

Characterization of Poly(*tert*-Butyl Acrylate) by SEC

In size exclusion chromatography (SEC) macromolecules are separated with respect to their hydrodynamic volume, which is proportional to a multiple of intrinsic viscosity $[\eta]$ and molecular weight M (cf. Ref. 1). This holds for all macromolecules, irrespective of their chemical structure and chain topology. SEC data can be transformed to the molecular weight distribution of the linear polymer undergoing analysis if for the given fractionating system the dependence of the parameter $J_i = [\eta]M_i$ on the elution volume $J_i = f(V_i)$, called universal calibration, is known and if constants of the Mark–Houwink–Sakurada (MHS) relation of this polymer in the eluent used are available. If this is not so, then it is necessary to characterize a few samples of the polymer by the viscometric method or by absolute methods of measurement. Using the known characteristics $[\eta]$, M_w , M_n , and those of SEC chromatograms, the MHS constants K and a should be determined according to Weiss and Cohn-Ginsberg,² as demonstrated in this note for the case of poly(*tert*-butyl acrylate) (PtBA).

EXPERIMENTAL

Polymer. Samples of PtBA were kindly donated by Polymer Standard Service GMBH, D-6500 Mainz (FRG).

Methods. High-speed SEC was performed by means of a liquid chromatograph (Laboratory Instruments, Prague) with differential refractometric detection. The original separation column HP (7.5/300 mm), packed with PL-GEL 10 μm MIX, was used. Tetrahydrofuran (THF) (flow rate 1 cm^3/min) was the mobile phase. A set of polystyrene standards [Polymer Laboratories (GB)] was used in the calibration of the separation system. The injected amount of solutions (conc. about 2 wt %) was 10^{-5} L. The universal calibration was calculated using the MHS equation for polystyrene in THF³— $[\eta] = 1.17 \times 10^{-2} M^{0.717}$. Viscosity was measured with a capillary Ubbelohde viscometer adapted for gradual dilution at 25°C. Osmometric measurements were performed in toluene at 40°C using an automatic membrane Wescan (USA) osmometer. Light scattering measurements of propylalcohol solutions ($dn/dc = 0.074$) were carried out with a Fica 40 000 photogoniometer in vertically polarized light with $\lambda = 546$ nm, angular range 30–150°.

RESULTS

The weight average (M_w) and the number average (M_n) molecular weight and the intrinsic viscosity $[\eta]$ of PtBA samples determined by absolute methods of measurement are summarized in Table I. They were used to calculate the parameters K and a using the relations²

$$X_\eta = \sum w_i J_i^{a/(a+1)} = K^{-1/(a+1)} [\eta] \quad (1)$$

$$X_n = \sum w_i J_i^{-1/(a+1)} = K^{1/(a+1)} \bar{M}_n \quad (2)$$

$$X_w = \sum w_i J_i^{1/(a+1)} = K^{1/(a+1)} \bar{M}_w, \quad (3)$$

in which w_i is the weight fraction of the monodisperse species separating at V_i . The search for real a and the corresponding K was performed with a computer using a reiterative program. First, the X_w , X_n , and X_η values were calculated from SEC data for all PtBA samples used in the analysis, each time for a certain a varying in the range 0.5–1.0. After that, for each chosen a the slope of

TABLE I
 Characteristics of Poly(*tert*-butyl acrylate) Samples

Sample	A	B	C	D
Viscometry: $[\eta]$ in THF, cm^3/g	25	34	56	125
Light scattering: $M_w \times 10^{-5}$	0.74	1.03	2.05	5.4
Osmometry: $M_n \times 10^{-5}$	0.53	0.79	1.40	4.0

the logarithmic form of Eq. (1) [Fig. 1(a)] or the slope of superimposed relations (2) and (3) [Fig. 1(b)] was calculated. The dependencies K and $d \log X_n/d \log [\eta]$, or $d \log X/d \log M$ on the chosen a given in Figure 2 should have a common solution if the required proportionalities given by relations (1) through (3) are satisfied, and the slopes are close to unity, which can be regarded as a reliable criterion of reality of the determined MHS parameters. This is particularly valid if independently obtained viscometric data are utilized [Eq. (1)].⁴ For PtBA in THF, two possible pairs of the MHS constants were found. The common solution of the dependencies in Figure 2(a) has the coordinates $K = 4.1 \times 10^{-3}$, $a = 0.78$. For the same a the slope $d \log X/d \log M$ is unity, while viscometric data are better satisfied by the exponent $a = 0.8$ [cf. Fig. 2(b)] and $K = 3.3 \times 10^{-3}$. Nevertheless, these MHS constants are consistent with the data published earlier for PtBA in other solvents.⁵ The accuracy of determination of the MHS constants by means of SEC, i.e., $\Delta a \sim 2\%$, $\Delta K \sim 24\%$, is in accordance with the usual practice because it may be affected by many factors, such as precision of universal calibration (the best procedure is that employing the same absolute technique of measurement), efficiency of the fractionation system, accuracy of the absolute methods of measurement, and last but not least, by the number of "standards"—homologs of the polymer that are available.

