamic parameters obtained from the Huggins equation indicate the applicability of HFIP for studying polyamide polymers. The molecular weight of these polymers was also determined by the gel permeation and low-angle laser light scattering technique (GPC–LALLS). The molecular weight data combined with the viscosity data provide the Mark–Houwink parameters. The agreement between these parameters and the same parameters obtained in tetrafluoropropanol (TFP) is excellent.

INTRODUCTION

The viscosity of dilute polymer solution provides important information, namely, molecular weight, chain dimension, polymer solvent interactions, aggregation, and branching. Therefore, viscosity and molecular weight measurement play a significant role in polymer characterization. One of the important parameters for characterizing a polymer is proper choice of solvent. It has been shown by Drott[1] that hexafluoroisopropanol HFIP is a very good solvent for studying polyamides, especially aliphatic polyamides. A survey of dilute solution properties of nylons[2-5] showed that a number of solvents were used to study various solution properties, but very few studies have been made with HFIP as a solvent for nylon polymers.[6] Moreover, no viscosity data exists in the literature for nylon 66 in HFIP. In this paper, the viscosity data of several nylon 66 polymers of varying molecular weight is presented. Molecular weight of these polymers was also determined by the gel permeation and low-angle laser light scattering (GPC–LALLS) technique. These data demonstrate the utility of HFIP as a solvent for studying nylon polymers.

EXPERIMENTAL

Nylon 66 exhibits a salt effect in HFIP. This can be conveniently eliminated by addition of $0.1 M$ sodium trifluoroacetate (NATFAT)[1]; therefore, all measurements of viscosity and molecular weight were done in HFIP with $0.1 M$ NATFAT. Viscosity was measured at 25°C in a Schott viscometer. The polymer solution was prepared and diluted to the appropriate concentration. Before measurement, the solution was passed through a 0.2 micron Millipore filter and allowed to stand in the viscometer to attain the proper temperature. After equilibrium was reached, the drop time was measured both for solvent and solution. The viscometer was microprocessor-controlled; therefore, filling of the viscometer bulb and drop time measurement were automatic.

Molecular weight was measured by the GPC–LALLS technique. DuPont bimodal columns, two pairs in series, and PL gel columns (10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} Å particle size) produced identical results. Though DuPont columns tend to last longer in HFIP, both performed extremely well. The GPC was equipped with a Waters 6000 series pump and U6K manual injection. Light-scattering intensity was recorded with a Milton Roy KMX-6 spectrometer. The concentration of polymer used was 2 mg/mL. The

amount of sample injected was 2×10^{-4} gm, and the pump flow rate was 1 mL/min. The concentration of the eluted fraction was measured by a differential refractometer. Eluted solution was collected in a flask equipped with distillation capability. After sufficient collection, the solvent was distilled and recycled to the storage tank. The system is nearly a closed loop. One comes in contact with the solvent only during the sample preparation. This is insignificant compared to the total measurement time. This arrangement practically eliminates exposure to the solvent.

VISCOSITY

The intrinsic viscosity, $[\eta]$, is a measure of the polymer hydrodynamic parameter, which is directly related to molecular weight and provides information about the thermodynamic quality of the solvent. Intrinsic viscosity is related to the molecular weight via an empirical equation:

$$[\eta] = KM^a \tag{1}$$

where K and a are constants at a given temperature. Classically, viscosity is measured experimentally by plotting η_{sp}/c or $\ln \eta_{rel}/c$ vs. c and extrapolating to zero concentration. The common equations used for dilute solution viscosity measurement are[7,8]

