

Size distribution as a function of branching in the pregelation stage for poly(methyl methacrylate) containing randomly distributed tetrafunctional units*

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Size distribution in methyl methacrylate polymers containing small amounts of randomly distributed dimethacrylate units was studied as a function of branching up to the point of gelation. Size distribution was determined by size exclusion chromatography with refractive index and low angle light scattering detection as well as by dynamic light scattering. Proper handling of experimental data to get precise size averages is critically discussed. Multiangle static light scattering was used to provide additional verification of data obtained from size exclusion chromatography and dynamic light scattering. Expansion factors were determined for further elucidation of the effect of crosslinking in terms of coil volume change. The results agree quite well with the Flory-Stockmayer theory of gelation. However, the prediction of modern scaling theories that the ratio of the static and dynamic radii for randomly branched copolymers would attain a value of unity or slightly below as the critical branching, i.e. the gel point, is approached was not confirmed. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The sol-gel transition in macromolecular branching processes has been the subject of considerable theoretical and experimental efforts during the last half century. However, the experimental support of the theories has not been decisive due to the high precision required and the need for very accurate knowledge of the molecular weight and size distribution. It was believed that the recently developed high-resolution modern computerized techniques could provide such precise experimental data. This would then allow a deeper analysis of the process of branching in relation to dynamic behaviour and gelation. As a model system, copolymers of methyl methacrylate with small amounts of randomly distributed tetrafunctional ethylene dimethacrylate units were selected. The degree of polymerization or branching was varied just up to the point where gelation begins.

In a nonlinear polymer system, high-performance size exclusion chromatography (SEC) can be used as a routine method for determination of the real weight distribution of radii of gyration¹, R_g (static coil dimension, determined, e.g. from angular dissymetry in a multiangle static light scattering experiment). The hydrodynamic coil volume controls the SEC separation according to the product $M[\eta]$, where M is the molecular weight and $[\eta]$ is the intrinsic viscosity. $M[\eta]$ is known as a universal calibration parameter which holds irrespective of topological structure of the polymer molecules². The weight distribution of radii

of gyration can be calculated if the existing universal calibration of a SEC system is transformed to R_g -calibration via the Flory-Fox relation³. The use of low angle laser light scattering (LALLS) detection on line with refractometric (RI) detection makes possible an 'intensity weighting' of SEC data and a comparison of results coming from SEC and dynamic light scattering (DLS) measurements, for instance in the form of a dimensionless ρ parameter, which is the ratio of square root of z -average mean square radius of gyration $\langle R_g^2 \rangle_z^{1/2}$ and inverse z -average hydrodynamic radius $\langle 1/R_h \rangle_z^{-1}$. This quantity was suggested as a more easily accessible measure of branching density⁴ than a hydrodynamic or a static shrinking factor.

DLS has become a technique⁵ often used to determine size distribution of polymers and dispersions. A translational diffusion coefficient, D , is measured by DLS and the hydrodynamic radius of the coil, R_h (i.e. the radius of an equivalent sphere having the same D) is inversely related to D through the Stokes-Einstein formula. The scattered light intensity from a very dilute solution of macromolecular particles with hydrodynamic radius R_h is proportional to the number of these particles per unit volume and to the square of their molecular weight, M , if the Mie effect is neglected. In a polydisperse system, each particle size contributes by its z -fraction to the total measured intensity of scattered light. A z -average diffusion coefficient⁶ results in this case and the intensity-defined distribution of D and the corresponding distribution of R_h (cf. Ref. ⁷) are obtained from the multiexponential autocorrelation function by the inverse Laplace transformation⁸. Hence, the inverse z -average hydrodynamic radius is obtained from DLS data.

As a first objective of this paper, average molecular weights and sizes and size distribution were determined by

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SEC with RI and LALLS detection as well as by DLS. Although DLS is a non-separation technique, it is often claimed as being competitive^{9,10} or even superior¹¹ to SEC for determination of molecular weight and size distributions. On the other hand DLS was stated to be not very promising⁶ in polydispersity analysis. The 'ill conditioning' of the inverse Laplace transformation¹² appears to be the weak point of the DLS here. Hence, this work has a second objective to compare the z -distributions of the static and dynamic dimensions, as obtained from SEC and DLS experiments, to present reliable relations between the average molecular parameters obtained and to examine ratios of the proper averages R_g/R_h of long-chain randomly branched systems. To deepen the insight into branched systems and as a further crosscheck of the information obtained from SEC and DLS, the R_g values and expansion factors were determined using multiangle static light scattering (MALS) and viscosity measurements.

