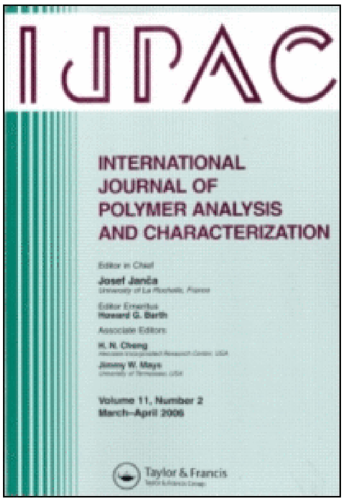

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Examination of the Universality of the Calibration Curve of Size Exclusion Chromatography by Using Polymers Having Complex Macromolecular Architectures

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The validity of the universal calibration curve (UCC) in size exclusion chromatography (SEC) was tested by using polymers having complex macromolecular architectures such as miktoarm stars (μ-stars) $(PS)_2PI$, $(PS)_2PBd$, $(PI)_3PS$, $(PS\text{-}PI)_2(PI\text{-}PS)_2$, (PS)(PI)(PBd), (PS)(PI)(PBd)(P4MeS), H-shaped $(PI)_2PS(PI)_2$, and π-shaped (PS)(PI)PI(PS)(PI), as well as a model linear tetrablock copolymer of the PS-PI-PS-PI type, where PS is polystyrene, PBd polybutadiene, PI polyisoprene, and P4MeS is poly(4-methyl styrene). It was found that the universality of the relation of log(M[η]) vs. peak elution volume (V_e), where M is molecular weight and [η] is intrinsic viscosity, is valid even for these complex molecules. The determination of the molecular weight of a polymer by using the UCC is very sensitive to the molecular and compositional homogeneity of the sample.

Keywords: Universal calibration; Miktoarm stars; SEC

Grubisic et al.[1], based on the Flory–Fox equation[2], expressed the hydrodynamic volume of a polymer in solution as the product of $M\,[\eta]$,

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where M is the molecular weight and $[\eta]$ the intrinsic viscosity of the polymer. They showed that the plot of $\log(M\,[\eta]) = f(V_e)$ can be used as a universal calibration curve, which is independent of polymer species and branching. The universality of this relationship has been examined for various polymeric systems such as linear homopolymers[3], block copolymers[3], symmetric star homopolymers[1], grafted copolymers[4,5], randomly branched homopolymers[6], and natural polymers such as cellulose[10].

Ambler et al.[7] found that low molecular weight poly(n-butyl isocyanate) fractions, as well as highly branched polystyrenes, deviate significantly from a common UCC. However, these polymers exhibited high molecular polydispersity, a key parameter for the determination of the molecular weight of the copolymers with the UCC.

Guixian et al.[8] presented a universal calibration curve made by using polydisperse samples. This was achieved by converting the weight average hydrodynamic volumes of the polydisperse samples to peak hydrodynamic volumes, and correlating them with the elution volume.

Huang et al.[9] found that the UCC was valid for well-defined poly (styrene-b-isoprene) star-block copolymers having up to 32 arms. Timpa[10], by using a chromatographic system equipped with a differential refractive index and a viscometric detector, was able to calculate the $[\eta]$ at each retention time of a polydisperse sample and determine the molecular weight and the polydispersity index (I) of a natural cellulose sample.

Recently, a new class of polymeric materials, the μ-star polymers (miktoarm stars), has been developed[11]. This term is attributed to star polymers that contain a junction point from which chemically different arms emanate. Each of these polymers exhibit high chemical and molecular weight asymmetry, and as a consequence are most appropriate for testing the universality of the UCC.

In this work the validity of the UCC was tested by using a linear tetrablock copolymer and branched block copolymers having complex macromolecular architectures.

