

This article was downloaded by:

On: 21 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

Dilute Solution Characterization of Statistical Poly(styrene-co-methylmethacrylate) Polymers as Applied to Liquid Chromatography under Limiting Conditions of Adsorption

Florence Sauzedde^a; David Hunkeler^a

^a Laboratory of Polyelectrolytes and Biomacromolecules, Swiss Federal Institute of Technology, Lausanne, Switzerland

To cite this Article Sauzedde, Florence and Hunkeler, David(2005) 'Dilute Solution Characterization of Statistical Poly(styrene-co-methylmethacrylate) Polymers as Applied to Liquid Chromatography under Limiting Conditions of Adsorption', *International Journal of Polymer Analysis and Characterization*, 10: 3, 205 – 224

To link to this Article: DOI: 10.1080/10236660500418013

URL: <http://dx.doi.org/10.1080/10236660500418013>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Dilute Solution Characterization of Statistical Poly(styrene-*co*-methylmethacrylate) Polymers as Applied to Liquid Chromatography under Limiting Conditions of Adsorption

Florence Sauzedde and David Hunkeler

Laboratory of Polyelectrolytes and Biomacromolecules, Swiss Federal Institute of Technology, Lausanne, Switzerland

Abstract: This study evaluates the dilute solution properties of model poly(styrene-*co*-methyl methacrylate) polymers with correlation established between the refractive index increment, second virial coefficient, and the radius of gyration to the molar mass and composition. Specifically, with the aim of studying the elution mechanism of liquid chromatography under limiting conditions of adsorption, two series of statistical copolymers, varying either in molar mass or in composition, have been employed. After having synthesized such models by radical solution polymerization, the experimental copolymer composition was determined by ^1H NMR and was found to be in good agreement with the theoretical composition, calculated with the monomer reactivity ratios. Static light scattering measurements were then performed in various solvents, such as dichloroethane, dimethylformamide, tetrahydrofuran, and toluene. By fitting the apparent molar mass versus reduced dn/dc with a squared equation, the weight-average molar mass of the copolymers and the copolymer heterogeneity were determined in the aforementioned conditions. The second virial coefficient was also examined as a function of copolymer molar mass and composition. Finally, the radius of gyration was evaluated in solvents corresponding to the eluents used for liquid chromatography under limiting conditions of adsorption.

Address correspondence to David Hunkeler, AQUA+TECH Specialities SA, Chemin du Chalet-du-Bac 4, CP 28, CH-1283 La Plaine, Geneva, Switzerland.
E-mail: david.hunkeler@aquaplustech.ch

Keywords: Compositional heterogeneity; Light scattering; Poly(styrene-*co*-methyl methacrylate); Second virial coefficient; Size exclusion chromatography; Specific refractive index increment; Statistical copolymers

INTRODUCTION

Size exclusion chromatography (SEC) is a powerful tool for the determination of the molar mass of macromolecules. Nevertheless, in the case of copolymers, since both molar mass and composition influence the hydrodynamic volume of the solute in solution, the retention volume does not depend only on steric parameters. Chromatography under limiting conditions of adsorption (LC LCA) is a new method that has been developed to overcome this problem and to perform a simultaneous determination of copolymer molar mass and composition as well as their distributions.^[1,2] For the purpose of separately studying molar mass and composition effect on the elution using LC LCA, two series of statistical poly(styrene-*co*-methyl methacrylate) polymers have been employed.

In this study, the preparation of poly(styrene-*co*-methyl methacrylate poly(S/MMA)) copolymers varying either in molar mass or in composition was carried out using radical solution polymerization and is described in detail. Since both series of copolymer were used as models, they required complete and accurate characterization of molar mass and composition. Static light scattering (LS) and nuclear magnetic resonance (NMR) were chosen as absolute methods to determine molar mass and composition, respectively. In order to determine the weight-average molar mass of the macromolecules using LS, the measurements were performed in four solvents: dichloroethane (DCE), dimethylformamide (DMF), tetrahydrofuran (THF), and toluene. The experimental data lead also to further analysis of the physicochemical copolymer properties, such as the determination of the second virial coefficient and the heterogeneity parameter under various conditions. To the authors' knowledge, such a systematic study, using standards varying in both composition and molar mass, has not been performed on poly(S/MMA).

EXPERIMENTAL SECTION

Materials

Unless stated otherwise, the solvents and reagents were used as received. Styrene (S), 99% purity, methyl methacrylate (MMA), 99% purity, α,α' -azobis-isobutyronitrile (AIBN), and 1-butanethiol (BuSH), 97% purity,

were purchased from Fluka (Germany). Tetrahydrofuran (THF) and *n*-hexane, both HPLC grade (SDS, France), were used without further purification. All other solvents of purum grade were used for copolymer synthesis and characterization: toluene, deuterated and protonated DCE, carbon tetrachloride (CCl₄), DMF, and THF were obtained from SDS.

Copolymer Synthesis

Two series of copolymers, varying either in molar mass or in composition, were prepared by radical solution polymerization in toluene at 60°C. The polymerization conditions are given in Table I. The syntheses were performed in a 0.8 L stainless-steel reactor equipped with a coil heating system and agitated with a mechanic stirrer at 200 rpm. Toluene was first degassed with a nitrogen stream for 1 h at 60°C to remove

