Determination of Mark–Houwink Constants for Polystyrene and Polyacrylonitrile Terpolymers

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SYNOPSIS

Mark–Houwink constants of polystyrene and polyacrylonitrile terpolymers containing acrylonitrile, methyl acrylate, and styrene sulfonic acid or methallyl sulfonic acid as the third comonomer have been calculated from gel permeation chromatography (GPC) and viscosity data. The data have been used to determine molecular weights of polyacrylonitrile terpolymers.

INTRODUCTION

Gel permeation chromatography (GPC) is a well-established technique for determining weight average molecular weight ($\overline{M_w}$), number average molecular weight ($\overline{M_n}$), and molecular weight distribution (MWD). If accurate Mark–Houwink constant data for the unknown polymer and polystyrene (PS) standards are available, z-average molecular weight ($\overline{M_z}$), viscosity average molecular weight ($\overline{M_v}$), and intrinsic viscosity [n] can also be calculated.[1] Since GPC provides retention time (or retention volume) vs. detector response, its correlation with molecular weight is required to determine actual molecular weights of the sample. Ideally, narrow-polydispersity samples of the same chemical composition as that of the unknown polymer should be used for calibration work. But, well-characterized narrow-dispersity samples other than PS are not available commercially and are difficult to prepare in laboratory. On the other hand, GPC detector response in respect to different polymers is different due to the difference in their molecular structure and size. Hence, GPC calibration is tedious and complicated.

The universal calibration concept, based on hydrodynamic volume, suggested by Benoit et al.[2] has been found to be extremely helpful for GPC calibration. Its practical application has been well documented.[3–5] The molecular weight of the unknown polymer is generally estimated on the basis of a series of narrow-dispersity PS standards. The relationship between the two molecular weights requires the knowledge of Mark–Houwink constants.

These constants are traditionally obtained by determining $\overline{M_w}$ and $\overline{M_n}$ by classical techniques of light scattering and osmometry of a number of narrow fractions obtained from the original polymer.[6] Since polymer fractionation and molecular weight determination by classical techniques are cumbersome and error prone, there is practically a dearth of Mark–Houwink constants data in the literature, especially for copolymers and other newly developed polymers.

Attempts based on GPC data and intrinsic viscosity measurements, recently reported in the literature, provide a rapid means for the determination of Mark–Houwink constants. Mahabadi[7] recently reported the use of hydrodynamic average molecular weight, M_x, suggested by Goldwasser et al.[8] for calculating the values of K and a. The calculations require GPC and intrinsic viscosity data of four or five wide-dispersity polymers of the same type as that of the unknown polymer. In case sufficient samples of wide polydispersity are not available, K and a can still be calculated from two polymers but only with the help of the method suggested by Morris.[9] The values of K and a for PS and polymethyl methacrylate have recently been calculated by applying these techniques.[10]

Certain polymers such as polyacrylonitrile, containing polar groups like nitrile and sulfonate, dissolve in highly polar solvents like N,N-dimethyl-

formamide, dimethylacetamide, dimethylsulfoxide, etc. The polar groups result in polymer chain coiling that changes the molecular geometry.[11,12] In addition to this, molecular forces do not allow exclusion of molecules according to their real size in solution.

Acrylic terpolymers consisting of acrylonitrile, methyl acrylate, and randomly distributed sulfonate groups form one such family of polymers. These terpolymers are extensively used as acrylic fiber that finds ultimate use in textile applications.[13] Recently, these polymers have assumed more importance due to their use as carbon fiber precursors.[14] Hence, their characterization has become very important. Cha[15] was probably first to investigate such polymers by GPC. He concluded that electrostatic attraction between polymer and solvent molecules resulted in the formation of very large molecular sizes but molecules contracted about five-fold on the addition of lithium bromide. Later, Coppola et al.[16] also investigated such polymers by viscometry–GPC and concluded that polymers having sulfonate groups behaved differently from those not containing such groups. Kamide et al.[17,18] also studied acrylonitrile–methyl acrylate polymer by fractionating it into several small fractions. No attempts have probably been made for determining K and a values necessary for absolute molecular weight determination of such polymers. In the present study, Mark–Houwink constants for sulfonate containing terpolymers of the type stated above have been determined.