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \tag{2}$$

$$\ln \eta_{rel}/c = [\eta] - k''[\eta]^2 c \tag{3}$$

where η_{sp} is the specific viscosity, η_{rel} is the relative viscosity, and c is the concentration (gm/dL). The

parameters k' and k'' are Huggins'[7] and Kraemer's[8] constants. From eqs. (2) and (3) and after some algebraic manipulation:

$$k' + k'' = 0.5 \tag{4}$$

Several equations are available for single-point viscosity measurement. These are

$$[\eta] = Sqrt[2(\eta_{sp} - \ln \eta_{rel})]/c \tag{5}$$

$$[\eta] = [\eta_{sp} + 3 \ln \eta_{rel}]/4c \tag{6}$$

Equation (5) was proposed by Soloman and Cuita as well as by Naar et al.,[9,10] and eq. (6), by Kuwahara.[11] All of them recommended a dilute solution concentration (0.2%). The range of k' is also applicable for single-point measurement.[12] We have calculated the viscosity using all the equations for several nylon 66 polymers and tested the above conditions to show the goodness of the fit. Experimentally measured viscosity was compared with the data obtained by all the above equations and their correlations are shown.

The concentration used for viscosity measurement was as high as 0.5 gm/dL and as low as 0.1 gm/dL. The viscosity data obtained by all the methods are shown in Table I. The correlation between graphical data and the least-squares fit of eqs. (2), (3), (5), and (6) is shown in Figure 1. The single-point data for individual polymers is the average of the single-point measurement for all concentrations. The correlation parameters are shown in Table II. The k' for all polymers is slightly lower than the lower limit, but all fall far below the upper limit ($.3 < k' < .4$). The sum of ($k' + k''$) is very close to the theoretical value.

Table I   Results for Nylon 66 in HFIP

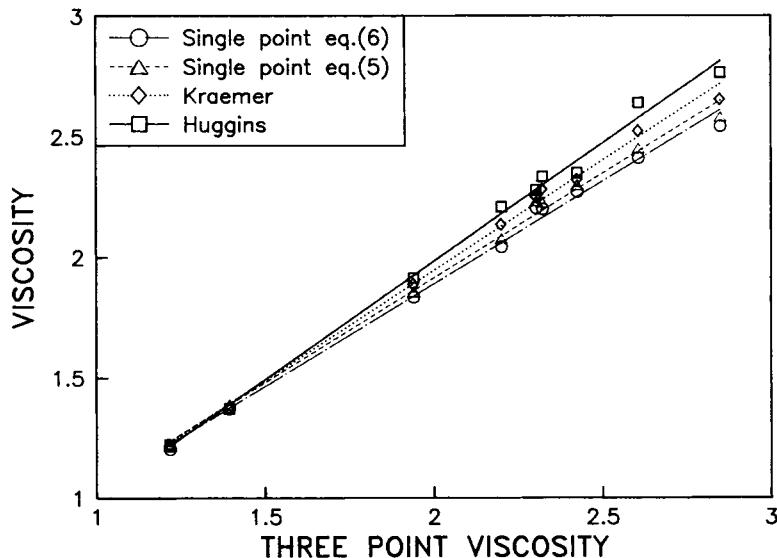| Mol. Wt.		Viscosities							
$\bar{M}_w$	$\bar{M}_w/\bar{M}_\eta$	Huggins [Eq. (2)]	Kraemer [Eq. (3)]	Expt	Single Point [Eq. (5)]	Single Point [Eq. (6)]	k'	k''	($k' + k''$)
25,910	1.8242	1.2192	1.2169	1.2173	1.2131	1.2021	0.3182	0.1665	0.4847
35,542	1.4952	1.3675	1.3708	1.3925	1.3859	1.3702	0.3922	0.1296	0.5218
54,983	1.4546	1.9114	1.8852	1.9400	1.8549	1.8338	0.2525	0.1832	0.4357
64,949	1.7022	2.3308	2.2784	2.3220	2.2243	2.1983	0.2079	0.1952	0.4031
69,844	1.6901	2.2053	2.1316	2.2000	2.0753	2.0422	0.2309	0.1751	0.4060
70,589	1.9491	2.2755	2.2479	2.3033	2.2295	2.2016	0.2924	0.1616	0.4540
78,271	1.8475	2.3464	2.3172	2.4250	2.2973	2.2699	0.2825	0.1676	0.4501
92,848	2.0526	2.6375	2.5198	2.6067	2.4491	2.4100	0.2329	0.1625	0.3954
104,630	1.8521	2.7649	2.6517	2.8500	2.5801	2.5415	0.2240	0.1669	0.3909

Figure 1   Correlation between viscosities.