EXPERIMENTAL

Polymers and solvents

All samples were prepared by radical copolymerization of methyl methacrylate [6.55 mol l^{-1}] with ethylene dimethacrylate [0.032 mol l^{-1}] initiated by 2,2'-azobis(isobutyronitrile) [0.197 mol l^{-1}] in toluene [2.82 mol l^{-1}] solution at 45°C (cf. Ref. ¹³). Samples differed from each other in degree of conversion (< 0.15) and/or in degree of branching. A linear polydisperse polymer having the length of the so-called primary chain³ was also prepared in the absence of the branching component. The sample 6 (the highest molecular weight fraction; $w = 0.035$) was prepared by precipitation with methanol from 1% acetone solution of sample 5. The purity of the solvents used, i.e. tetrahydrofuran (THF) and 2-ethoxyethanol (EE), was checked by gas chromatography (content of the impurities $< 0.1\%$).

Multiangle static light scattering

Measurements were performed with a photogoniometer (Fica, Le Mesnil-Sant Denis, France) with vertically polarized light, wavelength 546.1 nm, angular range $30\text{--}150^\circ$. The THF- and EE-solutions were purified in a Beckman L8-55 ultracentrifuge (rotor SW.1, 15,000 rpm, 1 h). The weight average molecular weight $\langle M \rangle_w$ as well as the z -average radius of gyration $\langle R_g^2 \rangle_z^{1/2}$ were obtained by the evaluation of experimental data using the Zimm method.

Membrane osmometry

An automatic membrane osmometer (MO) Wescan 231 (Wescan Instruments, Santa Clara, CA, USA) was used for osmometric measurements in toluene at 30°C . The number-average molecular weight $\langle M \rangle_n$ was calculated from the reduced osmotic pressure extrapolated to zero concentration.

Viscometry

Solution viscosities were measured in an Ubbelohde dilution capillary viscometer; the intrinsic viscosity $[\eta]$ was extrapolated using Heller's method. $[\eta]$ of linear poly(methyl methacrylate)—PMMA—was calculated using the Mark-Houwink-Sakurada equations $[\eta] = 1.08 \times 10^{-2} M^{0.702}$ valid at 25°C and $[\eta] = 4.9 \times 10^{-2} M^{0.51}$ at 28°C for THF¹⁴ and EE¹⁵, respectively.

Size exclusion chromatography

The chromatographic equipment used (Laboratory Instruments, Prague, CZ), consisted of a pump HPP 5001, an injection valve LC-30 with a $100 \mu\text{l}$ loop, a RIDK-102 differential refractometer and a LALLS detector (KMX-6, Chromatix, Sunnyvale, CA, USA), both detectors being connected through an A/D converter-2308 (Black Star Ltd, St. Ives, Huntingdon, U.K.) to an IBM compatible computer with a printout facility. The homemade software allows online data accumulation as well as calculation of M - or R_g -distribution and averages of M or R_g . A commercial stainless steel column HP (7.5/600 mm) packed with PLGel 10 μm MIX (Polymer Laboratories, Ltd, Shropshire, U.K.) was used with THF as eluent; sample concentrations were selected in the range $(2 - 3) \times 10^{-3} \text{ g cm}^{-3}$. In the universal calibration² the Mark-Houwink-Sakurada equation for PMMA in THF (cf. Ref. ¹⁴) was used. Under given experimental conditions of SEC separation the axial dispersion was negligible.

Dynamic light scattering

An Inova 70-series 4W argon-ion laser (Coherent Laser Division, Palo Alto, CA, USA) tuned to 514.5 nm was focused into a precision scattering cell (Hellma GmbH, Mullheim Baden, BRD). The optical components were mounted on a massive steel bench (Newport Research Corporation, Fountain Valley, CA, USA). The scattered photon flow was monitored at an angle of 90° using a commercially available Brookhaven photomultiplier unit and a 128 channel BI-8000 digital correlator (Brookhaven Instruments Corp., Holtsville, USA). The Brookhaven particle size distribution software package¹⁶ contains five of the most common size analysis procedures; Brookhaven CONTIN version 3.0 (including Mie correction) procedure was used here. For the DLS measurements the concentration of solutions of copolymers in THF was selected in the range $(5 - 10) \times 10^{-4} \text{ g cm}^{-3}$.

