

A correlation of the limiting viscosity number, molecular mass and composition of statistical linear styrene–methyl methacrylate copolymers

Zvonimir Matusinović, Marko Rogošić *, Helena Jasna Mencer

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, HR-10000 Zagreb, Croatia

Received 17 March 2005; accepted 13 May 2005

Available online 31 August 2005

Abstract

Statistical copolymers of styrene and methyl methacrylate of different compositions were synthesized by the radical solution copolymerization in a batch isothermal reactor. Copolymers were characterized by the size exclusion chromatography (SEC), elemental analysis and dilute solution viscometry. Experimental limiting viscosity numbers were described by the Mark–Houwink–Kuhn–Sakurada correlation as the function of the molar mass and by the Mendelson correlation as the function of both the molar mass and copolymer composition. A new correlation of the intrinsic viscosity number, molar mass and composition was developed, based on semiempirical considerations. The correlation takes into consideration all the effects which affect the dimensions of random linear copolymer coils in solvents. The new equation was found to be superior to the Mendelson's one in correlating the experimentally obtained intrinsic viscosities.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Statistical copolymers of styrene and methyl methacrylate; Intrinsic viscosity (limiting viscosity number); Molecular mass; Copolymer composition; Dilute solution viscometry

1. Introduction

The limiting viscosity number, $[\eta]$, is a viscosity parameter related to infinitely diluted polymer solutions. In the absence of strong specific polymer interactions, which may cause self-association of polymer molecules, $[\eta]$ would in principle reflect solely polymer–solvent interactions. In homopolymer solutions, $[\eta]$ depends on the type of polymer and solvent, temperature, molecular mass and polydispersity of a dissolved polymer.

The limiting viscosity number (intrinsic viscosity) of a copolymer will depend, besides above mentioned factors, on the average chemical composition, chemical composition distribution, sequence distribution etc. The development of a suitable correlation of the limiting viscosity number, molecular mass and copolymer composition would decrease the experimental effort needed for the determination of Mark–Houwink–Kuhn–Sakurada parameters in copolymer solutions. The correlation should take into consideration the majority of effects which could affect the limiting viscosity number of copolymer solutions. At the same time it should be relatively simple and related to other correlations found in literature in order to achieve a rather wide

* Corresponding author. Tel.: +385 1 4597 299; fax: +385 1 4597 250.

E-mail address: mrogosic@fkit.hr (M. Rogošić).

applicability. The correlation might find its application in the field of size exclusion chromatography (universal calibration [1] for copolymers). Moreover, it might be used for the estimation of absolute viscosity of copolymer additive solutions (common lubricants, for example [2,3]), etc.

2. Theoretical background

The intrinsic viscosity vs. molecular mass correlation is most commonly [4] described by the Mark–Houwink–Kuhn–Sakurada (MHKS) equation

$$[\eta] = KM^a \quad (1)$$

where K and a are empirical parameters, dependent on the polymer–solvent pair and temperature. The exponent a takes values between 0.5 and 0.8 for flexible chain polymers. Higher values correspond to the thermodynamically better solvents. One may say that parameter a , in a particular manner, quantifies the solvent quality. In principle, MHKS-correlation can be applied in copolymer solutions, too. However, the correlation parameters will depend on the chemical composition, chemical composition distribution, sequence distribution, etc.

Mendelson [5] set a simple empirical correlation of the intrinsic viscosity, molecular mass and chemical composition of copolymers, similar to the MHKS-equation. Mendelson identified the three effects that determine the intrinsic viscosity of a copolymer: the size difference of comonomer units, segment–segment interactions and copolymer segments–solvent interactions (thermodynamical quality of solvent changes with the change in copolymer composition). Mendelson considered the net effect of the last two contributions to be practically constant in certain and relatively wide range of copolymer composition. Therefore, he suggested the intrinsic viscosity of copolymer to be dependent only on the number of carbon atoms in the main chain (backbone) of copolymer macromolecule, Z

$$[\eta] = JZ^\beta \quad (2)$$

The number of carbon atoms in the vinyl chain backbone is

$$Z = 2\bar{M}_w \sum \frac{w_i}{M_{0i}} \quad (3)$$

The final form of correlation is given by

$$[\eta] = 2^\beta J \bar{M}_w^\beta \left(\sum \frac{w_i}{M_{0i}} \right)^\beta \quad (4)$$

The effect of size difference of comonomer units is taken into account by molecular masses of comonomer units, M_{0i} ; w_i is the mass fraction of i th comonomer unit and \bar{M}_w is the mass-average molecular mass of copoly-

mer. Mendelson's correlation may be formally identified with the MHKS-correlation: parameters J and β correspond to K and a -parameters, respectively.

One may imagine the main objection to Mendelson's correlation to be its applicability to the limited range of copolymer composition. The correlation, that would successfully describe the intrinsic viscosity for the entire copolymer composition range, should take explicitly into consideration the other two effects that influence the intrinsic viscosity: segment–segment interactions and copolymer segments–solvent interactions.

To include those two effects in the correlation, one has to consider how they affect the shape and the dimensions of polymer molecules in the solution, i.e., the equilibrium conformation of copolymer coils. An isolated homopolymer coil in solution will take the conformation governed by the polymer–solvent interactions. Polymer coils will expand in the thermodynamically good solvent, tending to increase the number of energetically favorable segment–solvent contacts. The tendency for expansion will be balanced by decreasing the entropy of the system as a result of polymer coil stretching. In addition, heterogeneous segment–segment contacts occur in a copolymer coil; these are usually energetically unfavorable (repulsive interactions). The number of such contacts may be minimized only by the further expansion of copolymer coils. The extent of expansion will increase as the number of unfavorable contacts is increased, so the maximum of expansion is expected at some intermediate copolymer composition.

The picture is not so clear for diblock-copolymers [6]. Some authors believe that the intermolecular phase separation takes place [7–9] in diblock-copolymer coils; others suppose that copolymer blocks interpenetrate, but the corresponding conformations are expanded when compared to the conformations of homopolymer molecules under similar conditions [10,11]. Some authors suggest the skin–core morphology as a physical picture of the macromolecule [12]. However, it seems that the block copolymer conformation is determined mainly by polymer–solvent interactions; the influence of repulsive interactions may be considered negligible [13–17]. Experiments confirm that block copolymer molecules are characterized by smaller dimensions in solution in comparison to statistical copolymers, regardless of the type of imaginary conformation [6,18]. This means that the number of energetically unfavorable heterogeneous segment–segment contacts will be greater for statistical copolymers than for block copolymers.