In poor solvent, polymer–polymer interaction rather than polymer–solvent interaction is strong enough to form aggregates.[13] This has an effect on $[\eta]$, but has a much stronger effect on k'. It is widely accepted and proven for several polymers that k' tends to increase with aggregation. But it is very much apparent from the k' values that no aggregation exists in HFIP in the molecular weight range studied. Moreover, k' tends to decrease with increasing solvent power. Therefore, it is not surprising to see that the k' value is slightly lower than theoretical value,[14] probably because of the contribution from the thermodynamic effect (solvating power of HFIP). If the thermodynamic effect is taken into account, then the k' would be

$$k' = k_h - 3K_1/[\eta] \qquad (7)$$

where k_h is the hydrodynamic part and K_1 is the thermodynamic part. To estimate K_1, one needs to know the relationship between K_1 and A_2 (Refs. 15–

18) (second virial coefficient). A lower value of k' is the most probable reason for good agreement in single-point viscosity, even at much higher concentration (0.5%). In good solvent, polymer–solvent interaction is prominent and should remain constant with molecular weight and dilution. This trend is generally seen in the data except for two low molecular weight samples, but both of them are well within the limiting values of k'. In some cases, a higher value of k' with decreasing molecular weight has been interpreted as a polyelectrolyte effect.[19] It is, however, not likely in the presence of NATFAT and, therefore, may be related to the some other interaction with the solvent. Values of k' obtained here are, in general, consistent with previous observations.[20,21]

Variations in polymer viscosity are ascribed to variations in the expansion factor of the polymer. If the solvent is good, the polymer will be more extended. Solvent dependence of viscosity is therefore related to the polymer–solvent interaction and chain

Table II   Straight-Line Correlation between Experimental and Viscosity Equations
(η_{expt} = constant + A $\eta_{equation}$)

	Huggins	Kraemer	sqrt[$2(\eta_{sp} - \ln \eta_{rel})$]/$c$	$(\eta_{sp} + 3 \ln \eta_{rel})/4c$
Constant	0.022	0.119	0.184	0.193
Std error (constant)	0.040	0.034	0.037	0.038
A coefficient	0.979	0.911	0.865	0.848
Std error in (A)	0.026	0.022	0.024	0.025
R^2	0.9949	0.9958	0.9944	0.9938

dimension in the particular solvent. According to Flory's excluded volume theory for dilute solution, polymer viscosity is related to molecular weight by

$$[\eta] = KM^{1/2}\alpha^3 \qquad (8)$$

where K is assumed to be the universal constant and α is the expansion factor. For a particular solvent, K should be a constant; this can be seen qualitatively by dividing both sides by the lowest viscosity and the corresponding molecular weight. A plot of normalized viscosity vs. normalized molecular weight would be linear if the expansion factor does not vary with molecular weight. The slope of that plot would be a ratio of the expansion factors. One such plot (shown in Fig. 2) is in agreement with the assumption that there is no contraction of the chains and no chain entanglement with increasing molecular weight in dilute solutions.