Table I. Summary of polymerization conditions

Copolymer code	BuSH (mmol/L)	AIBN (mmol/L)	f _S	Conv. (%W)	F _S Th	F _S ^{Exp}
Poly(S/MMA)18	0	0.53	0.46	8.9	0.50	0.50 ± 0.01
Poly(S/MMA)2	0	1.94	0.47	6.5	0.50	0.50 ± 0.02
Poly(S/MMA)3	1.0	2.14	0.48	4.5	0.50	0.52 ± 0.02
Poly(S/MMA)4	2.2	2.20	0.48	4.5	0.50	0.52 ± 0.01
Poly(S/MMA)6	3.5	2.10	0.47	5.4	0.50	0.50 ± 0.03
Poly(S/MMA)8*	14.0	14.40	0.47	13.3	0.50	0.48 ± 0.02
Poly(S/MMA)10	0	2.13	0.90	4.1	0.85	0.84 ± 0.01
Poly(S/MMA)9	0	2.10	0.72	3.5	0.65	0.68 ± 0.02
Poly(S/MMA)20	0	2.66	0.30	5.1	0.39	0.37 ± 0.02
Poly(S/MMA)11	0	2.00	0.28	3.2	0.35	0.32 ± 0.02
Poly(S/MMA)19	0	2.18	0.20	5.7	0.29	0.28 ± 0.01
Poly(S/MMA)16	0	2.18	0.20	6.2	0.28	0.27 ± 0.01
Poly(S/MMA)24	0	2.46	0.14	11.6	0.22	0.22 ± 0.01
Poly(S/MMA)23	0	2.35	0.09	11.5	0.15	0.16 ± 0.01
Poly(S/MMA)12	0	1.90	0.08	5.0	0.15	0.15 ± 0.01
Poly(S/MMA)21	0	2.45	0.06	9.1	0.12	0.12 ± 0.01
Poly(S/MMA)15	0	2.29	0.04	7.4	0.08	0.08 ± 0.01

BuSH: chain transfer agent concentration; AIBN: initiator concentration; f_S: initial molar fraction of styrene; F_STh and F_S^{Exp}: conversion and theoretical and experimental copolymer molar fraction of styrene respectively. All polymerizations were performed at 60°C unless noted by an asterisk, in which case the polymerization was carried out at 70°C.

oxygen. Monomers were then added and the total concentration was 4.2 mol/L. The 400 mL solution was then further degassed for 30 min prior to the introduction of AIBN as initiator dissolved in 1 mL of toluene. Reactions were terminated before overall conversion by adding 5 mg of hydroquinone dissolved in acetone, and monomer conversion was measured by thermogravimetry (Table I).

The initial molar fraction of styrene was varied in order to obtain copolymers with composition ranging from 0.08 to 0.85 molar fraction of styrene with a controlled molar mass of around 200,000 g/mol. The chain transfer agent (butanethiol) was introduced to produce the second series of copolymers having an identical composition of 0.5 molar fraction and various molar masses. All copolymers were then dissolved in acetone and purified twice by precipitation in methanol.

Determination of Copolymer Molar Mass

Static Light Scattering

Copolymer molar mass was measured by static light scattering with a Dawn DSP multi-angle laser photometer, equipped with a HeNe laser operating at 632.8 nm (Wyatt Technologies SA, Santa Barbara, California, USA). Specific refractive index increment (dn/dc) values were measured using an Optilab DSP interferometric refractometer (Wyatt) at a wavelength of 632.8 nm. All solvents and solutions were filtered using 0.22 μm and 0.45 μm pore size Teflon filters, respectively (Bioblock, France). Three reproducible measurements of molar mass and dn/dc were obtained in four different solvents (toluene, THF, DMF, and DCE).

Size Exclusion Chromatography

Pure THF was used as the eluent. A CGX 500 silica column with 10 μm particles and a pore size of 50 nm (Tessek, Praha, Czech Republic) was used as the stationary phase in all experiments. The liquid chromatograph consisted of an L-7100 isocratic pump (Hitachi Instruments, Tokyo, Japan) coupled with a Hitachi L-7400 UV detector and a Rheodyne 7100 injector with an injection loop of 20 μL . An operating wavelength of 260 nm was used for the copolymer and polystyrene (PS) with 235 nm for poly(methyl methacrylate) (PMMA), respectively. Chromatograms were analyzed using a D-7000 HPLC system manager interface and Merck-Hitachi software. The standard separation was carried out at 0.5 mL/min flow rate and a solute concentration of 1.0 mg/mL. All the experiments were performed at a controlled temperature of $25 \pm 0.1^\circ\text{C}$ in a Hitachi L-7300 Column oven.

Table II. ^1H NMR chemical shifts of the poly(S/MMA) copolymers

Peak	Chemical shift (ppm)	Chemical groups	Monomer
A	7.1	C_6H_5-	Styrene
D	2–1.2	$-\text{CH}_2-\text{CH}-$	
C	3.6–2.1	$-\text{O}-\text{CH}_3$	MMA
B	0.3–1.2	$-\text{CH}_3-$	
D	2–1.2	$-\text{CH}-\text{C}-$	

Polystyrene and poly(methyl methacrylate) standards were purchased from American Polymer Standards Corporation (USA), with a molar mass range of 9,000–370,000 g/mol and 6,000–350,000 g/mol, respectively.

Determination of Copolymer Composition

The theoretical composition can be estimated using the instantaneous copolymer composition:

$$F_S^{Th} = \frac{r_S f_S^2 + f_S f_{MMA}}{r_S f_S^2 + 2f_S f_{MMA} + r_{MMA} f_{MMA}^2} \quad (1)$$

where f_S , f_{MMA} are the monomer molar fractions, r_S and r_{MMA} are the reactivity ratios of S and MMA, respectively, and $r_S = 0.52$ and $r_{MMA} = 0.47$ at 60°C .^[3]

Copolymer composition was experimentally determined by ^1H NMR with a Brücker AC 200 Spectrometer (Germany). Copolymers were dissolved in a mixture of deuterated DCE and CCl_4 at a ratio of 1:2. The chemical shifts of P(S/MMA) are shown in Table II. The peak areas, S_A and S_B , corresponding to S and MMA monomer, respectively, were used to calculate the copolymer molar fraction of styrene (F_S) according to:

$$F_S^{Exp} = \frac{S_A/5}{S_A/5 + S_B/3} \quad (2)$$

RESULTS AND DISCUSSION

Radical solution polymerization can produce copolymer models in a simple and reproducible manner. NMR and light scattering can give absolute value of composition and molar mass, respectively, and can also lead to the understanding of copolymer behavior in various solvents, most particularly in those employed in liquid chromatography study.

