Size Exclusion Chromatographic Measurement of PVC Molecular Weight Distributions

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SYNOPSIS

Aggregates that may exist in poly(vinyl chloride) (PVC) solutions at ambient temperatures compromise the accuracy of SEC measurements of molecular weight distributions. Aggregate-free solutions can be produced in 1,2,4-trichlorobenzene (TCB) by controlling the dissolution time and temperature. SEC measurements were made in trichlorobenzene at 110°C after dissolution for 12 h at 120°C. An on-line continuous viscometer can be used to determine when aggregate-free solutions have been produced. The Mark–Houwink parameters ($K = 0.161$ mL/g, $\alpha = 0.762$) can be used for universal calibration procedures in TCB at 110°C. Complete dissolution of the PVC affects the high molecular weight end of the molecular weight distribution. Measured $\bar{M}_n$ values are not affected, but M_z's are much higher than those estimated, for example, from room-temperature SEC analyses in tetrahydrofuran. Molecular weight distributions are also seen to be broader, especially for higher molecular weight PVCs. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The presence of aggregates in apparently clear solutions complicates measurements of molecular weight distributions of semicrystalline polymers. Since procedures have been developed in this laboratory to reduce the severity of this problem with polyolefins, it was of interest to see whether variations on this theme might also be useful to characterize poly(vinyl chloride) (PVC).

Stable aggregates have been reported to present a problem in the molecular weight characterization of PVC.[1] Various procedures have been suggested to break up the aggregates that are of almost universal occurrence in PVC solutions prepared at ambient temperature.[2-7] Following the work of Hengstenberg and Schuch,[3] Gautron and Wippler,[4] Kobayashi,[5] Lyngaae-Jorgensen,[6] and Chan and Worman[7] found that heating tetrahydrofuran (THF) solutions at 120°C for 3 h destroyed aggregates in the case of commercial PVC polymers. This procedure is not believed to be effective for low-tem-

perature polymerized polymers,[8] but heating at 200°C for 2 h may suffice in this case if the thermal stability of the polymer is adequate. All the above methods are not very simple to perform and they all are somewhat hazardous, particularly since THF is a peroxide-forming ether. A specially equipped autoclave apparatus is required.

Here we report an alternative, simpler, and less hazardous method for preparing aggregate-free PVC solutions for SEC analyses. The analysis itself is carried out with a high-temperature SEC apparatus. The unit used here was equipped with a continuous viscometer (CV) for molecular weight measurements, but universal calibration procedures can also be employed with the Mark–Houwink constants that are reported here.

A simple and apparently reliable procedure for the preparation of aggregate-free solution of polyethylene has been reported from our laboratory.[9] A similar approach for PVC is shown to be successful in obtaining aggregate-free solutions of PVC in 1,2,4-trichlorobenzene. A log–log plot of corresponding values of intrinsic viscosity and molecular weight measured by the CV SEC system yields a set of Mark–Houwink constants, K and α, for the molecular weight range of the particular samples under study.

Trichlorobenzene (TCB) is not a common solvent for molecular weight analyses of PVC samples. It is widely used for polyolefins, however, and we have employed it for PVC because of the convenience of being able to analyze both polymer types without changing solvents or SEC columns. TCB is a relatively high boiling liquid and it is fairly simple and safe to rely on elevated temperatures to break up PVC aggregates. Polyolefin SEC is generally performed at 145°C. Here, we have carried out PVC SEC analyses at 110°C, in view of the greater thermal instability of this polymer type. Dissolution of the polymers was at 110°C or at 120°C, as noted below.

EXPERIMENTAL

All solutions for analysis were prepared in filtered TCB, the same solvent used as the SEC eluent. Polymer solutions were prepared by dissolving known quantities of PVC and diluting to the desired volume with the filtered TCB solvent. Dissolution of PVC samples was achieved by rotating the samples either at (i) 110°C for 12 h or (ii) 120°C for 12 h. To prevent oxidative degradation of the polymer, 0.1 wt % of a phenolic antioxidant was added in both cases. The mixed-bed column was calibrated using 30 polystyrene standard samples with molecular weights ranging from 580 to 15,000,000. Noise in the detector signals was not suppressed electronically and the calculated molecular weight distribution curves were not smoothed.