MOLECULAR WEIGHT

The polymer molecular weight was measured by the GPC–LALLS method. This is a rapid and accurate measurement procedure. The solvent used was HFIP with $0.1M$ NATFAT. This mixture satisfies all the criteria for accurate molecular weight measurement: (a) A given solvent–solute must have a high refractive index differential; (b) the solution should be free from a polyelectrolyte effect; and (c) dilute solution should be free from aggregates. Except for condition (b), all other conditions are ideal for nylon

66 in HFIP. However, the second condition can be met very easily with the addition of NATFAT. From viscosity measurements in HFIP, there was no aggregate effect observed in dilute solutions. Considering the above criteria, HFIP is an exceptionally good solvent for aliphatic polyamide characterization. In addition to molecular weight, light-scattering measurements provide another important thermodynamic parameter: the second virial coefficient (A_2). In dilute solution, the scattering intensity and molecular weight are related in the following way:

$$KC/\bar{R}_\theta = 1/\bar{M}_w + 2A_2C \qquad (9)$$

where K = optical constant (3.7914×10^{-7}) = $(2\pi^2 n^2/\lambda^4 N)(dn/dc)^2(1 + \cos^2\theta)$; A_2 = second virial coefficient; n = solvent refractive index = 1.2649 ($25°C$) at wavelength used (633 nm) (λ = 633 nm); N = Avogadro's number; $\bar{M}_w$ = molecular weight average; C = concentration of the solution; θ = angle of scattered light collection; and $\bar{R}_\theta$ = difference in Rayleigh factor (solution − solvent) (Rayleigh factor HFIP was 2.3–2.5×10^{-6}).

The refractive index increment for nylon 66 in HFIP is 0.241 (Ref. 22) at $25°C$. Molecular weight is obtained from the above equation by measuring the scattering intensity at several concentrations and plotting them with concentration and extrapolating to zero concentration. One such measurement for nylon 66 is shown in Figure 3. The second virial coefficient obtained in this way is used for all other polymers for the GPC–LALLS measurement.
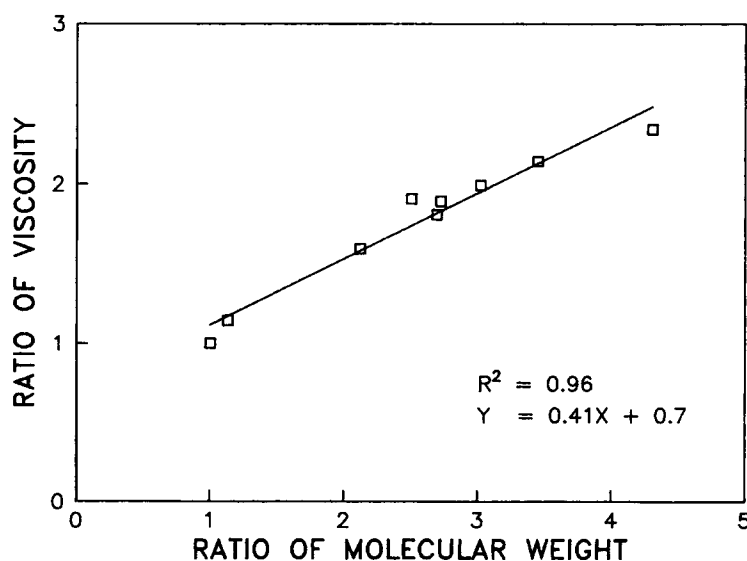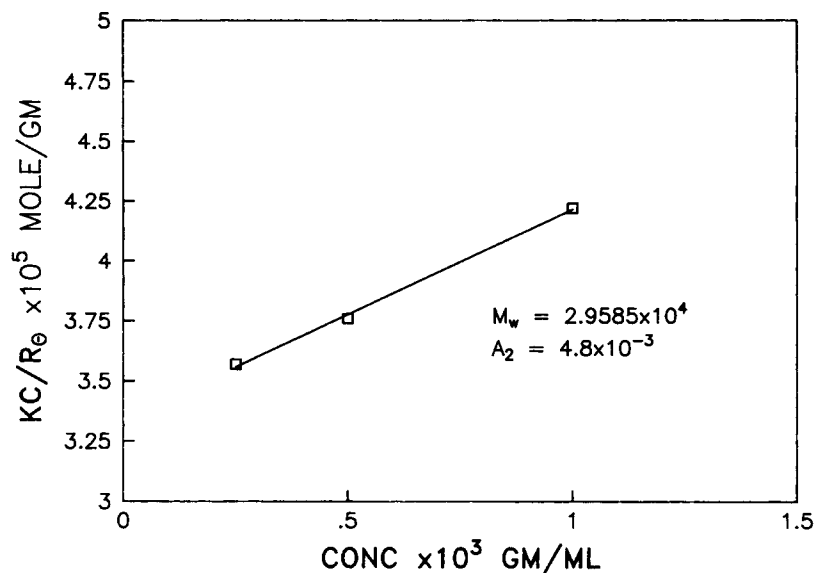