3. Development of a new correlation

By analyzing the above mentioned considerations, one may construct a procedure for deriving the desired empirical correlation of intrinsic viscosity, composition

and molecular mass of copolymers. Firstly, an adequate correlation for segregated block copolymers may be derived which primarily describes polymer–solvent interactions. Secondly, the obtained correlation may be modified for statistical copolymers by an expression that accounts for heterogeneous segment–segment interactions.

The solution for the first step is already found in the literature: Dondos and coworkers [19] have suggested the following expression for the limiting viscosity number of a segregated block copolymer in a θ -solvent:

$$[\eta]_{\theta} = \left\{ w_1 [\eta]_{\theta 1}^{2/3} + w_2 [\eta]_{\theta 2}^{2/3} \right\}^{3/2} \quad (5)$$

This is, in fact, the mixing rule for the limiting viscosity number in the θ -state, $[\eta]_{\theta}$. A mixing rule for the viscometric coefficient of expansion, α_{η}^3 , was introduced, too, to define the departure from the θ -state

$$\alpha_{\eta}^3 = w_1 \alpha_{\eta 1}^3 + w_2 \alpha_{\eta 2}^3 \quad (6)$$

The limiting viscosity number in good solvents is given by

$$[\eta] = \alpha_{\eta}^3 [\eta]_{\theta} \quad (7)$$

Hence, by combining Eqs. (5)–(7), one comes to the expression that describes the limiting viscosity of segregated block copolymers

$$[\eta] = \left(w_1 \alpha_{\eta 1}^3 + w_2 \alpha_{\eta 2}^3 \right) \left(w_1 [\eta]_{\theta 1}^{2/3} + w_2 [\eta]_{\theta 2}^{2/3} \right)^{3/2} \quad (8)$$

It may be worthwhile to replace the viscometric coefficient of expansion with a parameter that is abundant in literature. In the first approximation, one may accept the literature suggestion [20] that $[\eta]_{\theta}$ for linear flexible polymers is not a function of the solvent and temperature but only of the molecular mass. Thus, one may use the expression

$$[\eta]_{\theta} = K_{\theta} M^{0.5} \quad (9)$$

where K_{θ} is a constant for the polymer under consideration.

By combining Eqs. (8), (7), (9) and (1), the correlation for the limiting viscosity number of segregated block copolymers is obtained

$$[\eta]_{\theta} = \left(w_1 \frac{K_1 M^{a_1}}{K_{\theta 1}} + w_2 \frac{K_2 M^{a_2}}{K_{\theta 2}} \right) \left(w_1 K_{\theta 1}^{2/3} + w_2 K_{\theta 2}^{2/3} \right)^{3/2} \quad (10)$$

Hence, by knowing the constant K_{θ} and the MHKS-parameters K and a for corresponding homopolymers, it is now possible to evaluate the limiting viscosity number of block copolymers. The above mentioned constants are easily available for many systems, using the appropriate compiled tables, such as [21]. In principle, empirical MHKS-parameters depend on the solvent and temperature. However, they may vary with respect

to the molecular mass range and the method used for the molecular mass determination, too.

The expression that approximately describes the expansion of copolymer coils as a consequence of the heterogeneous segment interaction (the second step in the development of correlation), could be deduced by expanding Utracki–Simha's [22] expansion of Stockmayer–Fixman's [23] semiempirical equation

$$\frac{[\eta]}{M^{1/2}} = \Phi_0 (A^3 + 0.51 B M^{1/2}) \quad (11)$$

to the block and statistical copolymer case, respectively. Φ_0 is Flory's viscosity function for unperturbed chains. Short-range and long-range interaction parameters, A and B , respectively, are represented by the following equations:

$$A^2 M_0 = \sum_i x_i a_i^2 \quad (12)$$

$$B M_0^2 = \sum_i \sum_j \beta_{ij} x_i x_j \quad (13)$$

where M_0 stands for the molecular mass of polymer chain repetitive unit (one C–C bond in the chain backbone). The corresponding mixing rule is given by

$$M_0 = \sum_i x_i M_{0i} \quad (14)$$

The homopolymer interaction parameters, a_i and β_{ii} , respectively, are related to the corresponding values of A or B parameters by

$$A_i^2 = \frac{a_i^2}{M_{0i}} \quad (15)$$

$$B_i = \frac{\beta_{ii}}{M_{0i}^2} \quad (16)$$

Their values may be determined by viscometric measurements in homopolymer solutions. The cross-interaction parameter, β_{ij} , may be determined only by measurements in copolymer solutions and depends significantly on the tacticity of copolymer blocks [22].

The tacticity is less important in statistical copolymers. Short-range interactions are much more dependent on the microstructure (sequence distribution) of copolymer chain and they cannot be described by the simple arithmetic sum (15). Instead, the following expression is used:

$$A^2 M_0 = \sum_i \sum_j X_{ij} a_{ij}^2 \quad (17)$$

where a_{ij} denotes the short-range interaction parameter for $i-j$ sequence and X_{ij} is probability of finding such a sequence in the statistical copolymer chain.

The required probabilities may be calculated using a suitable radical copolymerization kinetic model. In the case of Mayo and Lewis [24] model, the corresponding

expression for describing the short-range interactions in binary statistical copolymers is

$$A^2 M_0 = a_1^2 x_1 p_{11} + a_2^2 x_2 p_{22} + 2a_{12}^2 x_1 (1 - p_{11}) \quad (18)$$

where p_{ii} stands for the conditional probabilities which are within the same copolymerization model defined by the equation

$$p_{ii} = \frac{r_i f_i}{r_i f_i + f_j} \quad (19)$$

r_1 and r_2 are the copolymerization model parameters, namely the copolymerization reactivity ratios; f_1 and f_2 are relative molar fractions of corresponding monomers in the reaction mixture.

Upon comparing Eqs. (18) and (12) one may obtain the expression for the “excess” short-range interaction parameter, i.e., the difference of interaction parameters of statistical and block copolymer as a reference state

$$M_0 (A_S^2 - A_B^2) = \frac{1}{2} (2a_{12}^2 - a_{11}^2 - a_{22}^2) X_{12} = C X_{12} \quad (20)$$

C may be regarded as a constant for the comonomer pair–solvent system under consideration. Its value will depend on the temperature, too.