EXPERIMENTAL

Narrow molecular weight distribution polystyrene standards were obtained from Pressure Chemical Co., USA, and Toyo Soda Co., USA. Tetrahydrofuran (THF) was purified over Na. The miktoarm stars were synthesized by Hadjichristidis et al.[12–17] using anionic polymerization, high vacuum techniques, and controlled chlorosilane chemistry[18]. With the exception of the H-type $(PI)_2PS(PI)_2$ copolymer, all μ-stars, the π-shaped copolymer, and the linear tetrablock copolymers all exhibited high degrees of molecular and compositional homogeneity.

Size exclusion chromatography (SEC) experiments were carried out at 30°C by using a Waters 600 pump, Waters Model 410 (Waters Corp., Milford, MA, USA) differential refractometer, and a 996 Diode-Array UV detector. In this instrument a high-resolution column setup was used, with 7 columns having a porosity range from 10^2 to 10^6 Å. THF was the carrier solvent at a flow rate of 1 ml/min. Since the amount of the polymer injected influences the peak elution volume, especially for the higher molecular weight samples, all the polymer solutions had the same concentration ($\sim 1 \times 10^{-3}$ g ml^{-1}).

The number average molecular weight (M_n) of the PS homopolymers and the μ-stars were measured using a Jupiter Model 231 Recording Membrane Osmometer (MO) at 35°C. Toluene distilled over CaH_2, was the solvent. The M_n values from the MO were obtained from the corresponding $(\pi/C)^{1/2}$ versus C plot where π is the osmotic pressure and C is the polymer concentration.

Viscometric data were analyzed using the Huggins equation:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c + \cdots \tag{1}$$

and the Kraemer equation

$$ln\,\eta_r/c = [\eta] + k_K[\eta]^2 c + \cdots \tag{2}$$

where η_r, η_{sp}, and $[\eta]$ are the relative, specific, and intrinsic viscosities, respectively, and k_H and k_K are the Huggins and Kraemer constants, respectively. Virtually identical intrinsic viscosities were obtained by the two methods. All the measurements were carried out at 30°C in THF using Cannon-Ubbelohde dilution viscometers with a Schott-Geräte AVS 410 automatic flow timer.

RESULTS AND DISCUSSION

The molecular characteristics of the polystyrene standards given by the two companies and measured by the MO in toluene are presented in Table I. Number average molecular weights measured by the MO were used for all samples, because only apparent weight average molecular weights can be obtained by light scattering for copolymers containing chemically different species. The PS standards have number average molecular weights covering the range from 2.72×10^4 up to 2.39×10^5 and exhibit narrow molecular weight distributions. The molecular characteristics of the linear tetrablock copolymer, the H- and π-shaped copolymers and μ-stars are given in Table II. The samples are shown schematically in Scheme 1.

The H-type copolymer exhibits higher polydispersity index (I) as obtained by SEC (1.15) (Figure 1). However, in order to examine the

TABLE I Molecular Characteristics of the PS Standards

Sample	$M_{\text{peak}} \times 10^{-3}$ [a]	$M_n \times 10^{-3}$ [b]	$M_n \times 10^{-3}$ [c]	I [d]
PS1	28.6	–	27.2	1.03
PS2	–	42.8	43.7	1.03
PS3	78.2	–	74.5	1.02
PS4	–	107	107	1.03
PS5	–	186	177	1.05
PS6	233	–	239	1.03

[a] Peak molecular weights provided by Pressure Chemical Co.
[b] M_n provided by Toyo Soda Co.
[c] by MO, toluene at 37°C.
[d] by SEC, THF at 30°C.

influence of I on the determination of the molecular weights by using the UCC, this sample will be used in this work.

The log[η] versus log M_n plot for the PS standards is shown in Figure 2, and the obtained data by viscometry and SEC are reported in Table III. The viscometric data can be described by the following equation:

$$[\eta] = 1.39 \times 10^{-2} M_w{}^{0.708} (\text{corr. coef.} = 0.996) \tag{3}$$

This equation is close to the one given by Fetters et al.[19] for a large number of PS standards in THF, covering a molecular weight range from 2.04×10^4 to 22×10^6 g mol^{-1}.

