Single-Point Determination of Intrinsic Viscosity of Wholly Aromatic Thermotropic Copolyesters in 1,1,1,3,3,3-Hexafluoro-2-Propanol

YONGJIAN LIU

Institute of Materials Science and Engineering, China Textile University, Shanghai 200051, China

ABSTRACT: A series of wholly aromatic thermotropic copolyesters based on 4-hydroxybenzoic acid, hydroquinone, and 2,6-naphthalene dicarboxylic acid were synthesized by direct melt polymerization with or without different added transesterification catalysts. Nine procedures for calculation of the intrinsic viscosities from a single viscosity measurement for polymer solutions, including a proposed one, were applied for the thermotropic copolyesters in 1,1,1,3,3,3-hexafluoro-2-propanol at 30°C. Various forms of the Huggins and Kraemer equations, singly or combined, yielded intrinsic viscosities that were in good agreement with extrapolated values obtained in the usual manner from multipoint viscosity measurements over a wide range of concentrations. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3396–3401, 2001

Key words: wholly aromatic thermotropic copolyester; intrinsic viscosity; single-point determination of intrinsic viscosity

INTRODUCTION

The usefulness of solution viscosity as a measure of polymer molecular weight has been recognized ever since the early work of Staudinger and Heuer.[1] It is empirically related to the molecular weight for linear polymers; the simplicity of the measurement and the reliability of the viscosity–molecular weight correlation, compared with other molecular weight methods, are so great that viscosity measurement constitutes an extremely valuable tool for the molecular characterization of polymers.

The method of dilute solution viscometry is often based on the use of the Mark–Houwink equation, which usually relates the intrinsic viscosity (or limiting viscosity number, $[\eta]$) to the the viscosity-average molecular weight (M_v), but sometimes the weight- (M_w) or number-average (M_n).

However, in the aromatic thermotropic copolyesters, which are gaining increasing commercial importance and academic values, few Mark–Houwink relations have been established because of the variety of compositions and the complicity of comonomer sequence distribution. The properties, including the constants K and α in Mark–Houwink relations, of thermotropic copolyesters depend not only on the composition but also on the comonomer sequence distribution. Thus, in practice, the $[\eta]$ (instead of M_v, M_n, or M_w) is often used as an indicator of the molecular weights of thermotropic copolyesters.

The intrinsic viscosity of a polymer solution is conventionally determined from the extrapolation to zero concentration of ln η_{rel}/C against the concentration C by means of the Kraemer equation[2] or η_{sp}/C versus C using the Huggins equation[3]:

$$\frac{\ln \eta_{\mathrm{rel}}}{C} = [\eta] + k''[\eta]^2 C \qquad (1)$$

$$\frac{\eta_{\mathrm{sp}}}{C} = [\eta] + k'[\eta]^2 C \qquad (2)$$

$$[\eta] = \lim_{c \to 0}\left(\frac{\ln \eta_{\mathrm{rel}}}{C}\right) = \lim_{c \to 0}\left(\frac{\eta_{\mathrm{sp}}}{C}\right) \qquad (3)$$

where η_{sp} is the specific viscosity, η_{rel} is the relative viscosity of the polymer solution compared with the solvent, C is the concentration of the polymer solution (g/dL), k'' is the Kraemer constant, and k' is the Huggins constant.

The extrapolation procedure for the determination of the intrinsic viscosity requires that the specific viscosity be measured at several concentrations in the region where the reduced specific viscosities may be extrapolated linearly. These operations underlying the determination of the value of $[\eta]$, if performed properly, are rather tedious and time consuming. To obviate these difficulties, measurements are frequently made at one dilute concentration and the η_{sp}/C value is considered to be the $[\eta]$. However, such determinations are only approximations and a method that would yield $[\eta]$ and not η_{sp}/C from the viscosity is desirable. Several alternative methods were reported for calculation $[\eta]$ from a single viscosity measurement at a known concentration. Hart[4] reported a graphic method (N curve), employing the following equation:

$$[\eta] = \frac{\eta_{\mathrm{sp}}}{C}\frac{N}{\eta_{\mathrm{sp}} + N} \qquad (4)$$