Utracki and Simha [22] showed that the long-range interaction parameter values are mutually comparable for block and statistical copolymers (if the influence of tacticity in block copolymers is excluded). Moreover, they do not depend on the composition. Stockmayer–Fixman’s expression (11) for block copolymer may be subtracted from the corresponding expression for statistical copolymer (both copolymers having the same overall composition and molecular mass). As a result, the departure of the limiting viscosity number of statistical and block copolymer will be determined by the difference of the corresponding short-range interaction parameters and it will be proportional to $M^{1/2}$

$$[\eta]_S - [\eta]_B = \Phi_0 (A_S^3 - A_B^3) M^{1/2} \quad (21)$$

The indices S and B denote the statistical and block copolymer, respectively. If A_S does not differ too much from A_B ($A_S \approx A_B$), one may write

$$[\eta]_S - [\eta]_B = \Phi_0 A_B (A_S^2 - A_B^2) M^{1/2} \quad (22)$$

By applying the corresponding mixing rules (12) and (17), the following expression is obtained:

$$[\eta]_S - [\eta]_B = \Phi_0 (w_1 A_1^2 + w_2 A_2^2)^{1/2} (A_S^2 - A_B^2) M^{1/2} \quad (23)$$

In θ -conditions, Stockmayer–Fixman’s expression for homopolymers (11) reduces to Eq. (9); thereout follows:

$$A = \left(\frac{K_\theta}{\Phi_0} \right)^{1/3} \quad (24)$$

Now Eq. (23) may be written as

$$[\eta]_S - [\eta]_B = \Phi_0^{2/3} \left(w_1 K_{\theta 1}^{2/3} + w_2 K_{\theta 2}^{2/3} \right)^{1/2} (A_S^2 - A_B^2) M^{1/2} \quad (25)$$

Finally, by combining Eqs. (25), (8), (20) and (14), the expression for the limiting viscosity number of statistical copolymer is obtained

$$[\eta]_S = \frac{K_E M^{1/2} X_{12} \left(w_1 K_{\theta 1}^{2/3} + w_2 K_{\theta 2}^{2/3} \right)^{1/2}}{M_0} + \left(w_1 \frac{K_1 M^{a_1}}{K_{\theta 1}} + w_2 \frac{K_2 M^{a_2}}{K_{\theta 2}} \right) \left(w_1 K_{\theta 1}^{2/3} + w_2 K_{\theta 2}^{2/3} \right)^{3/2} \quad (26)$$

where K_E is the interaction parameter, a product of constants

$$K_E = \Phi_0^{2/3} C \quad (27)$$

Eq. (27) is the desired correlation of the limiting viscosity number, molecular mass and copolymer composition. The comonomer unit size difference is characterized with M_0 -value; the copolymer segment–solvent interaction is described by the expression in the first parentheses of the second term on the right-hand side of the equation; the segment–segment interaction is taken into account by the $K_E X_{12}$ -product, namely, the interaction parameter multiplied by the probability of finding heterogeneous comonomer unit sequences within copolymer chain. The sequence distribution of copolymer chain may be found experimentally, by the nuclear magnetic resonance method [25,26], or may be calculated from the monomer (reaction) mixture composition and parameters of the copolymerization kinetic model. Particularly, the Mayo–Lewis [24] model is appropriate for predictive purposes because the necessary model parameters (r_1, r_2) are experimentally determined for a great number of comonomer pairs and systematically compiled [21] in literature. The expression for X_{12} within the framework of the Mayo–Lewis model is

$$X_{12} = 2X_1 p_{12} = \frac{2f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (28)$$

where

$$f_1 = (1 - f_2) \quad (29)$$

The major drawback of the correlation is the assumption that $A_S \approx A_B$. For a set of given values of $[\eta]_S - [\eta]_B$, M , Φ_0 , and K_0 ($5 \text{ cm}^3 \text{ g}^{-1}$, 100000 , 2.1×10^{23} and $75 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$, respectively), calculated A_S and A_B -values are 7.1×10^{-3} and 6.6×10^{-3} , respectively. Now the corresponding value of $(A_S^3 - A_B^3) = 7.5 \times 10^{-26}$ may be compared with $A_B (A_S^2 - A_B^2) = 4.8 \times 10^{-26}$. The discrepancy is, obviously, rather large. Therefore, in further considerations the C -constant must be regarded as an empirical, fitting parameter, which should compensate the error introduced in derivation. Thus, K_E becomes the adjustable parameter, too, used to fit the experimental data.

The correlation given by Eq. (26) is based on some specified assumptions. Firstly, the solvent, from the thermodynamic point of view, should be relatively good for both homopolymers. In the thermodynamically poor solvents one of the copolymer blocks may be in the collapsed state (the corresponding polymer would precipitate in the same conditions): In that case the definition of the block copolymer as a referent state for calculating the limiting viscosity number of statistical copolymer becomes meaningless. Besides, the strong specific interactions of copolymer segments (either homogeneous or heterogeneous) may disturb the statistical distribution of segments within a copolymer coil, a feature that is incorporated in the derivation of the correlation. In those cases the correlation will not satisfactorily describe the dependence of the limiting viscosity number on the molecular mass of copolymer. The limiting viscosity number value may be seriously affected by the eventual stereoregularity (tacticity) of copolymer; this effect was not taken into account within the correlation.

By taking all the above mentioned limitations into consideration, the statistical copolymers of styrene and methyl methacrylate (SMMA) were chosen as model systems to test the correlation. They are commonly synthesized by the radical solution copolymerization wherein the copolymer composition and molecular mass can be appropriately regulated by varying the synthesis recipes. SMMA copolymers are readily soluble in many solvents in the whole range of copolymer compositions. Styrene and methyl methacrylate comonomer units significantly differ in many of their properties, such as polarity, so their repulsive interaction within a copolymer chain will have an appreciable and measurable effect on the size of copolymer coil in solution. SMMA copolymers have already been investigated by the dilute solution viscometry [20,27,28]. Styrene and methyl methacrylate block copolymers (reference systems in this study) have been thoroughly studied in diluted solutions by the viscometry [7,10,19,29–32], osmometry [7,29], light scattering [10,11,13,14,31,33–35] and small angle neutron scattering [12,36] methods.

4. Experimental

4.1. Materials

Styrene (INA-OKI Zagreb, Croatia) and methyl methacrylate (Rohm and Haas) monomers were purified by distillation under reduced (atmospheric) pressure. Azobisisobutyronitrile (AIBN, AKZO Chemie, The Netherlands) was recrystallized repeatedly from cold methanol and dried in a vacuum oven. Toluene (Kemika, Zagreb, Croatia) was used as a solvent for syntheses and viscometric measurements.