RESULTS AND DISCUSSION

The results of MALS and MO measurements for linear 'primary' PMMA and four branched copolymers having different distances to the gel point as well as for the highest molecular weight fraction of a critically branched copolymer (sample 6) necessary for calculation of branching index

Table 1 Characteristics of branched systems

Sample	$\langle M \rangle_w$ $\times 10^5$	$\langle M \rangle_n$	γ	$\langle R_g^2 \rangle_z^{1/2}$ [nm]		$[\eta]$ [$\text{cm}^3 \text{g}^{-1}$]		α	α_η	$\alpha_{\eta,1}$
				THF	EE	THF	EE			
1	2.3	1.02	0.0			60	25		1.34	1.34
2	4.2	1.21	0.5			66	28		1.33	1.38
3	8.7	1.58	0.7	55	34	83	30	1.5	1.40	1.45
4	13.5	1.65	0.8	72	41	87	32	1.6	1.40	1.49
5	25.0	1.65	0.9	107	59	110	39	1.6	1.40	1.55
6	56.0	(12)		105	60	204	47	1.6	1.63	1.63

Note: Viscosity expansion factor $\alpha_{\eta,1}$ was calculated for linear polymer having identical $\langle M \rangle_w$ using proper Mark-Houwink relations^{14,15}.

γ are summarized in Table 1. Here, γ for a polydisperse polymer with random distribution of tetrafunctional branching points was calculated according to Kilb¹⁷ as $\gamma = \{(\langle M \rangle_w / \langle M \rangle_n) - 1\} / \{(\langle M \rangle_w / \langle M \rangle_n) - 0.5\}$ which holds for $\gamma < 1$, since in critical branching conditions $\langle M \rangle_w$ approaches infinity and γ approaches unity. To check possible changes in coil expansion due to branching, expansion factors of polymer chain $\alpha = (\langle R_g^2 \rangle / \langle R_g^2 \rangle_0)^{1/2}$ as well as viscosity expansion factors $\alpha_\eta = (\langle \eta \rangle / \langle \eta \rangle_0)^{1/3}$ were calculated from $\langle R_g^2 \rangle^{1/2}$ and $\langle \eta \rangle$ values in good and θ -solvent, THF and EE, respectively. ($\alpha_{\eta,1}$ values were calculated for linear polymer having identical $\langle M \rangle_w$ using proper Mark-Houwink relations^{14,15}.)

The SEC technique separates the branched macromolecules according to their hydrodynamic volumes ($[\eta]M$); i.e. molecules in a fraction of a given hydrodynamic volume eluting at a definite elution volume $V_{e,i}$ must be expected to have different branch lengths and different branching frequencies. Hence, within every slice along the elution volume axis², polymer coils having a given hydrodynamic size must be expected to have different molecular weights. Then the weight-average molecular weight, $\langle M_s \rangle_w$, for a definite hydrodynamic volume at a given $V_{e,i}$ is obtained from LALLS detection. To our knowledge, there is no correct way to transform SEC data to a true molecular weight distribution (MWD), because the mass fraction of macromolecules with a specific value of M is not unambiguously given in this case. On the other hand, the SEC separation mechanism can provide a real size distribution. Using broad linear PMMA, the universal calibration ($[\eta]M$ vs. V_e) was established from a SEC/LALLS experiment and then transformed to the corresponding universal calibration in terms of radii of gyration by means of relation

$$R_g = (1/6)^{1/2} [\eta]M/\phi \quad (1)$$

where the Flory universal constant³, $\phi = 2.2 \times 10^{23}$, recommended for linear polymer in good solvent¹⁸ was applied. Using this universally valid calibration (R_g vs. V_e) the common dependence $\log R_g$ vs. $\log \langle M_s \rangle_w$ for all branched copolymers (full line) along with this dependence for the corresponding linear primary chain coils (dashed line) could be obtained as shown in Figure 1. It is seen that the expected decrease in R_g due to branching is very small at lower $\langle M \rangle_w$ and a little more pronounced in the high molecular weight range where the slope of the dependence for branched