Maron[5] described a method based on the Kraemer and Huggins equations:

$$[\eta] = \frac{\eta_{\mathrm{sp}} + \gamma \ln \eta_{\mathrm{rel}}}{(1 + \gamma)C} \qquad (5)$$

Solomon and Ciuta[6] proposed the use of the following equation:

$$[\eta] = \frac{1}{C}\left[2(\eta_{\mathrm{sp}} - \ln \eta_{\mathrm{rel}})\right]^{1/2} \qquad (6)$$

Solomon and Gottesman[7] analytically derived another single-point equation:

$$\frac{C}{\eta_{\mathrm{sp}}} = -k'''C + \frac{1}{[\eta]} \qquad (7)$$

Gillespie and Hulme[8] further derived the following equation from eq. (6):

$$\frac{\eta_{\mathrm{sp}}}{C} = [\eta] + \frac{1}{3}[\eta]^2 C \qquad (8)$$

Varma and Sengupta[9] analytically derived a single-point equation from the empirical viscosity relation of Schramek[10]:

$$[\eta] = \frac{1}{C}\left[2(\eta_{\mathrm{sp}} - \ln \eta_{\mathrm{rel}})\right]^{1/2}\left(1 - \frac{\eta_{\mathrm{sp}}^2}{12}\right) \qquad (9)$$

Rafi'ee Fanood and George[11] calculated $[\eta]$ as the arithmetic mean of $[\eta]$ values obtained by the Kraemer and Huggins equations:

$$[\eta] = \frac{1}{2}\left([\eta]_{\mathrm{K}} + [\eta]_{\mathrm{H}}\right) \qquad (10)$$

and Schulz and Blaschke[12] reported a convenient equation,

$$\frac{\eta_{\mathrm{sp}}}{C} = [\eta] + k[\eta]\eta_{\mathrm{sp}} \qquad (11)$$

In these equations, N is the Hart constant, γ is the Maron constant, k''' is the Soloman–Gottesman constant; k is the Schulz–Blaschke constant; and $[\eta]_{\mathrm{K}}$ and $[\eta]_{\mathrm{H}}$ are the intrinsic viscosity determined by the Kraemer and Huggins equations, respectively.

The methods involving the use of eqs. (4)–(11) were applied only to specific polymer–solvent systems, not for general applications. Thus, the difficulty lies in the limited extent to which any particular equation is valid.

In this article a series of wholly aromatic thermotropic copolyesters based on 4-hydroxybenzoic acid (HBA), hydroquinone (HQ), and 2,6-naphthalene dicarboxylic acid (NDA) are synthesized by direct melt polymerization with or without different added transesterification catalysts. The accuracy of the above-reported methods, as well as a new proposed procedure, is assessed specifically for these wholly aromatic thermotropic copolyester samples in 1,1,1,3,3,3-hexafluoro-2-propanol at 30°C.

EXPERIMENTAL

Materials

The HBA and HQ were of AR-grade purity and were purchased from Shanghai Chemicals Com-

Table I Preparation of HBA/HQ/NDA Thermotropic Copolyesters

| Copolyester | Monomer Feed Ratio (mol %) | | | Transesterification Catalyst | LC | T_{cn}[a] (°C) | T_{d1}[b] (°C) | T_{d2}[b] (°C) | T_{d3}[c] (°C) |
	HBA	HQ	NDA						
I	50	25	25	—	N	318	390	455	460
II	50	25	25	Mn(Ac)$_2$	N	310	432	465	479
III	50	25	25	Sn$_2$O$_3$	N	305	440	470	480
IV	50	25	25	Sb(Ac)$_3$	N	307	451	483	485
V	50	25	25	TSA	N	298	435	484	489

N, Nematic as observed with an Olympus BH-2 polarized light microscope; Mn(Ac)$_2$, manganous acetate; Sn$_2$O$_3$, antimonous oxide; Sb(Ac)$_3$, antimonous acetate; TSA, *p*-toluenesulfonic acid.

[a] Determined by DuPont 910 Differential Scanning Calorimeter controlled by a Thermal Analyst 2000 system. The sample weight was approximately 8 mg; the heating rate was 20°C/min under nitrogen.