4.2. Copolymerization

Radical copolymerization of styrene and methyl methacrylate was conducted in an isothermal batch reactor using toluene as a solvent. Total monomer concentration was 2.5–3.0 mol dm⁻³. After preheating the monomer solution to the final reaction temperature of 60 °C, a selected quantity of the initiator was added. The variations in copolymer composition were achieved by changing the monomer feed composition; the variations in copolymer molecular mass were accomplished by varying the concentration of the initiator. Copolymerization reactions were interrupted at low monomer conversions (<10% by mass) to maintain the compositional homogeneity of prepared copolymers.

The reactions were interrupted by precipitation of reaction mixture in the tenfold volume of cold methanol. Synthesized polymers were purified by dissolving in toluene and precipitation in cold methanol; the procedure was repeated twice. Finally, the copolymer samples were dried in a vacuum oven at 60 °C to constant mass. Total monomer conversions were determined by weighing.

4.3. Elemental analysis

The compositions of the synthesized SMMA copolymers were determined by elemental analysis, using Perkin Elmer 2400, ser. 2 CHNS analyzer.

4.4. Size exclusion chromatography (SEC)

Molecular mass distributions of synthesized copolymers were determined by the size exclusion chromatography (SEC) method. The device consisted of the Waters 6000 A chromatographic pump, Waters U6K universal injector and Waters 150 C differential refractometer as a detector. For most of the samples, the separation unit consisted of the four μ -Styragel columns with exclusion limits of 10⁴, 10³, 10² and 50 nm, respectively; the columns were connected in a series. The samples with higher molecular masses (marked by $\times 2$ and $\times 4$, respectively) were analyzed by the same device (pump, injector and detector). However, the separation unit comprised the three PL-gel mixed B columns (30.0 \times 0.76 cm, 10 μ m), connected in a series. All the separations were performed at the ambient temperature of 20 \pm 1 °C. For molecular mass determinations the specific calibration curve for polystyrene was used.

4.5. Viscometry

Viscometric parameters of statistical SMMA copolymers (limiting viscosity numbers and Huggins' constants) were determined by the dilute solution viscometry method. The measurements were performed

in toluene solutions, using the Cannon-Ubbelohde viscometer type 50 L745, at 25 ± 0.02 °C. The measurements were performed in the copolymer concentration range of 0.002–0.008 g cm³.

5. Results and discussion

5.1. Synthesis and characterization of SMMA copolymer

Data relevant to the synthesis and characterization of SMMA copolymers are presented in Table 1.

5.2. Mendelson's correlation

Fig. 1 shows Mendelson's correlation of the limiting viscosity number, molecular mass and copolymer composition for our data (SMMA in toluene at 25 °C) as well as for the literature data [20] (SMMA in toluene at 30 °C). Corresponding correlation parameters are given in Table 2. A direct comparison of experimental and literature parameters is not entirely correct because the two sets of data were obtained at different temperatures. The linear regression coefficient (Table 2) is somewhat higher for the literature data because:

(1) investigated molecular mass range is significantly broader ($\overline{M}_w = 5–106 \times 10^4$ in comparison with $14.1–17.2 \times 10^4$),

(2) molecular mass distribution of copolymer samples is somewhat narrower (fractions, $I = 1.35–1.79$ in relation to whole samples, $I = 1.57–2$),

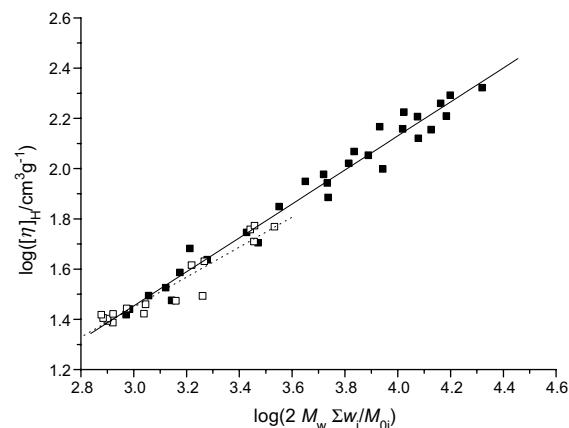


Fig. 1. Mendelson's correlation for SMMA copolymers in toluene at 25 °C: (□) experiment, (---) correlation; and for SMMA copolymer in toluene at 30 °C (literature data [20]): (■) experiment, (—) correlation.

Table 2
The parameters of Mendelson's correlation

Polymer	Solvent	$J/\text{cm}^3 \text{g}^{-1}$	β	R
SMMA	Toluene, 25 °C	0.456	0.597	0.955
SMMA	Toluene, 30 °C	0.266	0.676	0.986

(3) investigated copolymer composition range is significantly narrower ($x_2 = 0.29–0.70$ in comparison with 0–1).

Table 1
SMMA copolymer synthesis and characterization data

Sample	$c/\text{mol dm}^{-3}$	t/min	$X/\%$	f_1	x_1^{exp}	$[\eta]_H/\text{cm}^3 \text{g}^{-1}$	k_H	\overline{M}_n	\overline{M}_w
PS	3.000	190	9.44	1	1.014	24.40	0.644	24 500	43 400
SMMA 10	2.976	180	8.50	0.949	0.931	24.75	0.490	23 300	41 300
SMMA 20	2.943	120	5.61	0.881	0.835	25.31	0.382	24 000	41 200
SMMA 30	2.900	105	5.18	0.789	0.748	25.42	0.305	23 800	39 500
SMMA 40	2.851	100	4.90	0.668	0.650	26.16	0.169	23 800	38 700
SMMA 50	2.785	80	4.23	0.525	0.546	26.42	0.336	26 200	42 700
SMMA 60	2.724	70	4.72	0.377	0.426	27.76	0.325	29 900	47 900
SMMA 70	2.673	85	6.44	0.246	0.340	28.86	0.270	32 800	56 300
SMMA 80	2.632	80	6.81	0.142	0.229	26.47	0.352	34 500	55 300
SMMA 90	2.603	70	8.31	0.062	0.141	29.77	0.332	46 200	72 700
PMMA	2.579	210	34.78	0	-0.007	31.16	0.527	55 100	91 300
SMMA 20 × 2	3.000	240	4.09	0.842	0.786	41.28	0.529	43 800	85 600
SMMA 20 × 4	3.000	575	4.67	0.842	0.801	57.31	0.281	71 400	142 800
SMMA 50 × 2	3.000	160	2.85	0.453	0.465	42.79	0.533	53 300	94 400
SMMA 50 × 4	3.000	390	3.31	0.453	0.500	59.32	0.303	78 400	146 500
SMMA 80 × 2	3.000	240	6.91	0.113	0.175	51.29	0.247	78 300	144 000
SMMA 80 × 4	3.000	370	4.52	0.113	0.177	58.71	0.310	87 200	172 000

c —total monomer concentration; t —reaction time; X —total mass conversion of monomer; f_1 and x_1 —mole content of styrene and styrene units in reaction mixture and copolymer, respectively; $[\eta]_H$ and k_H —limiting viscosity number (intrinsic viscosity) and Huggins constant in toluene, respectively; \overline{M}_n and \overline{M}_w —number and mass-average molecular mass, respectively.