Complete dissolution of the polymers was assumed to have been achieved when the log–log plot of intrinsic viscosity and molecular weight obtained from the CV chromatogram did not exhibit an abnormal "drop" in the slope. At higher molecular weights, the slope of the curves will decrease to zero (or even become negative in extreme cases) if the high molecular weight species fail to dissolve completely.

The molecular weight of eluting species was derived from the polystyrene universal calibration curve (in terms of $[\eta]M$[10] or hydrodynamic volume[11] units) and the corresponding values of $[\eta]$ measured by the CV. A differential refractometer detector (DRI) served as the concentration detector. Since THF solutions are commonly used at room temperature for SEC analyses of PVC, we have made such measurements as well, for comparison with the modified procedures reported here.

In industrial practice, the molecular weight of PVC is inferred from dilute solution viscosity mea-

surements. These results are expressed in terms of specific viscosity $[(\eta - \eta_0)/\eta_0]$, inherent viscosity $[\log(\eta/\eta_0)]$, or Fikentscher K value. [Here, η_0 and η are the viscosities of the solvent and the PVC solutions at a specified concentration, c, respectively.] The K value[12] is calculated from

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{cK}{1000}\left(\frac{75K}{1.5cK + 1000} + 1\right) \quad (1)$$

In this study, we have examined suspension PVC polymers with K values between 60 and 95. Most commercial polymers will be within or close to this range.

RESULTS AND DISCUSSION

As mentioned, it has been reported[6,7] that a serious obstacle in SEC analyses of PVC is the difficulty of preparing true solutions. Since PVC contains a minor fraction of high-melting crystallites, the characterization of dilute solution properties of PVC depends upon how well one can prepare an aggregate-free solution.

Although our particular SEC apparatus is equipped with low-angle laser light-scattering (LALLS) and CV molecular weight detectors, only the latter could be used with PVC solutions. Raw LALLS traces of PVC solutions in THF were too noisy (evidence of incomplete dissolution[13]) to be useful, whereas the small refractive index difference between PVC and TCB made the LALLS signal too weak at the concentrations encountered in SEC analyses. The CV, on the other hand, provided a useful practical indication of solution quality from plots of intrinsic viscosity vs. molecular weight.

Figure 1 shows the plot of intrinsic viscosity vs. elution volume of two PVC samples ($60K$ and $66K$) from an SEC analysis in THF solution at 30°C. Solutions were prepared here by ultrasonic agitation, as recommended by Rudin and Benschop-Hendrychova.[2] It is interesting to notice that in both traces the slope of the intrinsic viscosity–molecular weight curve drops below zero in the high molecular weight region. The theoretical lower limit for the slope is 0.5, for theta solutions. This indicates that there may be undissolved aggregates present, which cannot be resolved by the column and which appear first in the elution profile. This observation agrees with results reported by the other researchers.[6,7] It is therefore an objective of this study to find alternate experimental conditions that could produce
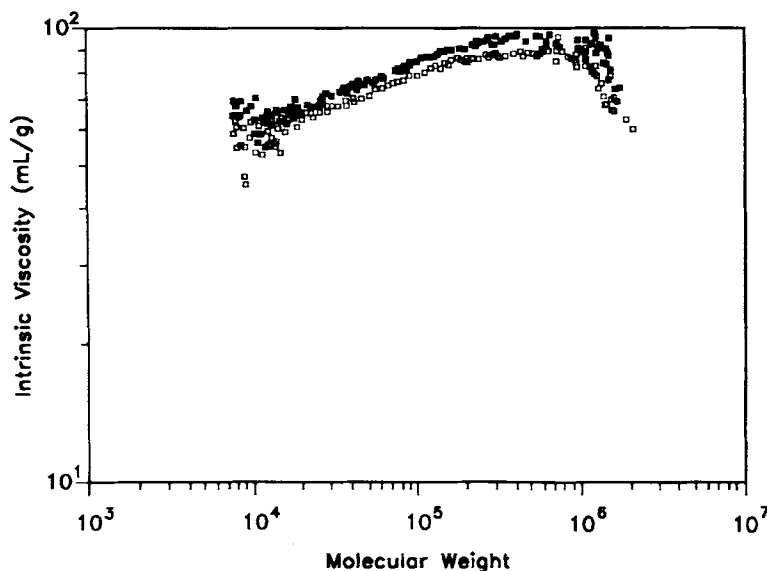
Figure 1   Intrinsic viscosity–molecular weight plots for 60K and 66K PVC samples; SEC analyses at 30°C in THF solution after 0.5 h treatment in ultrasonic cleaner bath.[2] Open symbols: 60K PVC; full symbols, 66K PVC.

aggregate-free PVC solutions without the tedious preparation procedures mentioned earlier. To achieve this without degradation of the PVC, a study was made of the effects of dissolution for 12 h in TCB at 110 and at 120°C. As before, the experimental results are quoted in terms of the intrinsic viscosity–molecular weight relations of the polymer from the CV analyses.