Figure 2 Effect of molecular weight on α.

Figure 3 Plot of KC/R_θ vs. concentration.

The molecular weight of all the polymers is shown in Table I.

Viscosity is related to the molecular weight given in eq. (1). This relationship is fulfilled by both fractionated and unfractionated polymers.[1,23] A plot of ln η and ln M is shown in Figure 4. The Mark–Houwink constants are K = 0.00198 and a = 0.63. The parameter a is the estimate of polymer–solvent interactions, and this is essentially independent of molecular weight distribution. But the value of K depends on the breadth of the distribution. Therefore, the accurate value of K is generally obtained with several fractions of the same polymer of equal breadth.[24] The parameters were obtained using whole polymers. The polymers used in this study are all condensation polymers; theoretically, their distribution is close to 2. From the light-scattering measurement, the ratio $(\bar{M}_w/\bar{M}_n)$ showed some variations for the two samples. Since, theoretically, their polydispersity is 2, the K value obtained in this way will not be far from the actual value. Moreover, it is reported in the literature that the value of K and a can also be obtained by using whole polymers.

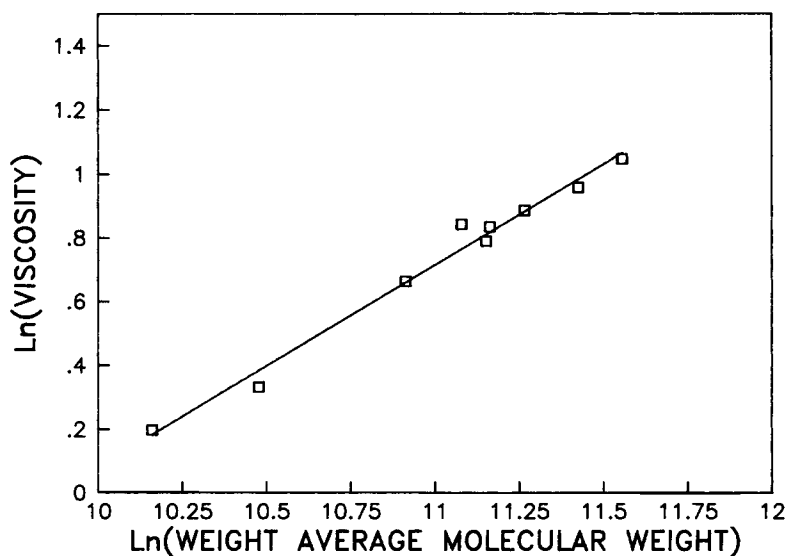The fact that the value obtained for a was well

Figure 4 Mol. wt. and viscosity; Mark–Houwnik relationship.

within the theoretical limit suggests nearly the same polymer–solvent interactions. But a similar explanation may not be given for K. However, the value available for nylon 66 in the literature for the fluorinated solvent using fractionated polymer agrees very well with the present estimate. The value of K obtained in HFIP is 1.98×10^{-3} vs. 1.14×10^{-3} in tetrafluoropropanol (TFP) and $a = 0.63$ (HFIP) vs. 0.66 (TFP).[1,25] The difference observed may well be reconciled with the difference in solvent used. Our measurement was performed with an unfractionated polymer compared to the fractionated polymer used for TFP.