However, Fig. 1 indicates that, qualitatively speaking, the dissipation for both sets of data may be considered rather similar.

5.3. New correlation

As already mentioned, the main objection to Mendelson's correlation may be found in its applicability for a limited range of copolymer composition. The correlation, capable of describing the intrinsic viscosity in the entire range of copolymer composition, should take into consideration all the effects that may affect the $[\eta]$ -value: the size difference of comonomer segments (the only effect explicitly accounted for in Mendelson's correlation), copolymer segment–solvent interaction, as well as segment–segment (hetero)interaction. Eq. (26) shows one possible form of the new correlation. Although it seems to be rather complicated, it includes common viscometric and kinetic parameters for corresponding copolymers. These parameters are normally determined from independent measurements, and good compilations for a wide variety of copolymer systems are available [21,37].

Eq. (10) describes the limiting viscosity number of block copolymer as a function of composition and molecular mass. To evaluate $[\eta]_B$, the literature data for MHKS-constants K and a for corresponding homopolymers in solvent under consideration as well as appropriate K_0 data are needed. Literature data for styrene and methyl methacrylate homopolymers as well as SMMA copolymers in toluene are shown in Table 3. The following values for the investigated system are chosen: $K = 10 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$, $a = 0.73$, $K_0 = 82 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ and $K = 7.5 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$, $a = 0.73$, $K_0 = 70 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ for PS and PMMA, respectively. The chosen values lay within limits of literature data and they produce a good match with experimental limiting viscosity numbers for PS and PMMA, as presented in Table 1. Fig. 2 shows the $[\eta]_S/[\eta]_B$ -ratio as a function of

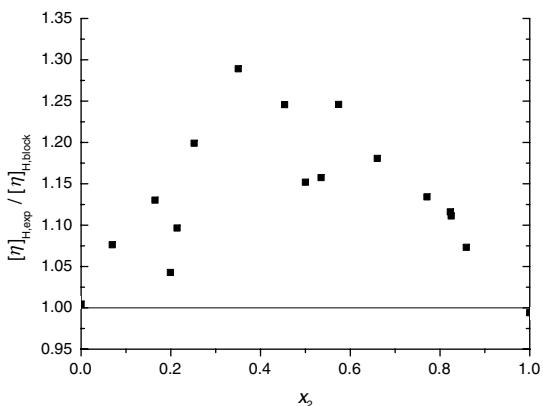


Fig. 2. Ratio of statistical and block copolymer intrinsic viscosities vs. SMMA copolymer composition; statistical copolymer values, $[\eta]_{H,\text{exp}}$, obtained experimentally, block copolymer values, $[\eta]_{H,\text{block}}$, obtained by calculation.

copolymer composition. $[\eta]_S$ -values are experimentally determined; $[\eta]_B$ -values are calculated using Eq. (10) for block copolymers having the same overall composition and molecular mass as the corresponding statistical copolymers. A similar diagram (Fig. 3) was created for literature [20] data regarding the SMMA copolymers in toluene at 30 °C, too. However, some parameter values used in the calculation of $[\eta]_B$ are changed. Namely, the authors have presented [20] experimental K_0 -values that decreased with an increase of methyl methacrylate content in SMMA. The three data points defined a linear composition dependence with corresponding intercepts of K_0 of $86 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ and $58 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ for PS and PMMA, respectively. These, newly defined K_0 -values again lay within the limits given by the literature (see Table 3). They were used in combination with above listed K and a -values for PS and PMMA to calculate the data points presented in Fig. 3.

Table 3
Selected literature [37] parameters of Mark–Houwink–Kuhn–Sakurada correlation in toluene, as well as viscometric constants K_0 for PS, PMMA and corresponding statistical copolymers

Polymer	$T/^\circ\text{C}$	$K/\text{cm}^3 \text{ g}^{-1}$	a	M_w range	$K_0/\text{cm}^3 \text{ g}^{-1}$	Reference
PS	25	7.50×10^{-3}	0.75	$12\text{--}280 \times 10^4$		279 in [37]
PS	25	8.48×10^{-3}	0.748	$4\text{--}52 \times 10^4$		289 in [37]
PS	25	10.50×10^{-3}	0.73	$16\text{--}100 \times 10^4$		294 in [37]
PS	30				$82 \pm 5 \times 10^{-3}$	3 in [37]
PMMA	25	7.10×10^{-3}	0.73	$4\text{--}330 \times 10^4$		174 in [37]
PMMA	25	8.12×10^{-3}	0.71	$5\text{--}41 \times 10^4$		177 in [37]
PMMA	25				$70 \pm 20 \times 10^{-3}$	3 in [37]
SMMA 30	30	8.32×10^{-3}	0.75	$5\text{--}55 \times 10^4$	$77 \pm 2 \times 10^{-3}$	[20] (614 in [37])
SMMA 44	30	13.20×10^{-3}	0.71	$4.8\text{--}81 \times 10^4$	$75 \pm 2 \times 10^{-3}$	[20] (614 in [37])
SMMA 71	30	11.40×10^{-3}	0.70	$7\text{--}106 \times 10^4$	$66 \pm 2 \times 10^{-3}$	[20] (614 in [37])

Note: The numbers added to the SMMA abbreviation denote the molar percentage of MMA units in copolymers.

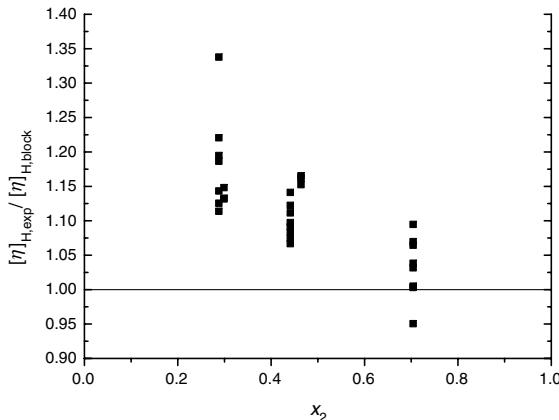


Fig. 3. Ratio of statistical and block copolymer intrinsic viscosities vs. SMMA copolymer composition; statistical copolymer values, $[\eta]_{H,exp}$, are literature [20] data, block copolymer values, $[\eta]_{H,block}$, obtained by calculation.