Intrinsic viscosity measurement experiments with synthetic elastomer polymers[10] have shown that solutions containing undissolved species produce an abnormal "drop" approaching a zero slope of the intrinsic viscosity molecular weight relation. Thus, the slope of the high molecular weight portion in a log–log plot of intrinsic viscosity vs. molecular weight can be used to show the presence or absence of poorly dissolved polymer. Lyngaae-Jorgensen[6] noted earlier that aggregation in THF solutions should produce a downward trend in $\log[\eta]$–$\log M$ plots if the solution has not been heat treated appropriately.

The same criterion was used to assess PVC solutions. As can be seen from Figure 2, at the high molecular weight portion, the slope of the log–log plot of the intrinsic viscosity vs. molecular weight for the 66K PVC samples made by dissolution for 12 h in TCB at 110°C exhibited the abnormal "drop" in slope at high molecular weights. Figure 3 shows that a solution of 66K polymer that was made by dissolution for 12 h at 120°C did not have the drop in the slope in the high molecular weight region.

The Mark–Houwink constants for the 60K and 66K samples that were properly dissolved were determined to be $K = 0.0161$ mL/g, $\alpha = 0.762$. The same constants are satisfactory for the 95K PVC. These parameters may be used for universal calibration SEC analyses of PVC in TCB at 110°C.

The cutoff lines present in the plots shown were determined by selecting the regions where the deviations (apparent oscillations in the trace) of the CV signal exceeded a preset threshold level ($\pm 5\%$ of the CV signal). In general, the cutoff at the low elution volume tail (high molecular weight) is governed by the strength of the DRI signals that are used as concentration data. Usually, at the high elution volume end, the cutoff is dictated by the strength of the CV signal. However, in the case of PVC, the cutoff at the high elution volume end is also dictated by the DRI signals. The strength of the DRI signal is relatively weaker in all cases and this determined the range of the usable CV data.