Composition Determination

Radical solution polymerization provided copolymers possessing both molar mass and composition distributions.^[4] In order to avoid a too broad distribution of chemical composition, the reactions were terminated at monomer conversions between 4 and 12% (Table I). The copolymer composition was determined experimentally by ¹H NMR using the peak area for each monomer (Table II). The NMR spectrum presented in Figure 1 shows the peak broadening of the chemical group, which is commonly observed in the case of polymers.

The copolymer composition depends on the initial monomer mixture composition and the monomer reactivity ratio (Eq. (1)). For the copolymer series varying in composition, the calculated and experimental composition values are compared in Figure 2. Good agreement is found between the theory and experimental data.

Molar Mass

In the case of copolymers, the experimental data provided by light scattering correspond to the apparent values, which are different from the real copolymer molar masses.^[5,6] These apparent molar masses, M_{app} , are related to the real weight-average molar masses, \overline{M}_w , of the copolymer according to:

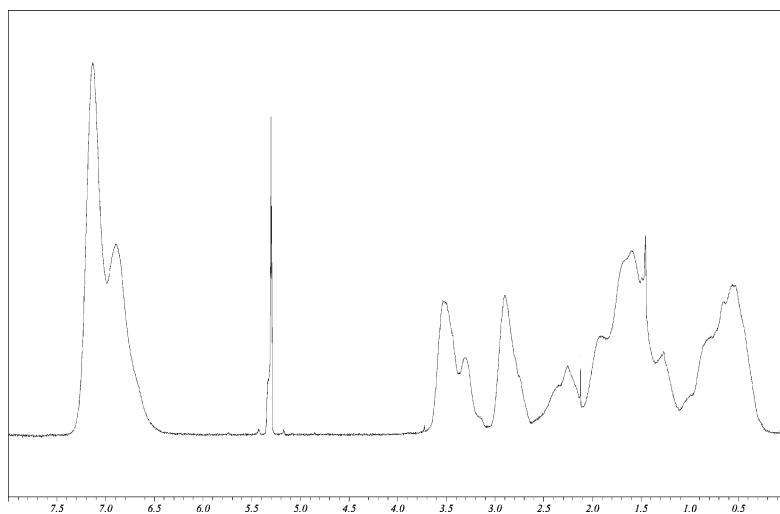
$$M_{app} = \frac{\delta_A \delta_B}{\delta_0^2} \overline{M}_w + \frac{\delta_A (\delta_A - \delta_B)}{\delta_0^2} x_0 \overline{M}_{wA} + \frac{\delta_B (\delta_B - \delta_A)}{\delta_0^2} (1 - x_0) \overline{M}_{wB} \quad (3)$$

where \overline{M}_{wA} and \overline{M}_{wB} are the weight-average molar masses of A and B species, respectively, $\delta = (dn/dc)$, and ∂_A , ∂_B , and ∂_0 are the specific refractive index increments of the species A, B, and copolymer solution, respectively, and x_0 is the weight fraction of A taking into account the composition distribution.

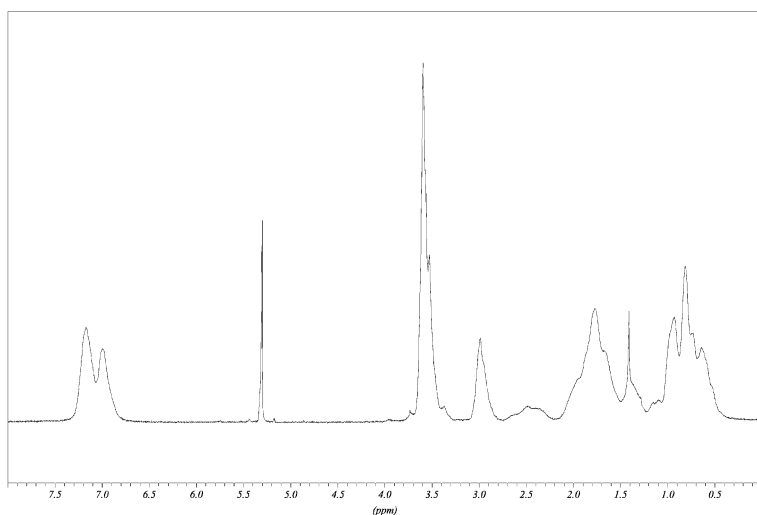
Equation (3) can be transformed into:

$$M_{app} = \overline{M}_w + 2P \left(\frac{\delta_A - \delta_B}{\delta_0} \right) + Q \left(\frac{\delta_A - \delta_B}{\delta_0} \right)^2 \quad (4)$$

where P and Q parameters are constants specific to the copolymer.^[7] P represents the composition variation of the copolymer depending on molar mass and Q is the composition variation of all macromolecules.^[7] When P and Q reach zero, the copolymer is homogeneous in composition. Since Q/\overline{M}_w is equivalent to the variance, it describes copolymer heterogeneity.^[8]



(a)



(b)

Figure 1. NMR spectra for two different copolymers with various molar fractions of styrene: (a) poly(S/MMA)18 ($f_s = 0.50$); (b) poly(S/MMA)24 ($f_s = 0.22$).

Three values of M_{app} and ∂ are required to solve Equation (4).^[6] The apparent molar mass and dn/dc values were measured under four different conditions, i.e., in four different solvents, to achieve reliable extrapolation of the parabolic equation.^[7] The solvents were chosen in