The log(M_n [η]) as a function of V_e of the PS standards, the linear tetrablock the H-shaped, the π-shaped, and μ-stars are shown in Figure 3. The line is the UCC and represents the linear regression fit of the data obtained from the PS standards. The UCC can be described by the following equation:

$$\log(M_n[\eta] = 13.4 - 0.214\, V_e \,(\text{corr. coef.} = 0.998) \tag{4}$$

A linear regression fit was chosen for these points, since the molecular weights of the PS standards are in the region in which the relation between the elution volume and the log(M_n) is linear. The viscometric and SEC data for the polymers having complex architectures and the linear tetrablock quaterpolymer are given in Table IV. In the same table, the molecular weights of copolymer samples, calculated from the UCC, and measured by the MO are also given.

In Figure 3 it is obvious that the points of the polymers with the complex architectures are randomly distributed close to the line, and in

TABLE II Molecular Characteristics of the Miktoarm Stars and the Linear Tetrablock Copolymer

Sample	M_n PS × 10^{-3} [a]	M_n PI × 10^{-3} [a]	M_n PBd × 10^{-3} [a]	M_n P4MeS × 10^{-3} [a]	M_{ntot} × 10^{-3} [a]	I [b]
PS-PI-PS-PI	36.1[c], 50.0[f]	52.6[d] 32.5[e],	–	–	103	1.03
$(PS)_2PI$	36.2	42.0	–	–	110	1.04
$(PS)_2PBd$	23.7	–	14.8	–	57.0	1.03
$(PI)_3PS$	59.3	11.7	–	–	92.3	1.02
$(PS\text{-}PI)_2(PI\text{-}PS)_2$	20.0[g] (37.3)[h]	17.9[i] (37.4)[j]	–	–	148	1.03
(PS)(PI)(PBd)#1	20.7	15.6	12.2	–	45.4	1.02
(PS)(PI)(PBd)#2	7.9	8.2	7.7	–	23.8	1.03
$(PI)_2PS(PI)_2$	52.2	22.1	–	–	227	1.15
(PS)(PI)PI(PS)(PI)	109	(3.9) 4.9[k]	–	–	231	1.04
(PS)(PI)(PBd)(P4MeS)	15.9	14.5	16.2	15.4	62.5	1.05

[a] by MO, toluene at 37°C.

[b] by SEC at 30°C.

[c] M_n of the first (PS) block.

[d] M_n of the second (PI) block.

[e] M_n of the last block (PI).

[f] M_n of the third (PS) block.

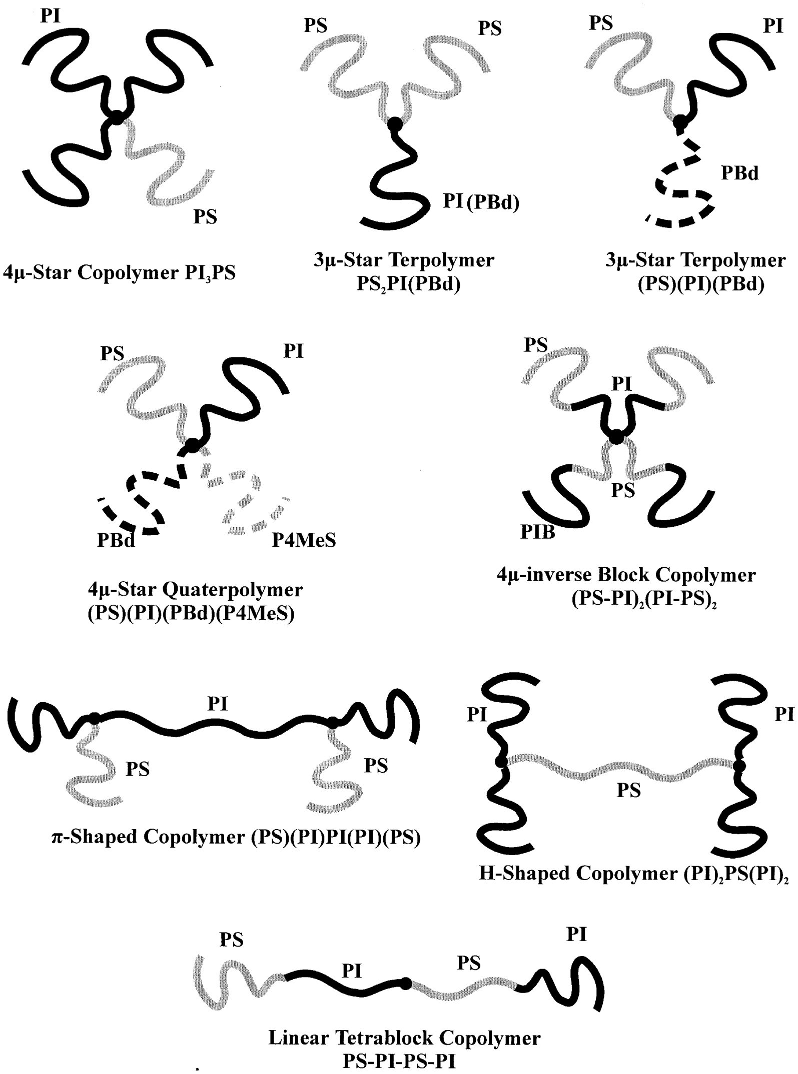
[g] M_n of the PS block of the PS-PI arm.