Table I shows the measured molecular weights and intrinsic viscosities of the 60K and 66K PVCs as measured in THF. Table II lists molecular weight averages of four PVCs measured in TCB. Dissolution at 120°C generally has little effect on $\bar{M}_n$, and even on $\bar{M}_w$, compared to values measured after dissolution at 110°C. Molecular weight averages per se do not usually provide much information on dissolution. This is especially true for $\bar{M}_n$ and $\bar{M}_w$, which are not very sensitive to the high molecular weight end of the distribution. Figures 4 and 5 show overlays
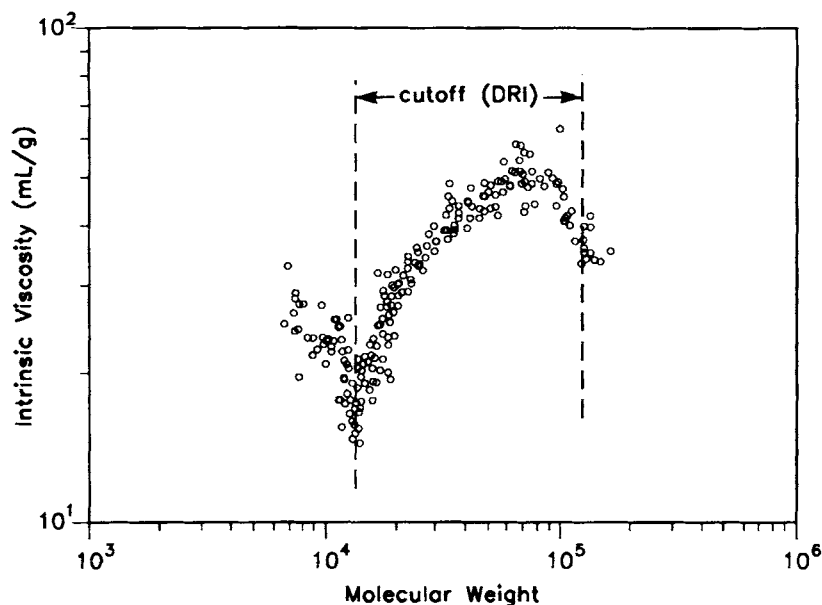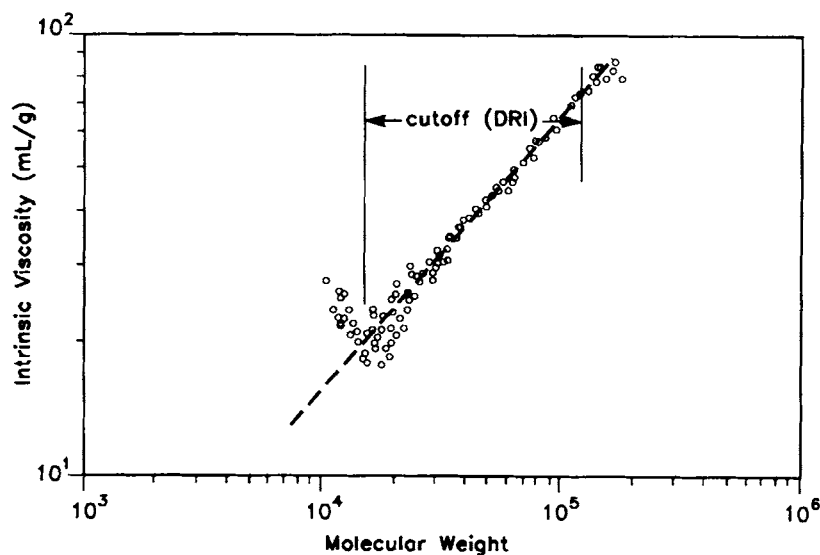
Figure 2 Intrinsic viscosity–molecular weight plot for 66K PVC sample; SEC analysis at 110°C in TCB after 12 h dissolution in TCB at 110°C.

of molecular weight distributions of 60K and 66K PVC samples in TCB (dissolution at 120°C) and THF solutions. In both cases, samples dissolved at 120°C in TCB showed the presence of high molecular weight species that were not detected in samples dissolved in THF.

The molecular weight distribution plots of the individual samples dissolved at 120°C showed distinctive differences, as shown in Figure 6. The dis-

crepancies in $\bar{M}_w$ and $\bar{M}_z$ values measured for all PVCs in TCB at 110 and at 120°C indicated that the higher dissolution temperature had resolved the undissolved aggregates. This observation agrees with the elimination of the drop in the slope of the log–log plot of the intrinsic viscosity vs. molecular weight at the high molecular region in both THF (at 30°C) and TCB (dissolution time of 12 h at 110°C) solutions, as previously noted.

Figure 3 Intrinsic viscosity–molecular weight plot for 66K PVC sample; SEC analysis at 110°C in TCB after 12 h dissolution in TCB at 120°C.

Table I Molecular Weight Averages of 60K and 66K PVC Samples from DRI and CV Analyses in the THF at 30°C

Sample	DRI				CV				Intrinsic Viscosity (dL/g)[a]
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	
PVC 60K 30°C THF	38,200	80,100	218,400	2.10	39,500 (41.380)	107,000	439,700	2.71	0.652 (0.655)
PVC 66K 30°C THF	39,150	88,400	279,200	2.26	41,700 (42,100)	110,600	565,800	2.65	0.787 (0.788)

[a] ( ) Values estimated from using the area under the chromatogram only with the Goldwasser method.[13]

In industrial practice, the dilute-solution viscosity of PVC polymers is normally used as an index of the molecular weight. The results are commonly expressed in terms of the Fikentscher K value or viscosity number [eq. (1)], but sometimes also as specific viscosity or inherent viscosity (logarithmic viscosity number). Currently, there are several test procedures and data representations based on the dilute solution viscosity measurement of PVC polymers. The ASTM standard (ATSM D1243-79) uses a 0.2 g/100 mL solution in cyclohexanone and expresses the result as inherent viscosity. The ISO standard uses 0.5 g/100 mL solution in cyclohexanone and reports the result as viscosity number. Many European manufacturers (DIN 53 726) prefer

to express results in terms of Fikentscher K value as stated above.