EXPERIMENTAL

Polymers and Chemicals

Narrow MWD PS standard polymers were obtained from Polymer Laboratories Ltd. (UK) and Waters Associates (USA). The three wide-dispersity polymer samples were obtained from commercial sources. Samples 1 and 2 were typical samples of normal molecular weight and high molecular weight (off grade), respectively, from acrylic fiber plant (IPCL) containing acrylonitrile, methylacrylate, and methallyl sulfonic acid. These polymers were prepared using a redox catalyst and monomer feed ratios of about 91.5 : 8.0 : 0.5, respectively. Sample 3 was obtained from E. I. Du Pont de Nemours & Co. and contained 93.6% acrylonitrile, 6.0% methyl acrylate, and 0.4% styrene sulfonic acid. HPLC grade N,N-dimethylformamide (S.D. Fine Chem., Bombay), containing $0.05 M$ lithium bromide was used as solvent throughout this study. The solvent was filtered through a 0.45-μm filter before being introduced into the GPC system.

Gel Permeation Chromatography

Waters Associates Model 150C GPC equipped with a differential refractive index detector and 730 data module was used. The concentration of polymer solution was generally kept at 0.1% except for high-molecular-weight polymers, where it was reduced to 0.05 or 0.075%. The GPC measurements were carried out at 60 and 100°C using a set of 10^5, 10^4, and 10^3 Ultrastyragel columns supplied by Waters Associates. The solvent flow rate was maintained at 0.8 mL/min. The calibration curve of PS standards was obtained by using a third-order polynomial, standard error and the correlation coefficient being < 0.1 and > 0.99, respectively. No adjustments for axial dispersion or band spreading were made.

Viscosity Measurements

The intrinsic viscosities of the polymers were determined at 60 or 100°C on a Lauda Viscomter bath using Ubbelohde Viscometer.

RESULTS AND DISCUSSION

PS calibration, necessary for the estimation of hydrodynamic volumes and ultimately K and a values of polyacrylonitrile terpolymers, was carried out in N,N-dimethylformamide (which contained $0.5 M$ lithium bromide) at 60 and 100°C. Thus, intrinsic viscosities and peak retention volumes of 12 narrow MWD PS standards were determined at the above temperatures (Table I). It is shown in Table I that retention volumes at 60°C are higher by about 1
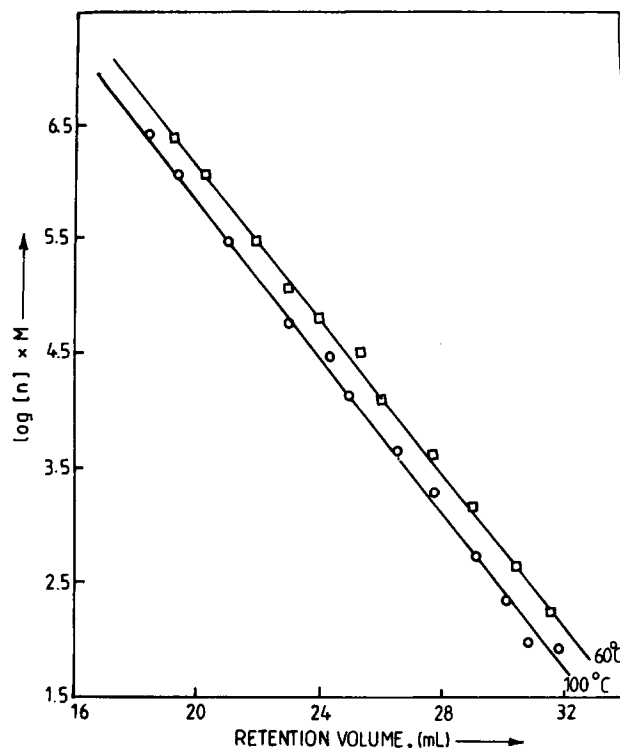
Table I Viscosity–Retention Volume–Molecular Weight Data