[h] M_n of the PS-PI arm.

[i] M_n of the PI block of the PI-PS arm.

[j] M_n of the PI-PS arm.

[k] M_n of the PI connector (parenthesis) and PI arm.



4μ-Star Copolymer PI$_3$PS

3μ-Star Terpolymer PS$_2$PI(PBd)

3μ-Star Terpolymer (PS)(PI)(PBd)

4μ-Star Quaterpolymer (PS)(PI)(PBd)(P4MeS)

4μ-inverse Block Copolymer (PS-PI)$_2$(PI-PS)$_2$

π-Shaped Copolymer (PS)(PI)PI(PI)(PS)

H-Shaped Copolymer (PI)$_2$PS(PI)$_2$

Linear Tetrablock Copolymer PS-PI-PS-PI

SCHEME 1

most cases they fall on the top of the UCC. The agreement between the UCC and the points of the copolymers is also supported by the small difference between the molecular weight calculated from the UCC compared to the one obtained by MO, which is in most cases less than 10%. However, there are some points that deviate more than the others,

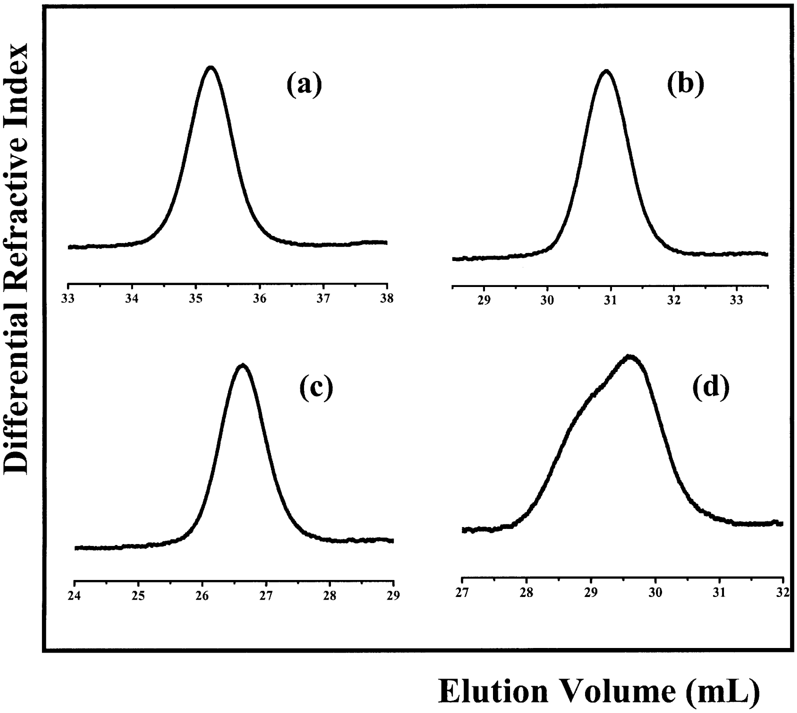


FIGURE 1 SEC chromatograms of the (PS)(PI)(PBd)#2 3-miktoarm star terpolymer (*a*), PS-PI-PS-PI tetrablock copolymer (*b*), π-shaped (PS)(PI)PI (PS)(PI) miktoarm copolymer (*c*), and of the H-shaped $(PS)_2PI(PS)_2$ miktoarm copolymer (*d*).