By examining Figs. 2 and 3, one may come to the conclusion that statistical copolymers exhibit higher intrinsic viscosities than corresponding block copolymers having the same overall composition and equal molecular mass. This observation was found by experiments [6,18] in other systems, too. Moreover, it seems that the ratio of intrinsic viscosities is a function of composition and shows a maximum at some intermediate copolymer composition (Fig. 2.). It is interesting to note that a similar maximum may be found in Table 3, regarding the literature values of MHKS-constant K for SMMA in toluene at 30 °C. By assuming the constant value of the a -parameter of 0.73 in the whole range of copolymer composition, the K -parameter values were evaluated using the MHKS correlation, Eq. (2), and the single pair of $[\eta]-\overline{M}_w$ for each copolymer composition. Estimated K -values are shown as a function of copolymer composition in Fig. 4. For the samples denoted by PS, SMMA 10–90 and PMMA, the K vs. x_2 dependence shows the maximum at $x_2 = 0.4$. Therefore, one may conclude that both MHKS and the new correlation describe the maximum of the expansion of copolymer coil at some intermediate composition qualitatively in the similar manner.

Eq. (26) may be used to evaluate the limiting viscosity number of a statistical copolymer. However, the equation includes the term X_{12} that has to be calculated by Eq. (28) using the appropriate values of copolymerization reactivity ratios, r_i . These values are, in this case, calculated from experimental data listed in Table 1, according to the copolymerization kinetics model of Mayo and Lewis [24]. A nonlinear regression analysis of data was performed using the algorithms of Tidwell–Mortimer [38] and Hagiopol–Frangu–Dumitru [39], respectively. The values of $r_1 = 0.61$ and $r_2 = 0.44$

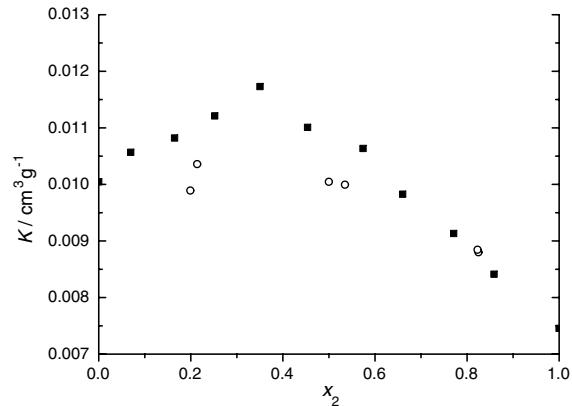


Fig. 4. K -parameter of MHKS correlation vs. copolymer composition (methyl methacrylate content, x_2); a -parameter assumed to be constant; (■) samples PS, SMMA 10–90, PMMA; (○) samples SMMA 20 \times 2, \times 4; 50 \times 2, \times 4; 80 \times 2, \times 4.

were obtained, that are in good accordance with literature [21] data for the same system. Table 4 lists all the parameters used in the analysis of experimental and literature [20] data, respectively, for SMMA in toluene.

The optimal value of the single fitting parameter K_E was obtained by minimizing the mean square deviation of experimental and calculated $[\eta]$ -values, according to the equation

$$OF = \sqrt{\frac{1}{N} \sum_{i=1}^n \left([\eta]_{S,i}^{\text{exp}} - [\eta]_{S,i}^{\text{calc}} \right)^2} = f(K_E) \quad (30)$$

The best match was found by the K_E -values of 8.24 and 3.36 for own and literature data, respectively.

It is not easy to visualize the new correlation, because in the series of samples the composition and molecular mass are simultaneously changing as independent variables and the limiting viscosity number as a dependent variable. Moreover, the same probability of finding the

Table 4

List of parameters used in the evaluation of the new correlation of limiting viscosity number, molecular mass and copolymer composition

Parameter	Own data	Literature data [20]
$K_{01}/\text{cm}^3 \text{g}^{-1}$	82×10^{-3}	86×10^{-3}
$K_{02}/\text{cm}^3 \text{g}^{-1}$	70×10^{-3}	58×10^{-3}
$K_1/\text{cm}^3 \text{g}^{-1}$	10×10^{-3}	10×10^{-3}
$K_2/\text{cm}^3 \text{g}^{-1}$	7.5×10^{-3}	7.5×10^{-3}
a_1	0.73	0.73
a_2	0.73	0.73
$M_{01}/\text{g mol}^{-1}$	104.15	104.15
$M_{02}/\text{g mol}^{-1}$	100.12	100.12
r_1	0.61	0.61
r_2	0.44	0.44

heterogeneous contacts in a copolymer chain, X_{12} , can be produced by different copolymer (or monomer mixture) compositions. So, a direct graphic comparison between experimental and calculated $[\eta]$ -values is probably the best solution of the problem. A corresponding numerical criterion is much easily constructed; the OF-value as calculated by Eq. (30) or (31) may serve as a measure of the success of the described correlation.

In Fig. 5 the comparison of experimentally determined and calculated $[\eta]$ -values is shown; both Mendelson's and the new correlation are considered. The relative mean square deviations of experimental and calculated data, defined by the equation

$$S = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{[\eta]_{\text{calc}} - [\eta]_{\text{exp}}}{[\eta]_{\text{exp}}} \right)^2} \quad (31)$$

are found to be 10.3% and 2.7% for Mendelson's and the new correlation, respectively. Fig. 6 is the analog of Fig. 5 for literature data [20]. In this case, the relative mean square deviations of experimental and correlated data are 11.0% and 15.4% for Mendelson's and the new correlation, respectively.

The results indicate that the new correlation gives much better results for the data presented in this paper. However, Mendelson's correlation performs somewhat better for the literature data. A relatively simple analysis will be presented to account for this fact. The $[\eta]_S/[\eta]_B$ -values for literature data were calculated and shown in Fig. 7 as functions of the copolymer molecular mass. The new correlation predicts that the $[\eta]_S/[\eta]_B$ -value should decrease as the molecular mass increases. Namely, the limiting viscosity number of the statistical copolymer is calculated essentially by the sum of two terms. The term that corresponds to the block copoly-

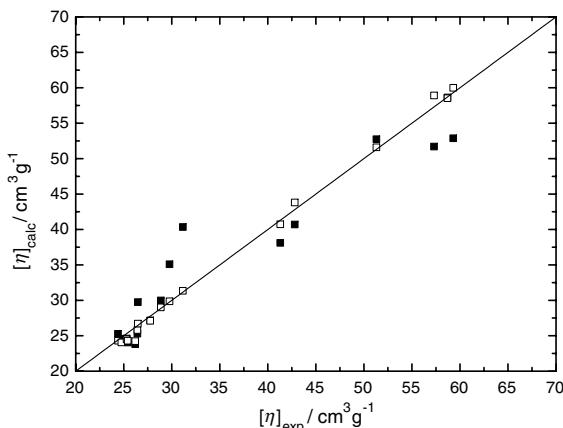


Fig. 5. Experimental (own data) vs. calculated intrinsic viscosity of SMMA copolymers; values calculated by Mendelson's correlation (■) and the new correlation (□).