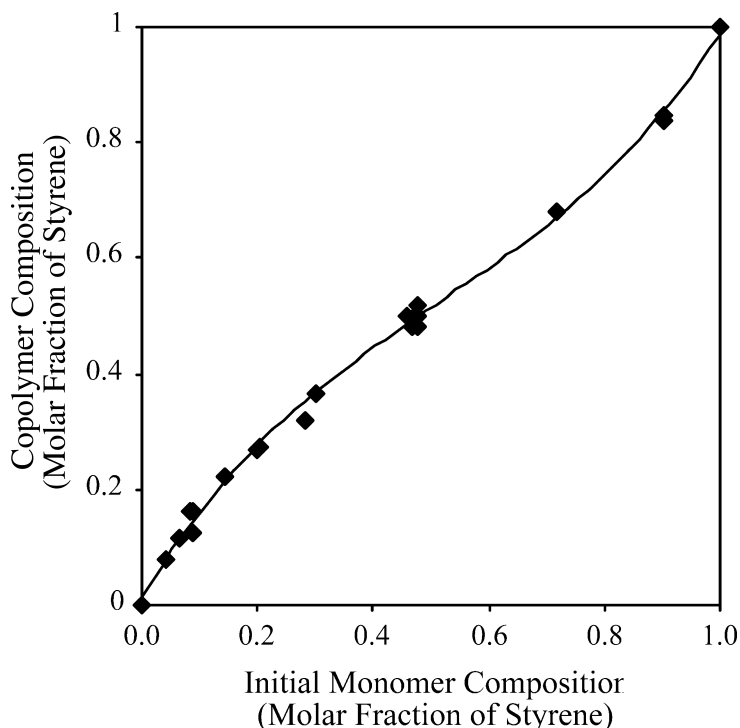


Figure 2. A comparison of theoretical (—) and experimental (◆) copolymer compositions as a function of feed composition.

order to satisfy a difference between dn/dc of the homopolymers above 0.06.^[7] The refractive index increment is molar mass independent in the studied range, between 15,000 and 250,000 g/mol. Although it depends strongly on copolymer composition, the refractive index increment should be measured in each solvent for each copolymer. The measured dn/dc corresponds to an average value in the case of a heterogeneous copolymer.^[7]

Experimentally, the copolymer refractive index increment was determined first and was found to be proportional to the copolymer composition as could be theoretically expected taking into account the additivity of the refractive index (Figure 3). Since the linear equations gave good regression coefficients, the dn/dc values confirm the copolymer composition determined by NMR. Moreover, the extrapolated values at 0 or 1 molar fraction of styrene are in good agreement with dn/dc of poly(MMA) and poly(S), respectively, given by other authors in Table III.^[9] Additionally, this plot permits the determination of dn/dc

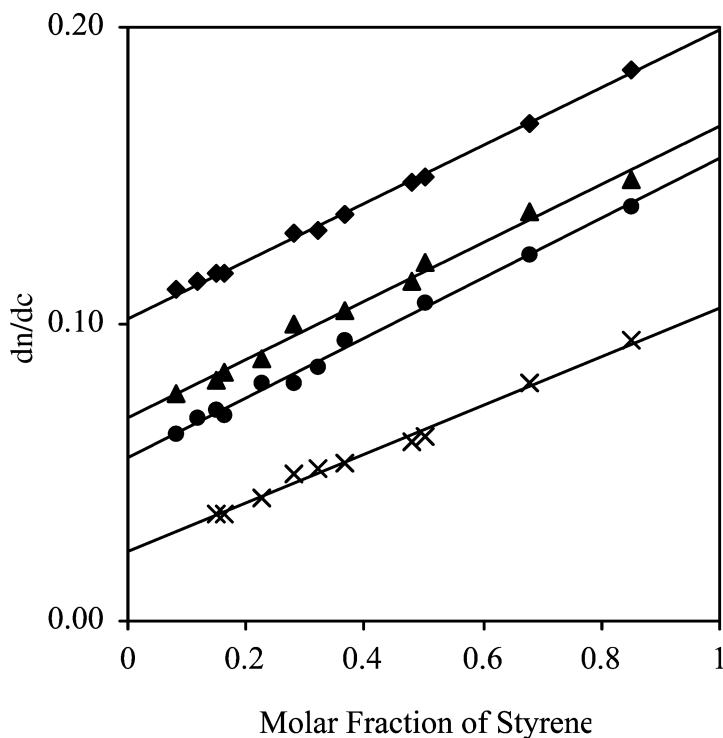


Figure 3. Specific refractive index increment (dn/dc) as a function of the copolymer composition (f_s) in various solvents: ● DCE, $dn/dc = 0.1002 f_s + 0.0555$, $R^2 = 0.993$; ▲ DMF, $dn/dc = 0.0983 f_s + 0.0684$, $R^2 = 0.983$; ◆ THF, $dn/dc = 0.0967 f_s + 0.1022$, $R^2 = 0.998$; × Toluene, $dn/dc = 0.0824 f_s + 0.0232$, $R^2 = 0.991$.

Table III. Specific refractive index increments

Polymer	dn/dc (This work) ^a	dn/dc (Literature) ^b	Solvent, conditions
Poly(MMA)	0.055	0.050	DCE, 25°C
	0.068	0.0630	DMF, 25°C
	0.097	0.0902	THF, 25°C
	0.023	0.003*	Toluene, 30°C
Poly(S)	0.156	0.158	DCE, 30°C
	0.167	0.165	DMF, 20°C
	0.199	0.193	THF, 25°C
	0.106	0.110	Toluene, 25°C

^aExperimental dn/dc values from this work measured at 633 nm, 40°C.

^b dn/dc values from different authors, measured at 25–30°C and at a wavelength of 633 nm excepted when noted by an asterisk, where wavelength is 546 nm.^[11]

dc of poly(MMA) in toluene. Indeed, this value is so close to zero that it is within the error domain of the apparatus. As a consequence, it is difficult to measure it using the homopolymers.

Based on the apparent molar mass values obtained in various solvents, the determination of the real average molar mass of the copolymers is performed by extrapolating to zero the parabolic fitting curve of molar mass versus the reduced refractive index increment, Λ , corresponding to the following ratio:

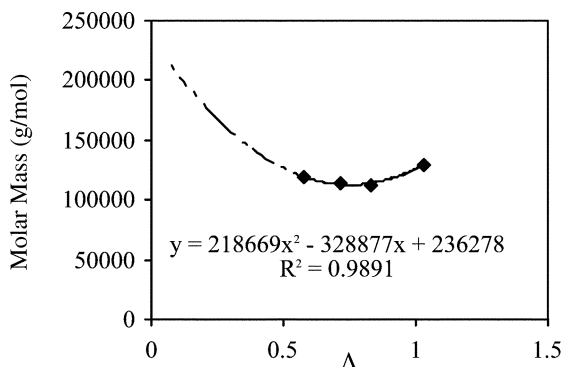
$$\Lambda = \frac{\partial_A - \partial_B}{\partial_0} \quad (5)$$