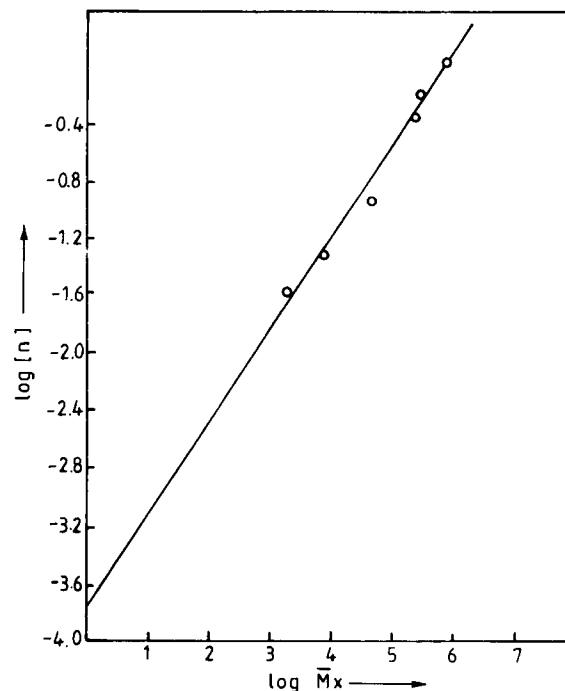| $M_p \times 10^{-3}$	Peak Retention Volume (mL) (60°C)	Peak Retention Volume (mL) (100°C)	$[n]_{60}$	$[n]_{100}$
3.1	31.92	30.82	0.027	0.032
5.0	31.65	30.21	0.035	0.044
9.0	35.50	29.20	0.048	0.058
19.0	29.06	27.81	0.075	0.102
34.5	27.73	26.61	0.118	0.131
68.0	26.08	25.04	0.185	0.186
115.0	25.49	24.40	0.270	0.269
170.0	24.02	23.06	0.365	0.343
240.0	23.04	—	0.455	—
450.0	21.97	21.04	0.675	0.625
1030.0	20.32	19.40	1.110	1.067
1750.0	19.33	18.48	1.400	1.498

count for all the polymers than at 100°C. This is attributed to the reduction in the solute–solvent interactions at higher temperature. The viscosities show a rather different behavior: Smaller molecules have more intrinsic viscosity at higher temperature, but gradually the difference narrows down with increasing M_w until it becomes almost equal for the M_w range 68,000–115,000; the viscosities then start reducing except for 1,750,000 M_w sample, where it is slightly higher at 100°C. Thus, it can be substantiated that lithium bromide, which is known to reduce the size of PS molecules,[16] has an adverse effect on smaller molecules when the temperature is raised from 60 to 100°C.

The hydrodynamic volume-retention volume variation with temperature is shown in Figure 1. Both curves are parallel, indicating a uniform reduction in the hydrodynamic volume throughout the entire M_w range. Since GPC separation takes place according to the size of molecules, this relationship shows uniform reduction in molecular size with the increase in temperature.

The Mark–Houwink constants of PS were first estimated at 60°C by using hydrodynamic molecular weight average, $\overline{M_x}$, and viscosity data at 60°C using the procedure of Mahabadi.[7] The log–log plot of

Figure 2 Hydrodynamic average M_w, $\overline{M_x}$ vs. intrinsic viscosity [n].

$\overline{M_x}$ vs. [n] gives a straight line relationship (Fig. 2).

The K and a values were obtained from the intercept and slope of the straight line. The values were: 1.85×10^{-4} dL/g and 0.635, respectively. The different values of δ and K obtained in respect of various PS standards were also quite close (Table II).

The determination of Mark–Houwink constants for polyacrylonitrile terpolymer samples could not be studied by the hydrodynamic molecular weight average method because different samples of wide dispersity did not have sufficient difference in the
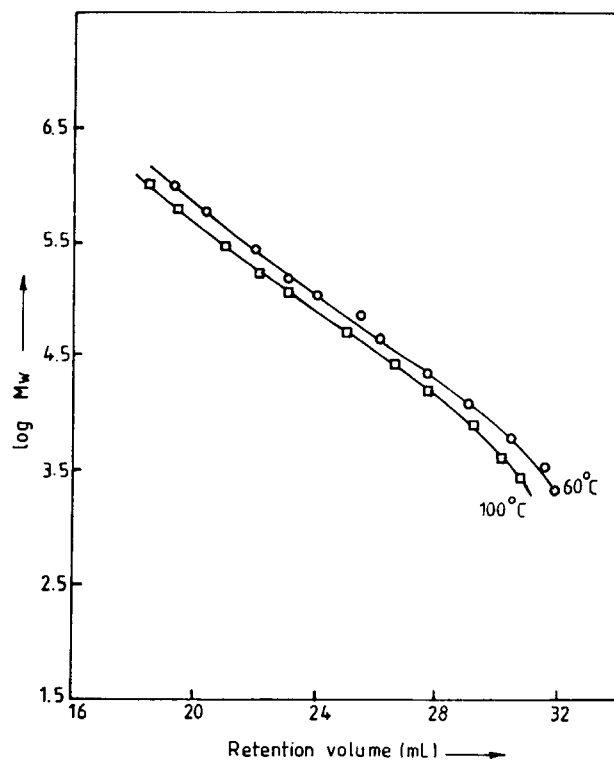
Figure 1 Hydrodynamic volume-retention volume relationship for polystyrene at 60 and 100°C.