Figure 7 shows the plot of the relationship between our measured average molecular weights, $\bar{M}_w$, and the corresponding Fikentscher K values supplied by the manufacturer (which were determined in cyclohexanone solutions of concentration 0.5 g/100 mL at 25°C). Figure 8 shows K values calculated from eq. (1) from specific viscosities measured in TCB at 110°C and literature values.[14] It is interesting that the slope of the TCB relation is almost the same as that of the cyclohexanone line. The K values in TCB are higher, for the same polymer, since this is a better solvent than THF.

Commercial PVC polymers are usually believed

Table II Molecular Weight Averages Measured in TCB at 110°C

Sample (Dissolution Temperature)	CV				Intrinsic Viscosity (dL/g)[a]	Specific Viscosity $(\eta - \eta_0)/\eta_0$
	$\bar{M}_n$[a]	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$		
PVC 60K [110°C TCB]	38,100 (37,200)	85,200	581,000	2.23	0.501 (0.495)	0.160
PVC 66K [110°C TCB]	43.000 (43,400)	128,100	681,000	2.97	0.548 (0.550)	0.200
PVC 69K [110°C TCB]	60,500 (59,900)	161,600	653,000	2.67	0.720 (0.713)	0.225
PVC 95K [110°C TCB]	81,100 (80,300)	384,300	750,100	4.74	0.880 (0.871)	0.501
PVC 60K [120°C TCB]	37,900 (36,400)	94,400	679,200	2.49	0.496 (0.480)	0.160 0.310[b]
PVC 66K [120°C TCB]	43,900 (42,600)	130,900	747,800	2.98	0.554 (0.542)	0.204 0.370[b]
PVC 69K [120°C TCB]	57,100 (56,000)	168,100	673,600	2.94	0.678 (0.668)	0.227 0.410[b]
PVC 95K [120°C TCB]	80,400 (79,100)	463,800	1,828,100	5.77	0.881 (0.870)	0.505

[a] ( ) Values estimated from using the area under the CV chromatogram only with the Goldwasser method.[13]
[b] Reported specific viscosity (0.5 g per 100 mL nitrobenzene at 25°C) for corresponding K values.[14]
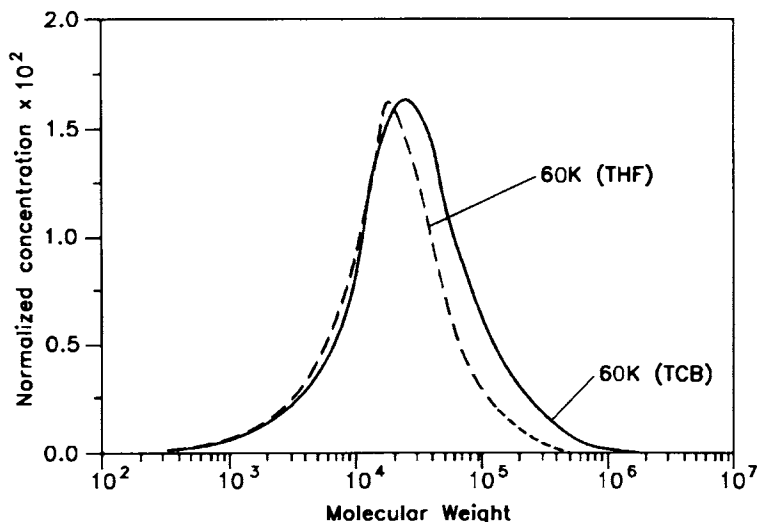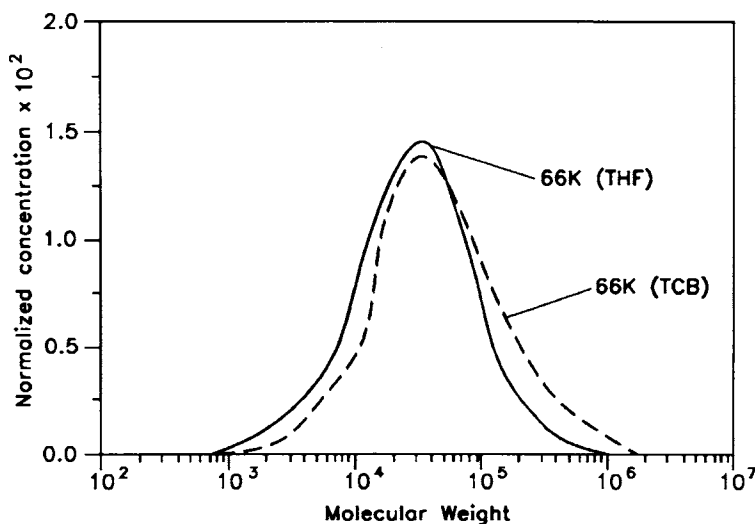
Figure 4 Molecular weight distribution overlay of 60K PVC samples from CV SEC analyses in THF (30°C) and at 110°C (120°C dissolution temperature).