The extrapolation of the parabolic curve is exemplified in Figure 4 for three different copolymers, poly(S/MMA)9, poly(S/MMA)2, and poly(S/MMA)24, having decreasing styrene content of 0.85, 0.50, and 0.22, respectively. For the copolymers, the regressed curves have a correlation coefficient between 0.96 and 1, permitting the calculation of accurate values of molar mass and the P, Q parameters,^[11] which are given in Tables IV and V. From the experimental Q/M_w values, it seems that the dispersity in chemical composition is reasonably low for both copolymer series. Since the difference between P/M_w and Q/M_w is weak, there is no composition drift according to molar mass. Nevertheless, different behaviors in solution, for example, between poly(S/MMA)10 and poly(S/MMA)23, can be expected, the latter ones presenting a very narrow chemical composition distribution. The homogeneity of the copolymers is otherwise illustrated by the shape of the parabolic curve, which tends to a linear dependence when Q tends to zero as shown in Figure 4 and Tables IV and V.

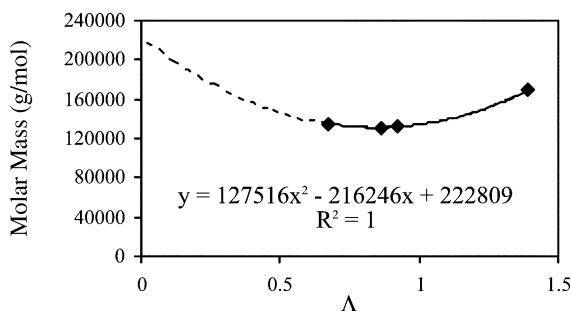
Weight-average molar masses were also measured by SEC (M_w^{SEC}) performed in pure THF, using a calibration curve constructed using polystyrene standards. The relative difference (ΔM_w) between both methods is given by the ratio

$$\Delta M_w = \frac{M_w^{LS} - M_w^{SEC}}{M_w^{SEC}} \quad (6)$$

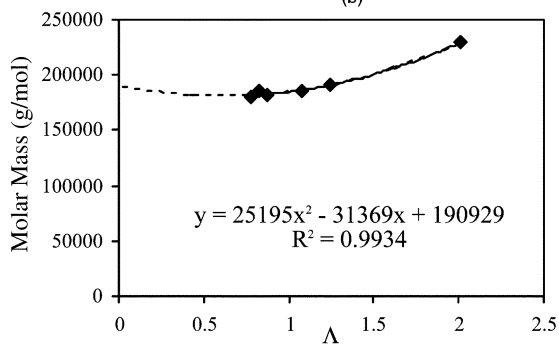
Tables IV and V reveal the molar mass difference between light scattering and SEC averages. The influence of the multivariate distribution on elution behavior of copolymers could be an explanation for the disagreement between the chromatographic and photometric data. Furthermore, the polydispersity index (PI) measured by SEC is approximately 1.5. This is an acceptable value for copolymers used as broad liquid chromatography standards.



(a)



(b)



(c)

Figure 4. Molar mass versus Λ , for three different copolymers having increasing MMA content: (a) poly(S/MMA)9; (b) poly(S/MMA)2; (c) poly(S/MMA)24.

Second Virial Coefficient in Various Solvents

Light scattering measurements also provide other information concerning copolymer and solvent interactions. According to Flory,^[10] the

Table IV. Molar mass characterization of copolymers varying in molar mass

Copolymer code	M_W^{LS} g/mol	P/ M_W	Q/ M_W	M_W^{SEC} g/mol	PI	ΔM_W
Poly(S/MMA)18	237,000	0.16	0.27	261,000	1.36	-0.15
Poly(S/MMA)2	223,000	0.48	0.57	201,100	1.56	0.09
Poly(S/MMA)3	136,000	0.65	0.72	135,600	1.61	0.01
Poly(S/MMA)4	69,800	0.32	0.27	75,400	1.59	-0.07
Poly(S/MMA)6	46,700	0.34	0.43	57,900	1.55	-0.19
Poly(S/MMA)8	25,000	0.65	0.76	18,600	1.28	0.35
Average values		0.4	0.5			0.15

Weight-average molar mass of poly(S/MMA) copolymers determined by LS (M_W^{LS}) as well as relative values of P and Q and by SEC (M_W^{SEC}), the polydispersity index (PI), and the relative difference between both methods (ΔM_W).

second virial coefficient can be related to the intrinsic viscosity as follows:

$$\frac{A_2 \times M_w}{[\eta]} = C_1 \quad (7)$$

where M is the molar mass, $[\eta]$ is the intrinsic viscosity, and C_1 is a constant.

Table V. Molar mass characterization of copolymers varying in composition.

Copolymer code	M_W^{LS} g/mol	P/ M_W	Q/ M_W	M_W^{SEC} g/mol	PI	ΔM_W
Poly(S/MMA)10	244,000	0.45	0.94	210,000	1.50	0.11
Poly(S/MMA)9	236,000	0.58	0.75	200,900	1.52	0.17
Poly(S/MMA)20	161,500	0.06	0.13	219,500	1.40	0.26
Poly(S/MMA)11	221,000	0.36	0.39	258,800	1.61	0.15
Poly(S/MMA)19	261,000	0.29	0.25	197,200	1.44	0.32
Poly(S/MMA)24	192,000	0.08	0.13	214,500	1.40	-0.10
Poly(S/MMA)23	237,000	0.03	0.02	254,000	1.38	-0.07
Poly(S/MMA)12	201,000	0.17	0.27	296,000	1.60	-0.32
Poly(S/MMA)21	219,000	0.31	0.28	230,000	1.43	-0.05
Poly(S/MMA)15	262,000	0.30	0.44	258,000	1.49	-0.02
Average value*	220,000	0.25	0.35	230,000	1.48	0.15
	$\pm 30,000$			$\pm 32,000$	± 0.08	

Weight-average molar mass of poly(S/MMA) copolymers determined by LS (M_W^{LS}) as well as relative values of P and Q and by SEC (M_W^{SEC}), the polydispersity index (PI), and the relative difference between both methods (ΔM_W).