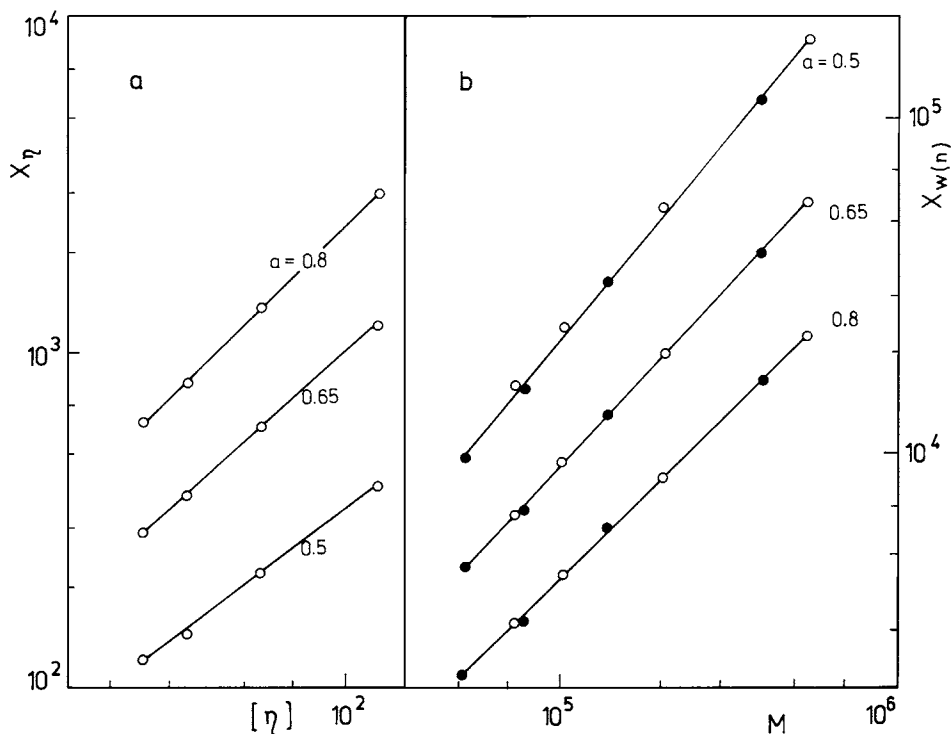


Fig. 1. Dependence of (a) $\log X_n$ on $\log [\eta]$ [Eq. (1)]; (b) $\log X$ on $\log M$ [Eqs. (2) and (3)] for given MHS exponents a ● X_n ; M_n , ○ X_w ; M_w .

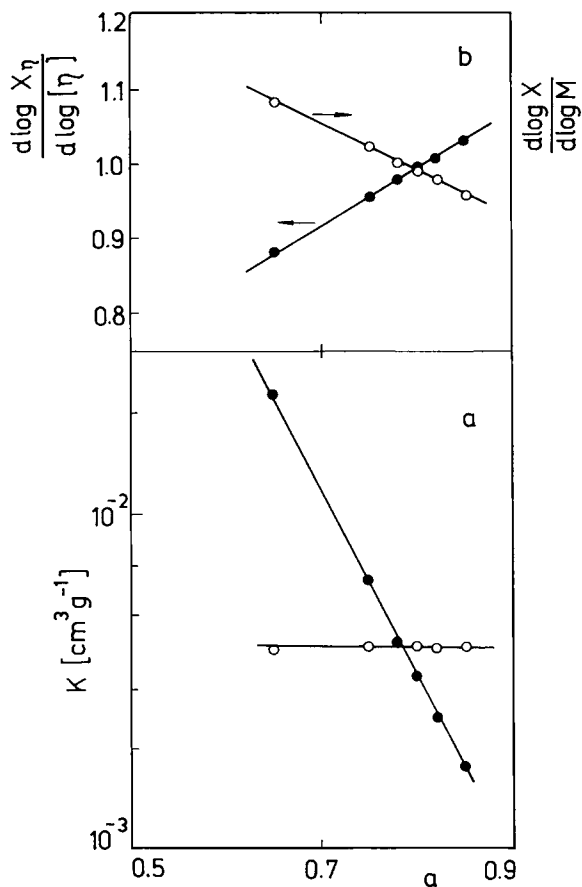


Fig. 2. (a) Dependence of K and (b) of slope values ● in Eq. (1), ○ Eq. (2) and (3) on chosen α .

The authors are deeply indebted to Polymer Standard Service GMBH, D-6500 Mainz (BRD), for providing the PtBA samples, and also thank Dr. L. Lochmann for the help in contacting the supplier.

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Received July 24, 1989
Accepted October 2, 1989