[b] The T_{d1} and T_{d2} are the temperatures corresponding to 2 and 5% weight loss, respectively, that were obtained from thermogravimetric analysis curves. The sample weight was 8–10 mg. Evaluation was carried out with DuPont 951 Thermogravimetric Analyzer controlled by a Thermal Analyst 2000 system under nitrogen (50 mL/min) at a heating rate of 20°C/min.

[c] The T_{d3} is the decomposition temperature, and it was found using an Olympus polarizing microscope (BH-2) equipped with a Stanton–Redcroft hot stage (TH600) fitted with a nitrogen purge. Samples were placed between glass coverslips under a load of 0.27 N. The heating rate was 20°C/min.

pany. The NDA (fiber-grade purity, Amoco) and 1,1,1,3,3,3-hexafluoro-2-propanol (Sigma) were used without further purification. The AR-grade purity transesterification catalysts included manganous acetate, antimonous oxide, antimonous acetate, and *p*-toluenesulfonic acid; these and other reagents were obtained commercially and used as received.

Preparation of 4-Acetoxybenzoic Acid, and HQ Diacetate[13,14]

The HBA (100 g, 0.725 mol), acetic anhydride (300 mL), and sulfuric acid (1 mL) were stirred at 130°C for 2 h. After cooling to room temperature, the reaction mixture was filtered. A white crystal was collected and washed with 1 L of an aqueous 3% sodium hydroxide solution and pure water and then dried. Recrystallization was carried out twice by using chloroform as a solvent and dried under a vacuum for 72 h. The purity of the monomer was checked with DSC (yield: 80.5%; mp, 194°C). The HQ diacetate was prepared by the same procedure except using 50% aqueous ethanol as the recrystallization solvent (yield: 90%; mp, 125°C).

Synthesis of HBA/HQ/NDA Thermotropic Copolyesters

The HBA/HQ/NDA thermotropic copolyesters were prepared from 4-acetoxybenzoic acid and equimolar combinations of HQ diacetate and NDA on a 0.1 mol scale with or without different transesterification catalysts added for the copolymerization. The preparation of copolyester I is described as an example. 4-Acetoxybenzoic acid (9.0000 g, 0.05 mol), HQ diacetate (4.8500 g, 0.025 mol), and NDA (5.4000 g, 0.025 mol) were placed in a specially designed flask fitted with a stainless stirrer, nitrogen inlet, and vacuum outlet. After the reaction flask was evacuated and purged with dry nitrogen 3 times to remove air, the mixture was heated to 270°C to start the reaction and acetic acid was soon distilled out slowly. After the reaction was conducted for about 2 h, the vacuum was gradually applied to reach about 40 Pa in 3 h. During that time, the temperature was gradually raised to 300°C. Polymerization was continued at 320 and 340°C for 3 and 2 h, respectively, until the reactants began to be pulled from the flask wall and climbed along the stirrer. The reaction was stopped by immersing the flask into liquid nitrogen. The resulting copolyester was taken out by breaking the flask, ground into a fine powder, and then dried at 80°C in a vacuum oven for 72 h. The other copolyesters were prepared by the same procedure except using different transesterification catalysts, which are listed in Table I.

The as-prepared HBA/HQ/NDA copolyesters were purified before use. They were first dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol and the solution was filtered to remove the undissolved solid particles. Then the copolyesters were precipitated by adding methanol, leading to the formation of floccule-like entities. This procedure was repeated 3 times. The resulting copolyesters were

extracted with methanol for 72 h and finally dried at 80°C in a vacuum oven for 72 h.

Viscometry

Viscometric measurements were carried out at concentrations of 0.10, 0.20, 0.30, 0.40, and 0.50 g/dL, respectively, in 1,1,1,3,3,3-hexafluoro-2-propanol at 30 ± 0.02°C using an Ubbelohde dilution viscometer. The solutions were made up with magnetic agitation but without heating. The flow times were the averages of 10 tests, each time being within the vicinity of 0.2 s. For each sample the plots of η_{sp}/C versus C and ln η_{rel}/C versus C were made. If, by extrapolation to zero concentration, a common intercept was obtained, the intrinsic viscosity was equal to this common intercept [procedure (a)]. If a common intercept was not obtained by the above extrapolations a mean $[\eta]$ value was reported, and values of k' and k'' were calculated from the two slopes [procedure (b)].