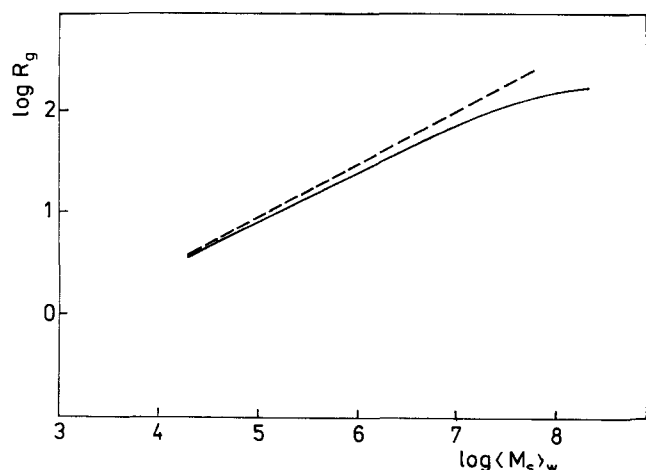


Figure 1 Dependence of particle size (R_g) on $\langle M_s \rangle_w$ corresponds to fractions at $V_{e,i}$ for linear PMMA (dashed line) and branched MA copolymers (solid line)

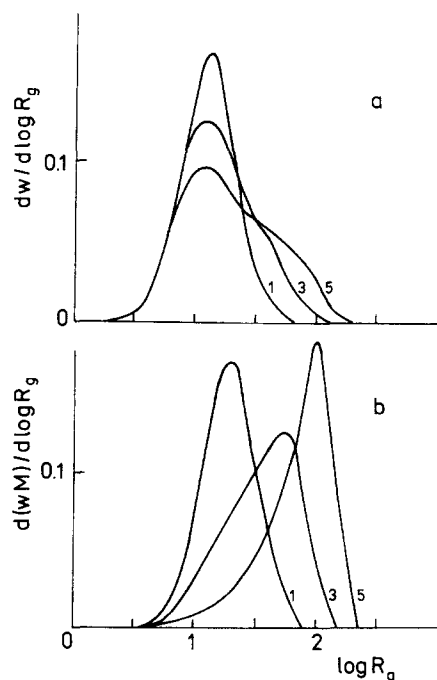


Figure 2 Weight-(a) and intensity- (z-) defined (b) normalized R_g -distributions denoted with sample numbers (see Table 1)

samples gradually decreased. The expansion properties of these branched coils only slightly differ as compared to the corresponding linear polymer (Table 1). This could be considered as a natural consequence of the presence of a small amount of branching points within the coil, i.e. only a very small decrease of the coil density results due to branching in our case.

Weight- and z-defined R_g -distributions were then calculated from the corresponding concentration and molecular weight profiles, the z-fraction z_i being defined as $z_i = (w_i M_i) / \sum w_i M_i$. Figure 2 illustrates a change in the differently weighted R_g -distributions during the pregelation period. Curves are normalized for easy shape comparison. The position of the maximum of the starting weight distribution of R_g related to the primary chain [Figure 2(a), sample 1] remained relatively constant, but progressively a broader shoulder developed and the height of the maximum decreased with increasing γ . A distortion (bimodality) observed here is due to the SEC mechanism as follows from the curvature of the plot shown in Figure 1, while MWD of the same system constructed after precipitation-dissolution fractionation was shown to be smooth and unimodal¹³, in agreement with theory¹⁷. Owing to intensity weighting, the maxima of the z-distribution are shifted to higher sizes [Figure 2(b)]; the increase in γ results in an increased reverse asymmetry as compared with weight distributions. The features of the z-distributions of R_g are less obvious in the case of R_h -distributions as calculated by the CONTIN procedure (Figure 3). To compare z-distributions from SEC and DLS data, the R_g -distributions were transformed into the same scale as obtained from CONTIN (the maximum ordinate is unity). For a linear polymer chain it was experimentally shown that $R_h \approx R_g$ (cf. Ref. 18). This is seen to be valid during the initial process of network buildup in the region of higher sizes (Figure 3). Since DLS loses sensitivity at low sizes due to intensity weighting, the R_h -distributions are known usually to be biased^{8,9,12} to some extent. Then the fractions of lower size should be underestimated and the related differences between R_h and R_g become smaller or even reverse ($R_h > R_g$, cf. Figure 3).