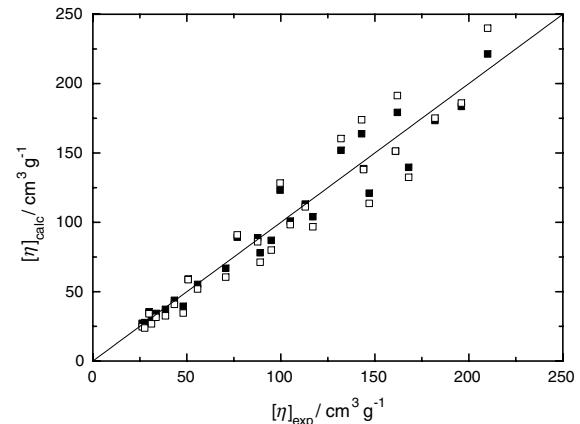


Fig. 6. Experimental (literature data [20]) vs. calculated intrinsic viscosity of SMMA copolymers; values calculated by Mendelson's correlation (■) and the new correlation (□).

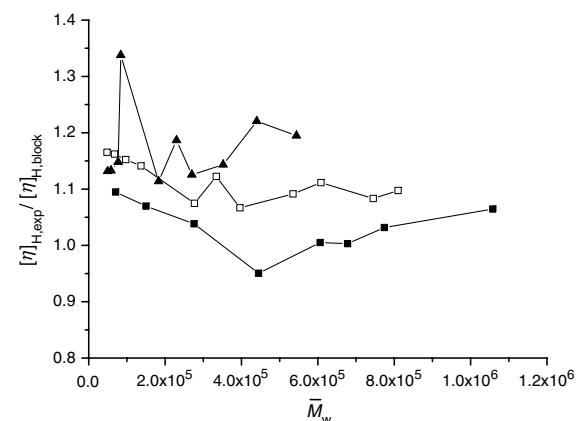


Fig. 7. Intrinsic viscosities of the statistical copolymers (literature data [20]) divided by the intrinsic viscosities of the corresponding block copolymers (predicted) as functions of the copolymer molecular mass. (▲) SMMA 30, (□) SMMA 44; (■) SMMA 71. Data points are connected with lines for the sake of clarity.

mer intrinsic viscosity increases with the molecular mass raised to the power of a (i.e., the arithmetic mean of the MHKS-exponent a). The “excess” intrinsic viscosity, $[\eta]_S - [\eta]_B$, is connected with the properties of copolymer chains in the θ -state; it does not depend on the solvent and increases with the molecular mass raised to the power of $0.5 < a$. The “excess” term will therefore exhibit a slower increase than the $[\eta]_B$ -term, pointing to the diminishing of $[\eta]_S/[\eta]_B$ -value with molecular mass. Fig. 7 indicates that there is no explicit trend of decreasing the $[\eta]_S/[\eta]_B$ -value for literature data, and the new correlation fails. Our experimental data agree well with

the above mentioned trend, indeed with the significantly narrower area of investigated molecular masses.

6. Concluding remarks

Statistical copolymers of styrene and methyl methacrylate of different compositions and molecular masses were synthesized by the radical copolymerization in the batch isothermal reactor. Copolymers were characterized by the elemental analysis, by the size exclusion chromatography (SEC) and by the dilute solution viscometry.

The Mark–Houwink–Kuhn–Sakurada *K*-parameter values were evaluated. With the assumed constant value of the MHKS *a*-parameter, the *K*-parameter exhibits the maximum at some intermediate copolymer composition, pointing to the repulsive interactions of comonomer segments in the copolymer chain.

The parameters of Mendelson's correlation of the limiting viscosity number, molecular mass and copolymer composition were calculated for the prepared SMMA copolymers, as well as for the literature data set. The two set of data are comparably well described by Mendelson's correlation.

The new correlation of the limiting viscosity number, molecular mass and copolymer composition was developed. The new correlation takes explicitly into consideration the size difference of comonomer units dimensions (like Mendelson's correlation) as well as the other two important effects, the repulsive segment–segment interaction and copolymer segment–solvent interaction. Suitable theoretical background was applied to describe the three effects. However, the parameter which describes the repulsive segment–segment interaction retained an empirical character. Other correlation parameters are easily available in the literature.

The new correlation was found to be superior to Mendelson's correlation regarding the experimental data presented in this work.