such as the one corresponding to the H-type $(PI)_2PS(PI)_2$ copolymer and the 4-μ inverse star copolymer of the $(PS\text{-}PI)_2(PI\text{-}PS)_2$ type. The larger deviation is also denoted by the difference between the calculated molecular weights and the one obtained by the MO, which are 23% and 15%, respectively. In the case of the $(PS\text{-}PI)_2(PI\text{-}PS)_2$ copolymer, the deviation could be due to experimental errors coming from SEC (~10%), MO (~5%), and viscometry (~5%). The deviations for these copolymers cannot be attributed to the chemical and the molecular weight asymmetry of the molecules, which is known to be controlled. The polymer that presents the highest molecular weight asymmetry is the π-shaped (PS)(PI)PI(PS)(PI) copolymer due to the large difference between the arms (109×10^3 for the PS arm, 4.9×10^3 for the PI arm, and 3.9×10^3 for the PI connector), and the one with the highest chemical asymmetry is the

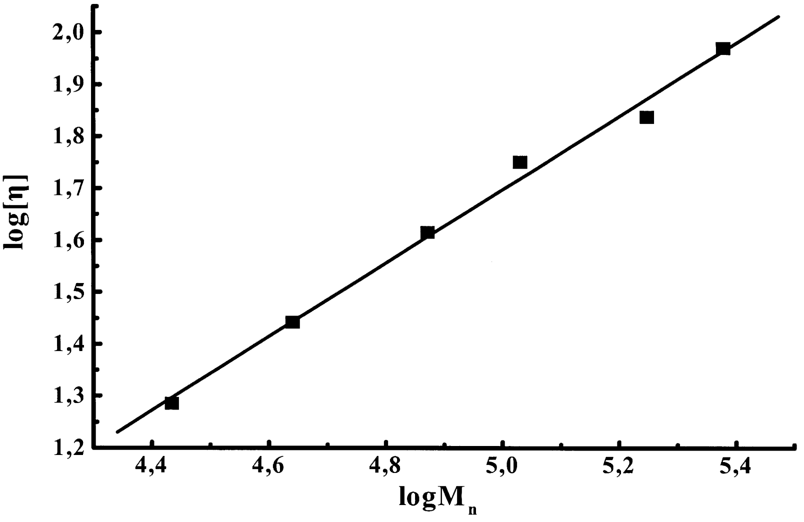


FIGURE 2 $\log[\eta]=f(\log(M_n))$ plot of the PS standards.

4-μ star quaterpolymer of the (PS)(PI)(PBd)(P4MeS) type, due to the four chemically different arms.

In the case of the H-type $(PI)_2PS(PI)_2$ copolymer, the SEC chromatogram presents a large shoulder that increases the polydispersity index and implies a higher molecular weight and compositional heterogeneity. Since V_e is the peak elution volume, the 23% difference of the molecular weights may be due to the lower V_e used, due of the asymmetry of the peak (Figure 1), which would lower the calculated molecular weight. Therefore, the methodology used is accurate only for samples with low molecular and compositional polydispersity.