Table II   Viscosity—M_x Data of PS Standards in DMF (Containing 0.05M LiBr) at 60°C

$M_p \times 10^{-3}$	$\overline{M_x} \times 10^{-3}$	[n] (dL/g)	δ	$K \times 10^4$ (dL/g)
2.9	1.85	0.027	0.89	2.08
8.5	7.48	0.049	0.83	2.31
35.0	44.07	0.119	0.87	2.13
233.0	242.55	0.460	0.82	2.27
470.0	303.05	0.653	0.78	2.37
1030.0	758.65	1.113	0.78	2.39

$K = 2.26 \times 10^{-4}$.

intrinsic viscosities and $\overline{M}_x$ values to get a straight line log–log plot. The intrinsic viscosities of these samples also did not correspond to the GPC molecular weights. Hence, the procedure suggested by Price et al.[10] was followed. The viscosities of polyacrylonitrile terpolymers and GPC analysis were carried out at 60 and 100°C. The molecular weights of different PS fractions, as recalculated by using K and a values of PS and polyacrylonitrile terpolymer at 60 and 100°C, against retention volumes are shown in Figure 3, where it can be seen that corresponding molecular weights at 100°C are lower as compared to those at 60°C. The $\overline{M}_w$, $\overline{M}_n$, and polydispersity values of the three polyacrylonitrile terpolymers recalculated on the basis of calibration curves (Fig. 3) are given in Table III. Although no authentic information regarding actual molecular weights of these samples is available, sample 1 is believed to have $M_w \sim 80,000$ and sample 3 $\sim 100,000$.

It is observed that the values of $\overline{M}_w$ and $\overline{M}_n$ have reduced at 100°C in all three samples, indicating that the molecular sizes reduce by increasing the temperature. The polydispersity values $(\overline{M}_w/\overline{M}_n$

Table III Molecular Weight Data (M_w and M_n) of PAN Samples

	Temperature(°C)	Sample 1	Sample 2	Sample 3
$M_w \times 10^{-5}$	60	1.078	1.518	1.400
	100	0.989	1.383	1.199
$M_n \times 10^{-4}$	60	3.019	4.805	3.400
	100	3.307	3.702	3.484
M_w/M_n	60	3.6	3.2	4.1
	100	3.0	3.7	3.7

$K_{ps} = 2.259 \times 10^{-4}$; $K_{pan,60} = 3.311 \times 10^{-4}$; $K_{pan,100} = 1.032 \times 10^{-4}$; $a_{ps} = 0.635$; $a_{pan,60} = 0.681$; $a_{pan,100} = 0.761$.

ratios) have also changed with the increase in temperature, considered to be due to nonuniform reduction in the different molecular sizes as observed for PS. Temperatures higher than 100°C were not considered feasible as the polymer solutions became yellow after about 4 h at 100°C. Though the sample solutions were injected within 1 h of their dissolution, slight degradation during analysis is also expected at higher temperature. It is evident that molecular interactions and associations are not eliminated totally even at 100°C and after the addition of 0.05 M lithium bromide. An interesting feature of the study is that $\overline{M}_w$ values of polyacrylonitrile terpolymers are greatly affected with the increase in temperature while $\overline{M}_n$ values have negligible effect. It substantiates that larger molecules have more association at lower temperatures than smaller molecules, which is true for PS also.

Figure 3 Retention volume–log M_w for polystyrene at 60 and 100°C.

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