The intrinsic viscosity can be calculated from the Mark-Houwink-Sakurada equation:

$$[\eta] = K \times \overline{M}_w^a \quad (8)$$

where K and a are the coefficients. As a result, A_2 can be related to the molar mass:

$$A_2 = C_2 \times M^{a-1} = C_1 \times M^b \quad (9)$$

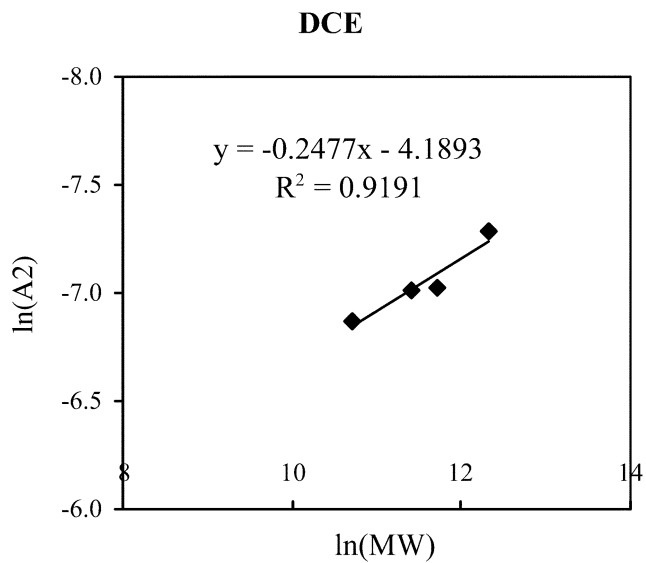
Plots of $\ln A_2$ versus $\ln M_w$ obtained in various solvents are presented in Figures 5–8. A linear relation was observed as expected. The experimental Mark-Houwink-Sakurada exponent can be calculated from the slope of the mentioned linear dependence for statistical poly(S/MMA) copolymers having a constant composition of 0.5 ± 0.02 molar fraction of styrene. The experimental values are in a good agreement with the literature values as presented in Table VI.^[11]

The influence of the composition was also analyzed with the second copolymer series having constant molar mass of $250,000 \text{ g/mol} \pm 50000$. Plots of $\ln A_2$ versus composition are presented in Figures 5–8 and show that the second virial coefficient can be considered as essentially constant over the entire composition range.

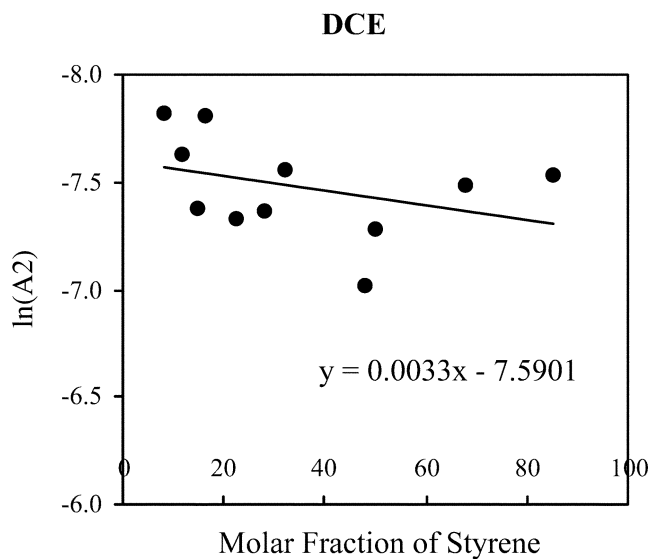
Upon examination of Figures 5–8 it is clear that there is a slight, though obvious trend of decreasing second virial coefficients with the styrene content of the copolymer. This is particularly true over the 0–20 mol% range. While it is certainly not unusual that A_2 varies with composition, we should note that both THF and toluene are poorer solvents for PS than for PMMA, as has been evidenced by recent LC LCA experiments.^[1,2] The LC LCA experiments of Sauzedde and Hunkeler^[2] also reveal the strongest dependence of solvency over the same range of styrene contents. Therefore, the virial coefficient data, while somewhat noisy, seem to reflect the general solution behavior of such copolymers.

RADIUS OF GYRATION IN LC LCA ELUENT

In order to simulate copolymer behavior in the eluent used for LC LCA, average R_g values have been calculated for one copolymer solution, in a THF/*n*-hexane solvent mixture varying in composition. The plot of R_g versus THF content is presented in Figure 9. A small addition of *n*-hexane (0.8 volume fraction of THF) has no influence on the radius of gyration. This implies that the macromolecules would present the same hydrodynamic volume in this mixture as in pure THF. In the investigation of LC LCA, a shift of retention volume is first observed using

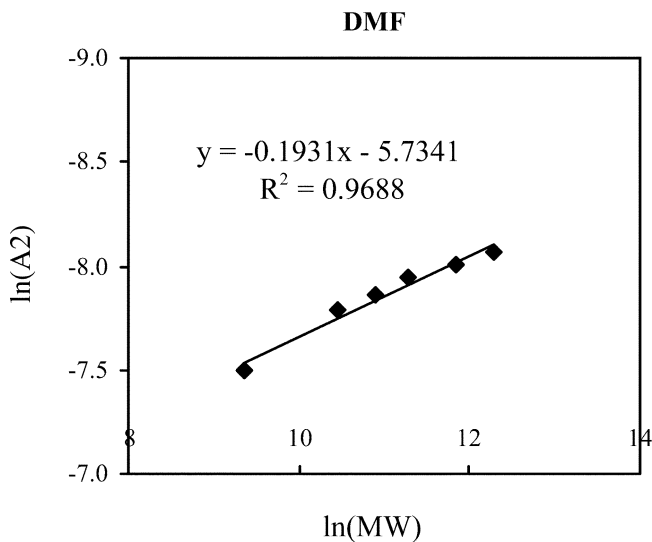


(a)