to have relatively narrow molecular weight distributions, with $\bar{M}_w/\bar{M}_n$ values (polydispersity) of suspension polymers typically within the range 2–2.5 (reducing with increasing polymerization temperature). In the polymerization process for PVC polymers, molecular weight increases with decreasing temperature. However, in this study, we found that the polydispersity of PVC polymers could be larger than 2.5 for two PVCs with high K values, as shown in Table II. We believe that this discrepancy can be attributed to the dissolution problem of PVC polymers in conventional GPC solvents. PVC polymers of very high molecular weight may require intensive heating in the solvent for complete dissolution when solutions are being prepared for viscosity measurements or GPC determinations. As a result, many reported polydispersity figures are possibly erroneously narrow.

CONCLUSIONS

Aggregates may exist in PVC solutions in THF at 30°C. Intrinsic viscosity measurements over the SEC chromatogram, especially in the high molecular


Figure 5 Molecular weight distribution overlay of 66K PVC samples from CV SEC analyses in THF (30°C) and TCB at 110°C (120°C dissolution temperature).
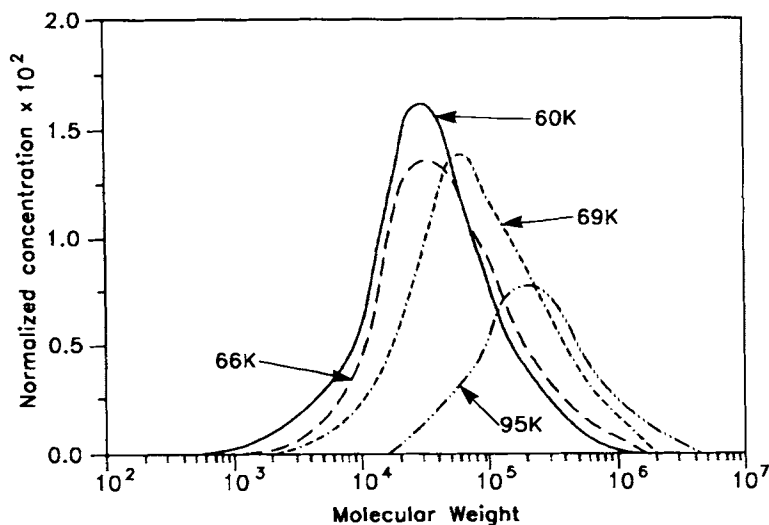
Figure 6 Molecular weight distributions of the various PVC samples. Measurements in TCB at 110°C after dissolution at 120°C.

weight region (or early elution times), are particularly compromised by the existence of such aggregates. A simple dissolution procedure can be used to remove aggregates in PVC solutions without the tedious approaches that are commonly used. Aggregate-free solutions of PVC can be produced in TCB by controlling the dissolution temperature and time. An on-line SEC continuous viscometer can be used to determine when aggregate-free solutions have