TABLE III Viscometric and SEC Results of the PS Standards

Sample	$[\eta]$ (mL/g)	k_H	k_k	$\log[\eta]$	$\log(M_n[\eta])$	V_e (mL)
PS1	19.3	0.48	0.06	1.285	5,720	36.09
PS2	27.7	0.39	0.12	1.441	6,083	34.44
PS3	41.2	0.46	0.09	1.614	6,487	32.3
PS4	56.3	0.40	0.12	1.750	6,779	30.91
PS5	68.9	0.41	0.11	1.838	7,086	29.73
PS6	93.3	0.38	0.13	1.969	7,348	28.52

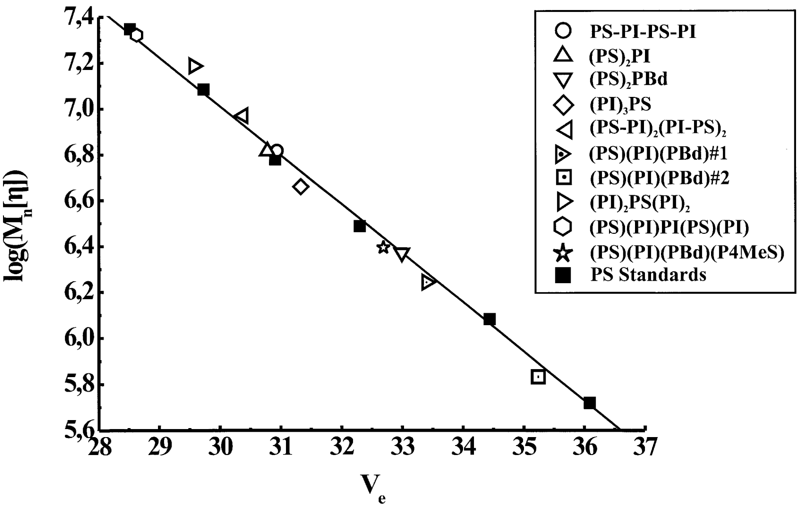


FIGURE 3 $\log(M_n[\eta]) = f(V_e)$ plot of the PS standards along with the miktoarm stars and the linear tetrablock copolymer. The line represents the linear regression fit plot of the PS standards.

CONCLUSIONS

The universal calibration curve of the SEC, which is expressed by the relation $\log(M\ [\eta])$ vs. V_e, is valid for molecules with complex macromolecular architectures that present high chemical and molecular weight asymmetry such as linear tetrablock copolymers μ-stars, H-shaped, and π-shaped copolymers. It has been shown that in the case of polymers with higher polydispersity index, the deviations from the UCC become significant. As a consequence, the molecular and compositional homogeneity of the samples is a very important parameter for the evaluation of the molecular weight of a polymer by using SEC and the UCC method, and maybe this is the reason of the large deviations from the UCC reported in some early works.

TABLE IV Viscometric and SEC Results of the Linear Tetrablock and Miktoarm Stars

Sample	$[\eta]$ (mL/g)	k_H	k_k	$\log(M_n[\eta])$	V_e (mL)	$M_{\mathrm{ntot}} \times 10^{-3}$ [a]	$M_{\mathrm{ncalc}} \times 10^{-3}$ [b]
PS-PI-PS-PI	63.8	0.47	0.06	6,817	30.94	103	94.2
$(PS)_2PI$	59.4	0.47	0.06	6,815	30.78	110	109
$(PS)_2PBd$	41.2	0.46	0.08	6,370	32.99	57.0	53.0
$(PI)_3PS$	49.5	0.47	0.06	6,659	31.33	92.3	100
$(PS\text{-}PI)_2(PI\text{-}PS)_2$	63.1	0.47	0.08	6,970	30.38	148	126
(PS)(PI)(PBd)#1	38.5	0.40	0.11	6,242	33.4	45.4	46.4
(PS)(PI)(PBd)#2	28.6	0.44	0.10	5,832	35.24	23.8	25.2
$(PI)_2PS(PI)_2$	67.8	0.43	0.09	7,187	29.57	227	174
(PS)(PI)PI(PS)(PI)	90.7	0.50	0.06	7,321	28.63	231	207
(PS)(PI)(PBd)(P4MeS)	39.6	0.57	0.03	6,394	32.69	62.5	64.1

[a] by MO, toluene at 37°C.

[b] calculated from V_e, $[\eta]$ and UCC.

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