RESULTS AND DISCUSSION

General Properties of HBA/HQ/NDA Copolyesters

Table I summarizes the results of the preparation of HBA/HQ/NDA copolyesters synthesized under different conditions. The polymerization conditions were not optimized, and no attempt was made at this stage to compensate for the loss of volatile monomers,[15,16] which in this case would be the HQ diacetate. During the first stage the stillhead was kept cold to diminish the evaporation of sublimation of the monomer. Monomers and even oligomers sublimated and condensed on the upper parts of the flask wall; but the sublimated materials were duly heated, enabling them to return to reactants. Additionally, the nitrogen flow was slow enough at the early stage of polymerization to prevent monomers from being blown off. High molecular weight copolyesters were obtained under all the polymerization conditions, as indicated by the intrinsic viscosities (see below), which were sufficiently high for a meaningful evaluation of the properties of these materials. All the copolyesters were opaque and exhibited a nematic phase above the flow temperature and persisted until the onset of decomposition, which was observed with a polarized light microscope.

All of the copolyesters showed good thermal stability (Table I), as expected for wholly aromatic polymers. The onset of decomposition observed by a hot-stage microscope ranged from 460 to 489°C, and the temperature T_{d2}, which corresponds to 5% weight loss, was between 455 and 484°C. Typically, the temperature corresponding to 2% weight loss T_{d1} was between 30 and 50°C below T_{d2}. However, copolyester I showed a larger difference between T_{d1} and T_{d2}; this was ascribed to the loss of low molecular weight species, which took place before the onset of decomposition. From the TGA evidence, in conjunction with the acceptable values of the solution viscosities, it was concluded that the compositions of the copolyesters did not differ substantially from those calculated from the concentrations of the monomers.

Determination of Intrinsic Viscosity and Associated Constants Using Multipoint Data for Eqs. (1), (2), (7), and (11)

Equations (4) and (11) are in fact of the same nature. Equation (5) is based on the assumption that a common intercept is always obtained by Huggins and Kraemer plots[5]; however, this was not generally true in our experiments, and thus eq. (5) was not used for multipoint or single-point determination of $[\eta]$. Equations (6), (8) and (9), which contain no constants characteristic of a polymer–solvent system, could be used directly for single-point determination of the intrinsic viscosity.

It was first necessary to calculate the constants involved in eqs. (1), (2), (7), and (11) by analysis of multipoint data before applying them to single-point determinations of $[\eta]$. So, ln η_{rel}/C versus C, η_{sp}/C versus C, C/η_{sp} versus C, and η_{sp}/C versus η_{sp} were plotted to obtain the corresponding $[\eta]$ values and related constants, and the results are presented in Table II.

Table II shows that the error in the $[\eta]$ values using eqs. (7) and (11) were relatively high compared with the $[\eta]$ value found by procedure (a) or (b).

Single-Point Determination of Intrinsic Viscosity Using Various Equations

The $[\eta]$ can be calculated as the positive root of the quadratic equations for each single point from the Kraemer equation:

$$[\eta]_K = \frac{(1 + 4k'' \ln \eta_{rel})^{1/2} - 1}{2k''C} \qquad (12)$$

Table II [η] Values Using Eqs. (1), (2), (7), and (11)

Copolyester	[η]^a (dL/g)	Eq. (1)		Eq. (2)		Eq. (7)		Eq. (11)	
		[η] (dL/g)	$-k''$	[η] (dL/g)	k'	[η] (dL/g)	k'''	[η] (dL/g)	k
I	0.606	0.630	0.138	0.582	0.420	0.677	0.312	0.700	0.284
II	0.655	0.651	0.117	0.659	0.320	0.724	0.265	0.754	0.432
III	0.658	0.658	0.161	0.658	0.334	0.753	0.188	0.751	0.375
IV	0.664	0.664	0.176	0.664	0.332	0.752	0.300	0.805	0.330
V	0.668	0.660	0.103	0.676	0.301	0.802	0.218	0.802	0.462

^{a} Obtained by procedure (a) or (b).