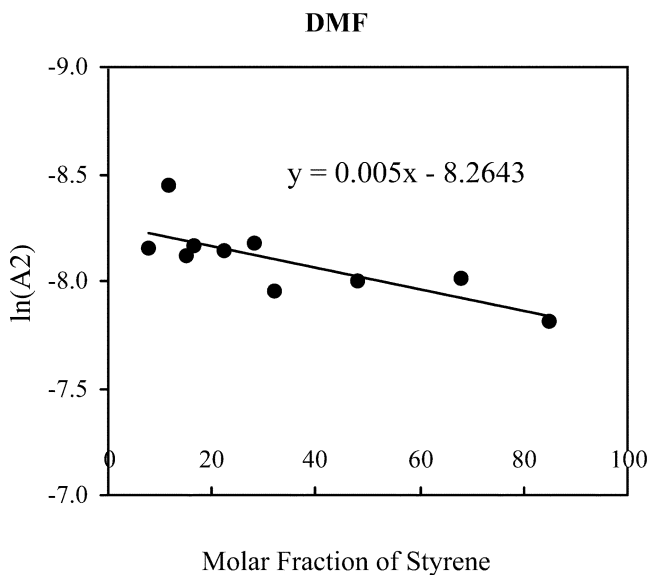


(b)

Figure 5. (a) $\ln A_2$ versus $\ln M_w$ and (b) $\ln A_2$ versus copolymer composition in DCE.

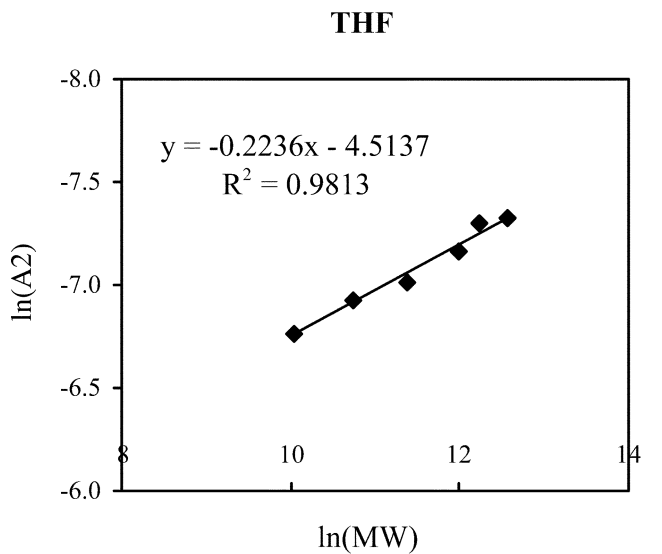


(a)

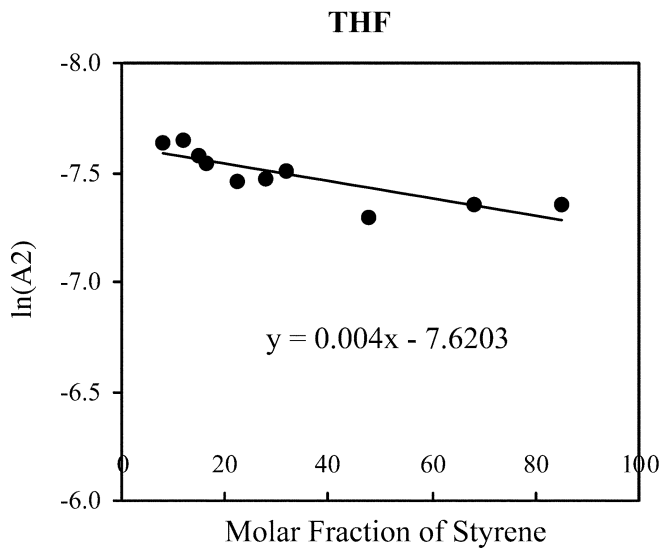


(b)

Figure 6. (a) $\ln A_2$ versus $\ln M_w$ and (b) $\ln A_2$ versus copolymer composition in DMF.

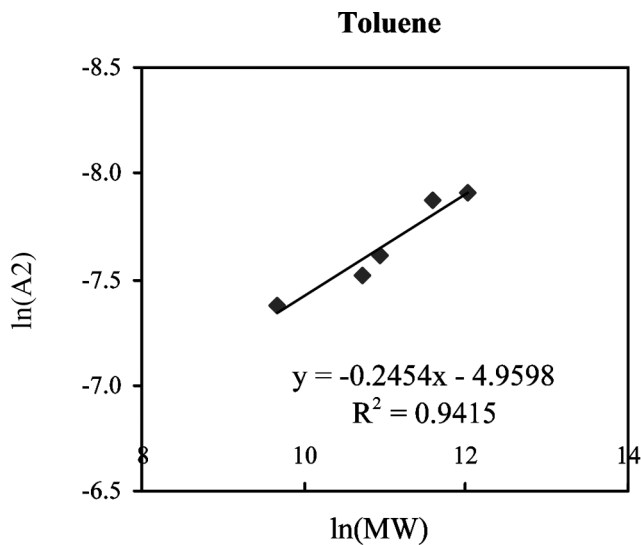


(a)

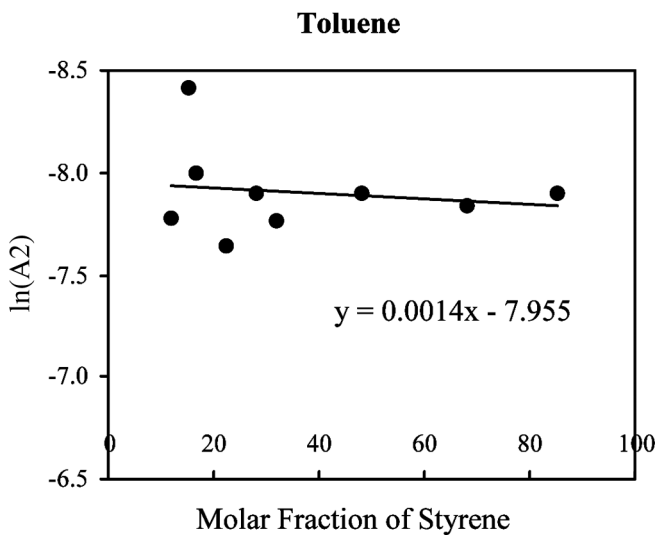


(b)

Figure 7. (a) ln A₂ versus ln M_w and (b) ln A₂ versus copolymer composition in THF.