References

- [1] Yau WW, Kirkland JJ, Bly DD. Modern size exclusion liquid chromatography. New York: Wiley; 1979.
- [2] Janović Z, Sarić K, Sertié-Bionda K. Polymerization and polymer properties of some alkylmethacrylates as lubricating oil viscosity modifiers. *Chem Biochem Eng Q* 1998;12:19–24.
- [3] Vidović E, Sarić K, Janović Z. Copolymerization of styrene with dodecyl methacrylate and octadecyl methacrylate. *Croatica Chem Acta* 2002;75:769–82.
- [4] Bohdanecký M, Kovář J. Viscosity of polymer solutions. In: Jenkins AD, editor. Polymer science library 2. Amsterdam: Elsevier; 1982.
- [5] Mendelson RA. Generalized intrinsic viscosity relations for copolymers and higher multispecies polymers for SEC universal calibration. I. Specific relations for SAN and S/MA/MM polymers. *ACS Symp Ser* 1987;352:263–80.
- [6] Kent MS, Tirrell M, Lodge TP. Properties of polystyrene–poly(methylmethacrylate) random and diblock copolymers in dilute and semidilute solutions. *J Polym Sci, Part B, Polym Phys* 1994;32:1927–41.
- [7] Burnett GM, Meares P, Paton C. Styrene + methyl methacrylate block copolymers. Part 2—Behaviour in dilute solutions. *Trans Faraday Soc* 1962;58:737–46.
- [8] Dondos A, Froelich D, Rempp P, Benoit H. Étude des copolymères en solution. Effet des interactions entre segments de nature différente sur les configurations de différents types de copolymères. *J Chim Phys* 1967;64: 1012–8.
- [9] Girolamo M, Urwin JR. Thermodynamic parameters from osmotic studies on solutions of block copolymers pf polyisoprene and polystyrene. *Eur Polym J* 1972;8:299–311.
- [10] Krause S. Dilute solution properties of a styrene–methyl methacrylate block copolymer. *J Phys Chem* 1964;68: 1948–55.
- [11] Utiyama H, Takenaka K, Mizumori M, Fukuda M. Light-scattering studies of a polystyrene–polymethyl methacrylate two-block copolymer in dilute solutions. *Macromolecules* 1974;7:28–34.
- [12] Han CC, Mozer B. Conformation of PS–PMMA diblock copolymer in toluene by small angle neutron scattering. *Macromolecules* 1977;10:44–51.
- [13] Tanaka T, Omoto M, Inagaki H. Conformation of block copolymers in dilute solution. 3. Determination of the center-to-center distance between the two blocks by light-scattering. *Macromolecules* 1979;12:146–52.
- [14] Tanaka T, Kotaka T, Inagaki H. Intermolecular correlation in light-scattering from dilute solutions of block copolymers. *Macromolecules* 1974;7:311–9.
- [15] Matsushita Y, Nakao Y, Shimizu K, Noda I, Nagasawa M. Conformations of diblock copolymers in dilute solutions. *Macromolecules* 1988;21:2790–3.
- [16] Tanaka T, Omoto M, Inagaki H. Conformation of isolated block copolymer molecules. *J Macromol Sci Phys B* 1980;17:229–48.
- [17] Matsushita Y, Shimizu K, Noda I, Chang T, Han CC. Chain conformation of block copolymers in dilute solutions measured by small-angle neutron scattering. *Polymer* 1992;33(11):2412–5.
- [18] Tanaka T, Kotaka T, Ban K, Hattori M, Inagaki H. Conformation of block copolymers in dilute solution. The molecular dimension/block architecture relationships. *Macromolecules* 1977;10:960–7.
- [19] Dondos A, Rempp P, Benoit H. Segregation and conformational transitions in triblock copolymers in dilute solution: 3. Viscometric investigations in solvent mixtures. *Polymer* 1975;16:698–702.
- [20] Kotaka T, Murakami Y, Inagaki H. Dilute solution properties of styrene–methyl methacrylate random copolymers. *J Phys Chem* 1968;72:829–41.
- [21] Greenley RZ. Free radical copolymerization reactivity ratios. In: Brandrup J, Immergut EH, Grulke EA, editors. *Polymer handbook*. 4th ed. New York: Wiley; 1999. p. II/181.

[22] Utracki LA, Simha R. *Macromolecules* 1968;1:505.

[23] Stockmayer WH, Fixman M. On the estimation of the unperturbed dimensions from intrinsic viscosities. *J Polym Sci* 1963;1:137–41.

[24] Mayo FR, Lewis FM. Copolymerization. I. A basis for comparing the behavior of monomers in copolymerization: the copolymerization of styrene and methyl methacrylate. *J Am Chem Soc* 1944;66:1594–601.

[25] Hill DJT, Lang AP, O'Donnell JH. The study of the copolymerization of styrene and acrylonitrile to high conversion. Application of low conversion reactivity ratios. *Eur Polym J* 1991;27:765–72.

[26] López-González MMC, Fernández-García M, Barrales-Rienda JM, Madruga EL. Sequence distribution and stereoregularity in methyl methacrylate–methyl acrylate copolymers at high conversions. *Polymer* 1993;34:3123–8.

[27] Stockmayer WH, Moore LD, Fixman M, Epstein B. Copolymers in dilute solution. I. Preliminary results for styrene–methyl methacrylate. *J Polym Sci* 1955;16:517–30.

[28] Podesva J, Bohdanecký M, Kratochvil P. Unperturbed dimensions of random and alternating styrene-*n*-alkyl methacrylate copolymers. *J Polym Sci* 1977;15:1521–36.

[29] Kotaka T, Ohnuma H, Inagaki H. Thermodynamic and conformational properties of styrene–methyl methacrylate block copolymers in dilute solution. II. Behavior in theta solvents. *Polymer* 1969;10:517–29.

[30] Ohnuma H, Kotaka T, Inagaki H. Thermodynamic and conformational properties of styrene–methyl methacrylate block copolymers in dilute solution. III. Viscometric behavior relation to incompatibility of parent homopolymers. *Polymer* 1970;1(6):716–26.

[31] Tanaka T, Kotaka T, Inagaki H. Thermodynamic and conformational properties of styrene–methyl methacrylate block copolymers in dilute solution. V. Light-scattering analysis of conformational anomalies in *p*-xylene solution. *Polymer* J 1972;3(3):338–49.

[32] Dondos A. Conformation “ségrégée” et conformation “statistique” dans les copolymères à trois séquences PMM-PS-PMM en solution diluée. *Makromol Chem* 1971;147:123–34.

[33] Kotaka T, Tanaka T, Hattori M, Inagaki H. Block copolymer micelles in dilute solution. *Macromolecules* 1978;11:138–45.

[34] Utiyama H, Takenaka K, Mizumori M, Fukuda M, Tsunashima Y, Kurata M. Light-scattering studies of a polystyrene–poly(methyl methacrylate) two-block copolymer in mixed solvents. *Macromolecules* 1974;7:515–20.

[35] Tanaka T, Kotaka T, Inagaki H. Conformation of block copolymers in dilute solution. Monte Carlo calculations and light-scattering studies on diblock copolymer systems. *Macromolecules* 1976;9(4):561–8.

[36] Matsushita Y, Noda I, Nagasawa M, Lodge TP, Amis EJ, Han CC. Expansion factor of a part of a polymer chain in a good solvent measured by small-angle neutron scattering. *Macromolecules* 1984;17:1785–9.

[37] Kurata M, Tsunashima Y. Viscosity–molecular weight relationships and unperturbed dimensions of linear chain molecules. In: Brandrup J, Immergut EH, Grulke EA, editors. *Polymer handbook*. 4th ed. New York: Wiley; 1999. p. VII/1.

[38] Tidwell PW, Mortimer GA. An improved method of calculating copolymerization reactivity ratios. *J Polym Sci* 1975;A3:369–87.

[39] Hagiopol C, Frangou O, Dumitru L. A nonlinear method for the estimation of reactivity ratios in copolymerization processes. *J Macromol Sci Chem* 1989;A26(10):1363–79.