Similarly, for the Huggins equation, [η] can be calculated as follows:

$$[\eta]_H = \frac{(1 + 4k'\eta_{sp})^{1/2} - 1}{2k'C} \tag{13}$$

Also, the average value of the intrinsic viscosity ([η]$_{av}$) from eqs. (12) and (13) was calculated as

$$[\eta]_{av} = ([\eta]_K[\eta]_H)^{1/2} \tag{14}$$

where [η]$_K$ and [η]$_H$ are the [η] values obtained from the Kraemer and Huggins equations, respectively. Thus, the average of the positive roots of eqs. (12) and (13) yields

$$[\eta]_{av}$$
$$= \frac{[(1 + 4k'' \ln \eta_{rel})^{1/2} - 1]^{1/2}[(1 + 4k'\eta_{sp})^{1/2} - 1]^{1/2}}{2C(k'k'')^{1/2}}$$
$$\tag{15}$$

Single-point determinations of [η] were calculated using eqs. (6), (7), (8), (9), (10), (11), (12), (13), and (15) and the values of the appropriate constants shown in Table II. The average modulus percentage of error in the values of [η] obtained by these methods were compared, for reference, with the values of [η] found by procedure (a) or (b) in Table III.

Equation (6) has a general limitation that ($k' - k''$) must equal 0.5.[17,18] Equation (6) can be used for a single-point determination for copolyesters III and IV because ($k' - k''$) = 0.495 and 0.508, respectively. Equation (8) is the Huggins equation with $k' = 1/3$, and it gives better results for copolyesters III and IV where k' is 0.334 and 0.332, respectively, than for copolyesters I, II, and V where k' is 0.420, 0.320, and 0.301, respectively. For all copolyesters eq. (9) gives fairly ac-

curate values of [η] at low concentration; at higher concentration, however, the deviation from the extrapolated values of [η] is considerable. This large error was due to neglect of higher order terms in the derivation of this equation.

Equations (7) and (11), which involve constants, were subject to considerable error. This was because the constants, although independent of the intrinsic viscosity for a particular polymer–good-solvent system at a given temperature, were not actually constant except over a rather limited range of specific viscosities. When the constants were above a certain value, this single-point method gave results for [η] that were higher than the values obtained by the multipoint method; when the constants were below a certain value, the value of [η] determined by these procedures was less than that determined by the multipoint method. Thus, eqs. (7) and (11) could not both be used for single-point determination of the intrinsic viscosity in our experiments.

The results in Table III indicate that, compared with procedure (a) or (b) for obtaining [η], the Kraemer and Huggins equations, used singly or in a combined form [eqs. (10), (12), (13), and (15)], can be used successfully for single-point determination over a wide range of concentrations.

CONCLUSIONS

A number of viscosity functions have been proposed that have the important property that for many polymer solutions their numerical value is almost independent of the concentration; hence, a good estimate of the intrinsic viscosity can be obtained from one measurement of the relative viscosity at a convenient concentration. The particular equation, which fits the data best, depends

Table III   Percentage Errors in [η] Values Determined by Various Single-Point Procedures