(a)



(b)

Figure 8. (a) $\ln A_2$ versus $\ln M_w$ and (b) $\ln A_2$ versus copolymer composition in toluene.

Table VI. Mark-Houwink-Sakurada exponents

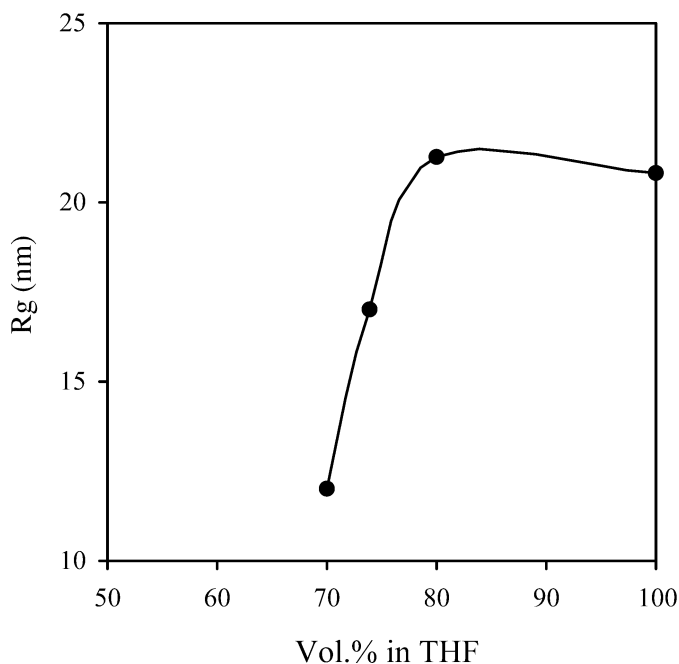
M-H-S exponent (This work) ^a	M-H-S exponent (Literature) ^b	Solvent
0.75	0.77 poly(MMA) 0.69 poly(S)	DCE
0.81	0.603 poly(S)	DMF
0.78	0.72 poly(MMA) 0.72 poly(S)	THF
0.75	0.72 ± 0.01 poly(MMA) 0.75 ± 0.03 poly(S)	Toluene ^c

^aMark-Houwink-Sakurada experimental exponents of statistical poly(S/MMA) copolymer having a styrene molar fraction of 0.48 measured by LS at 25°C.

^bLiterature values of Mark-Houwink-Sakurada experimental exponents measured at 25°C taken from Lechner et al.^[11]

^cIn toluene, the value corresponds to an average between several values from different studies as compiled in Lechner et al.^[11]

an 80/20 THF/*n*-hexane eluent compared to pure THF. This shift can be attributed to the modification of interaction between the solute and the stationary phase with the introduction of *n*-hexane. With decreasing

**Figure 9.** R_g measured in various solvent mixtures of *n*-hexane/THF.

THF (below 0.80), the radius of gyration dramatically decreases. This effect can take place in the chromatographic column in addition to the previous effect. Molar volume of the solute and the interaction between the stationary and mobile phase are both modified. However, it was not possible to obtain interpretable data at a solvent composition of 0.66 volume fraction of THF due to the formation of aggregates. In the presence of *n*-hexane, macromolecular coil shrinkage and the modification of the interactions between both phases influence the elution, which becomes independent of copolymer composition.

CONCLUSIONS

Both NMR and light scattering measurements have permitted the determination of the molar mass and composition of copolymers, without any assumptions. Moreover, the methods employed reveal that the copolymers do not present large distributions in molar mass and composition and can reasonably be used as standards. In the case of the solvent employed in the SEC study, such as THF and a mixture of THF and *n*-hexane, the experimental radius of gyration analysis corroborates liquid chromatographic observations.^[2]

REFERENCES

- [1] Bartkowiak, A. and D. Hunkeler. (2000). Liquid chromatography under limiting conditions of solubility. *Int. J. Polym. Anal. Charact.* **5**, 475–489.
- [2] Sauzedde, F. and D. Hunkeler. (2001). Determination of the composition of statistical copolymers by liquid chromatography under limiting conditions of adsorption. *Int. J. Polym. Anal. Charact.* **6**, 295–314.
- [3] Madruga, E. L., J. San Roman, and M. A. J. Del Puerto. (1979). Preparation of poly(tert-butyl acrylate-g-styrene) as precursors. *Macromol. Sci. Chem.* **A 13**, 1015–1115.
- [4] Stockmayer, W. H. J. (1945). Distribution of chain lengths and compositions in copolymers. *Chem. Phys.* **13**, 199–207.
- [5] Bushuk, W. and H. Benoit. (1958). Hydrodynamic properties of model 3-miktoarm star copolymers. *Can. J. Chem.* **36**, 1616–1626.
- [6] Leng, M. and H. Benoit. (1962). Diffusion de la lumière par les solutions de copolymers. *J. Poly. Sci.* **57**, 263–273.
- [7] Spatorico, A. L. (1974). Evaluation of the light-scattering technique for determining compositional heterogeneity in copolymers. *J. Appl. Polym. Sci.* **18**, 1793–1804.
- [8] Kratochvil, P. (1972). *Light Scattering from Polymer Solutions*. London: Academic Press.

- [9] Huglin, M. B. (1989). *Polymer Handbook*. Indianapolis, IN: Wiley Interscience.
- [10] Flory, P. J. (1953). *Principles of Polymer Chemistry*. Ithaca, NY: Cornell University Press.
- [11] Lechner, M. D., L. Nordameier, and D. G. Steinmeier. (2003). In *Polymer Handbook*, 4th Edition, eds. J. Brandup, E. H. Immergut, E. A. Grulke, and D. Bloch. Indianapolis, IN: Wiley Interscience.