The viscosity and molecular weight data obtained and the good agreement with the theoretical criteria emphasize that HFIP is a good solvent for an aliphatic polyamide study. Though the solvent is expensive, recycling can reduce the cost to less than the cost of solvent usually used. Moreover, the very low refractive index of this solvent makes (dn/dc) very large and therefore makes it sensitive to the light-scattering measurement; therefore, the molecular weight values obtained are more accurate. The solvent is very easy to distill (bp 59°C). An almost closed-loop system practically eliminates solvent contact and solvent evaporation to the laboratory atmosphere. By following good laboratory practices, this solvent can be used very effectively for nylon characterization. The common solvent for nylon 66 is formic acid, which has a much lower dn/dc (0.136), making it less sensitive to light-scattering measurement. Finally, excellent agreement between viscosity and molecular weight suggests that no branching is apparent in the higher molecular weight samples. The molecular weight ranges used in this study were much higher at the high end compared to the previous study.[25]

REFERENCES

1. E. E. Drott, *Chromatograph. Sci.,* **8,** 41 (1977).
2. Z. Tuzar, P. Kratochvil, and M. Bohdanecky, *Advances in Polymer Science,* Vol. 30, Springer-Verlag, Berlin, Heidelberg, New York, 1979.
3. C. A. Veith and R. E. Cohen, *Polymer,* **30,** 942 (1989).
4. P. J. Wong and R. J. Rivard, *J. Liq. Chrom.,* **10,** 3059 (1987).
5. M. A. Dudley, *J. Appl. Polym. Sci.,* **16,** 493 (1972).
6. G. Costa and S. Russo, *J. Macromol. Sci.,* **A18,** 299 (1982).
7. M. L. Huggins, *J. Am. Chem. Soc.,* **64,** 2716 (1942).
8. E. O. Kraemer, *Ind. Eng. Chem.,* **30,** 1200 (1938).
9. F. O. Solomon and I. Z. Ciuta, *J. Appl. Polym. Sci.,* **6,** 683 (1962).
10. R. Z. Naar, H. H. Zabusky, and R. F. Heitmiller, *J. Appl. Polym. Sci.,* **9,** S30 (1963).
11. N. Kuwahara, *J. Polym. Sci.,* **9,** 2395 (1963).
12. R. N. Shroff, *J. Appl. Polym. Sci.,* **9,** 1547 (1965).
13. P. Doty, H. Wagner, and S. Singer, *J. Phys. Coll. Chem.,* **51,** 32 (1947).
14. W. R. Moore and M. Murphy, *J. Polym. Sci.,* **56,** 519 (1962).
15. M. Bohdanecky, in *International Symposium on Macromolecular Chemistry,* Prague, 1965.
16. H. Yamakawa, *J. Chem. Phys.,* **34,** 1360 (1961).
17. T. Kawai and K. Saito, *J. Polym. Sci.,* **26,** 213 (1957).
18. W. R. Krigbaum, *J. Polym. Sci.,* **26,** 222 (1957).
19. H. McCormick, *J. Colloid Sci.,* **16,** 635 (1961).
20. F. Rybnikar, *J. Polym. Sci.,* **29,** 519 (1958).
21. P. R. Saunders, *J. Polym. Sci.,* **A3,** 1221 (1965).
22. E. E. Ramsen, private Communication, Monsanto, St. Louis, MO.
23. W. R. Moore, *Progress in Polymer Science,* Vol. 1, A. D. Jenkins, Ed., Pergamon Press, Oxford, 1967.
24. W. R. Moore and R. Hutchinson, *Nature,* **200,** 1095 (1963).
25. J. J. Burke and T. A. Orifino, *J. Polym. Sci.* **A2**(7), 1 (1969).