been produced. This occurs when the slope (alpha value) in the measured Mark–Houwink plot does not drop below a limiting value of 0.5 in the high molecular weight region in the SEC analysis. Number-average ($\bar{M}_n$) molecular weight and intrinsic viscosities have been shown to be quite insensitive to the presence of aggregates in the solutions, but $\bar{M}_w$ (for samples with high Fikentscher K values, i.e., > 70) and particularly $\bar{M}_z$ are not. The exact
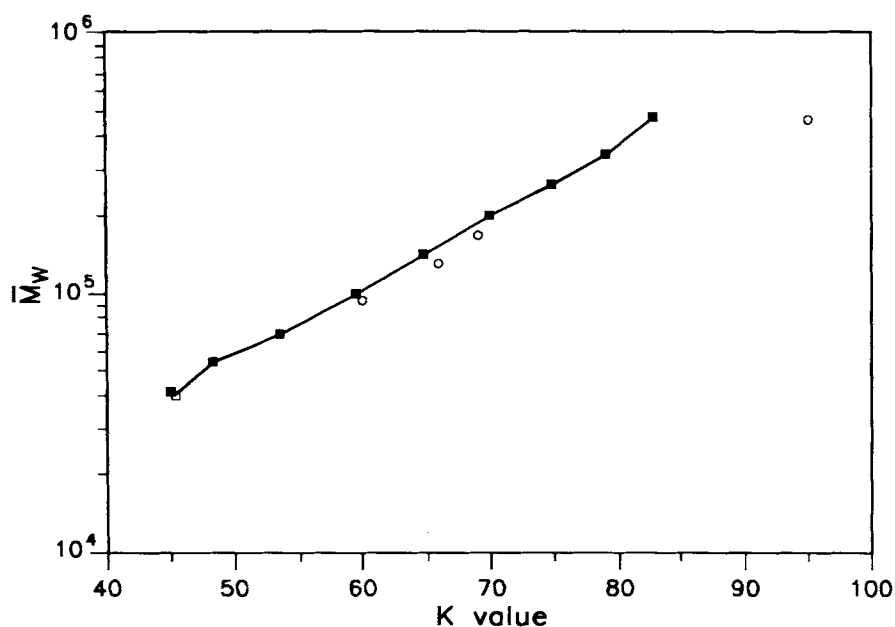
Figure 7 Relationship between $\bar{M}_w$ and K values (measured in cyclohexanone at 25°C): (O) present data from TCB analyses at 110°C.
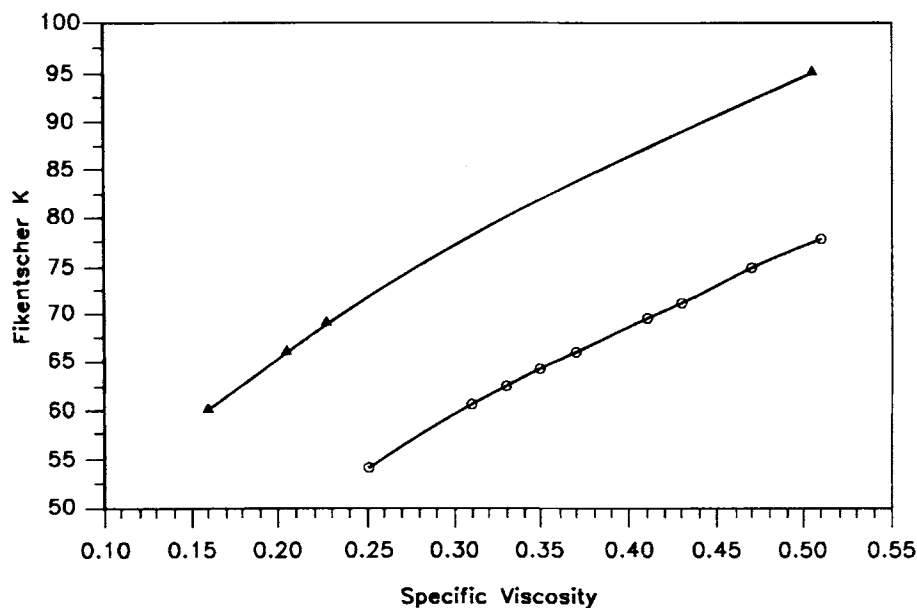
Figure 8 Relationship between K value [eq. (1)] and specific viscosity (O) in nitrobenzene at 26°C and (▲) in TCB at 110°C.

time needed for dissolution and freedom from degradation at high temperature could vary somewhat with the polymer molecular weight distribution and the nature and concentration of stabilizers used. Very high molecular weight polymers may require a very careful procedure for obtaining an aggregate-free solution.

The Mark–Houwink parameters obtained in this study ($K = 0.0161$ ml/g; $\alpha = 0.762$) in TCB at 110°C can be used to estimate the molecular weights from DRI data alone using the universal calibration method.

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