Copolyester	Concentration (g/dL)	Equation								
		(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(15)
I	0.10	11.0	8.00	7.30	3.60	1.84	8.90	1.75	2.12	1.50
	0.20	15.0	11.20	7.30	4.70	2.67	12.3	3.50	4.98	2.42
	0.30	22.0	14.70	10.2	9.20	4.28	15.6	6.12	6.62	3.83
	0.40	17.0	18.20	12.8	14.6	6.09	20.7	7.09	8.92	5.67
	0.50	25.0	23.40	16.9	18.2	7.88	23.3	8.50	9.48	6.48
II	0.10	13.0	6.30	8.80	4.30	1.89	10.0	2.72	1.59	1.62
	0.20	18.0	7.20	10.2	6.40	2.90	12.4	3.47	2.86	2.70
	0.30	25.0	10.5	12.5	10.7	3.94	15.1	4.27	4.08	3.48
	0.40	20.0	14.0	13.7	16.5	6.87	18.9	6.59	7.68	4.09
	0.50	30.0	21.8	15.8	21.6	8.00	24.5	7.80	8.42	5.27
III	0.10	3.20	8.20	2.50	3.40	2.87	11.2	3.78	2.56	2.39
	0.20	4.80	10.8	3.80	7.20	3.92	13.8	4.27	4.04	3.84
	0.30	5.30	14.5	8.70	11.2	5.06	14.2	5.06	4.93	4.76
	0.40	6.00	19.5	9.90	18.2	6.84	17.3	7.21	6.52	6.09
	0.50	6.20	23.6	11.2	28.1	7.98	27.8	7.92	7.86	7.47
IV	0.10	3.80	5.50	2.10	2.80	2.60	14.2	2.86	2.90	2.43
	0.20	5.00	9.70	2.00	7.50	3.93	18.6	4.23	3.72	3.59
	0.30	5.70	13.2	6.40	13.6	4.90	21.2	5.87	5.45	4.80
	0.40	6.50	20.8	8.20	18.2	6.85	28.4	7.54	6.39	5.49
	0.50	6.80	26.7	8.00	30.1	7.29	30.7	8.01	8.23	6.00
V	0.10	15.0	8.70	10.2	4.10	2.88	16.2	2.78	2.92	2.51
	0.20	20.0	14.5	11.9	9.20	3.67	18.9	3.84	3.47	3.52
	0.30	27.0	20.0	13.8	15.2	4.82	20.1	4.44	5.08	4.90
	0.40	25.0	25.0	15.1	21.3	6.55	27.5	6.29	7.49	6.00
	0.50	35.0	28.1	19.2	28.4	8.90	38.6	8.38	9.07	6.87

on the value of the associated constant and the behavior of the higher order terms that have been neglected in obtaining the corresponding equation.

For the single-point determination of the intrinsic viscosity of wholly aromatic HBA/HQ/NDA thermotropic copolyesters in 1,1,1,3,3,3-hexafluoro-2-propanol, the Soloman–Ciuta equation [eq. (6)] was valid when (k' − k'') was around 0.5; the Varma–Sengupta equation [eq. (8)] could only be used at low concentration. The Gillespie–Hulme equation gave better results when k' was around 0.333. Various forms of the Huggins and Kraemer equations [eqs. (10), (12), (13), and (15)], singly or combined, yielded intrinsic viscosities in good agreement with those extrapolated values obtained in the usual manner from multipoint viscosity measurements over a wide range of concentrations.

REFERENCES

1. Staudinger, H.; Heuer, W. Ber Dtsch Chem Ges 1930, B63, 222. [in German].
2. Kraemer, E. O. Ind Eng Chem 1938, 30, 1200.
3. Huggins, M. L. J Am Chem Soc 1942, 64, 2716.
4. Hart, V. E. J Polym Sci 1955, XVII, 215.
5. Maron, S. H. J Appl Polym Sci 1961, V, 282.
6. Solomon, O. F.; Ciuta, I. Z. J Appl Polym Sci 1962, VI, 683.
7. Solomon, O. F.; Gottesman, B. S. J Appl Polym Sci 1968, 12, 971.
8. Gillespie, T.; Hulme, M. A. J Appl Polym Sci 1969, 13, 2031.
9. Varma, T. D.; Sengupta, M. J Appl Polym Sci 1971, 15, 1599.
10. Schramek, W. Makromol Chem 1955, 17, 19.
11. Rafi'ee Fanood, M. H.; George, M. H. Polymer 1987, 28, 2244.
12. Schulz, G. V.; Blaschke, F. J Prakt Chem 1941, 158, 130.
13. Brydon, D. L.; Fisher, I. S.; Emans, J.; Smith, D. M.; MacDonald, W. A. Polymer 1989, 30, 619.
14. Cao, J.; Karayannidis, G.; McIntyre, J. E.; Tomka, J. G. Polymer 1993, 34, 1471.
15. Brown, P. J.; Karacan, I.; Liu, J.; McIntyre, J. E.; Milburn, A. H.; Tomka, J. G. Polym Int 1991, 24, 23.
16. Erdemir, A. B.; Johnson, D. J.; Tomka, J. G. Polymer 1986, 27, 441.
17. Elliott, J. H.; Horowitz, K. H.; Hoodock, T. J Appl Polym Sci 1970, 14, 2947.
18. Maron, S. H.; Reznik, R. B. J Polym Sci (A-2) 1969, 7, 309.