Having access to the R_g -distributions, the conventional statistical averages could be calculated:

$$\langle R_g \rangle_w = \sum w_i R_{g,i} / \sum w_i \quad (2)$$

$$\langle R_g \rangle_z = \sum w_i M_i R_{g,i} / \sum w_i M_i \quad (3)$$

The DLS-average hydrodynamic radius is defined^{19,20} as the inverse z -average

$$\left(\sum w_i M_i / R_{h,i} \right) / \sum w_i M_i = \langle 1/R_h \rangle_z \quad (4)$$

and, except for a 'monodisperse' polymer, $\langle R_h \rangle_z > \langle 1/R_h \rangle_z^{-1}$. The relative width of the z -distribution of diffusion coefficients (z -average normalized variance), ω_h , in terms of R_h

$$\omega_h = (\langle (1/R_h)^2 \rangle_z - \langle 1/R_h \rangle_z^2) / \langle 1/R_h \rangle_z^2 \quad (5)$$

where

$$\langle (1/R_h)^2 \rangle_z = \left(\sum w_i M_i / R_{h,i}^2 \right) / \sum w_i M_i \quad (6)$$

is also obtained from DLS data through the use of cumulants and inverse Laplace transform techniques⁸. Replacing R_h by R_g in equations (4) and (5), the analogous R_g and ω_g values were also evaluated. Finally, the well-known structure-sensitive parameter⁴

$$\rho = \langle R_g^2 \rangle_z^{1/2} \langle 1/R_h \rangle_z \quad (7)$$

which combines static LS and DLS data was calculated, $\langle R_g^2 \rangle_z$ being defined²¹ as

$$\langle R_g^2 \rangle_z = \sum w_i M_i R_{g,i}^2 / \sum w_i M_i \quad (8)$$

The conventional ρ parameter has been shown to increase with polydispersity and to decrease with branching⁴. In polydisperse randomly branched systems both effects are counteracting. Eventually they might be balanced and no dependence on branching may be detected. To eliminate the interfering polydispersity effect, the ρ' parameter was calculated from proper averages, i.e.

$$\rho' = \langle 1/R_g \rangle_z^{-1} \langle 1/R_h \rangle_z \quad (9)$$

All size averages, polydispersity criteria and values of the parameter ρ and ρ' obtained from SEC and DLS data are summarized in Table 2. Examining $\langle R_g^2 \rangle_z^{1/2}$ values in Tables 1 and 2 one finds that the agreement between independent size evaluation from MALS and SEC data is satisfactory and supports the eligibility of the ϕ value in equation (1). Also the ρ value of the so called primary chain ($\rho = 1.9$), as determined in this work, conforms to published experimental ρ values of poly(methyl methacrylate)s with $\langle M \rangle_w / \langle M \rangle_n < 2$ in good solvent²². Some extremely broad branched samples found in literature²³ have ρ values as high as 2.2.

Molecular weights, branching indices and all accessible size parameters of samples 1–6 were correlated as shown in Table 3. Experimental correlation exponents obey the prediction of the Flory-Stockmayer (FS) gelation theory^{3,24} quite well. The predicted power law relation between $\langle M \rangle_w$ or $\langle 1/R_h \rangle_z$ and the distance from the critical point ($1 - \gamma$) are, within the experimental error, adequate

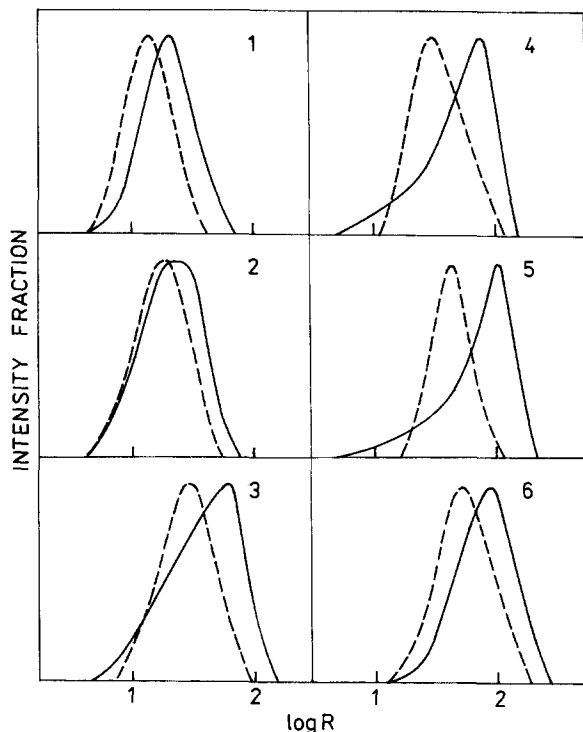


Figure 3 Comparison of z -distributions of (dashed line) hydrodynamic R_h and (solid line) static R_g size denoted with sample numbers (Table 1)

Table 2 Average size parameters of branched systems

Sample	$\langle R_g \rangle_w$ [nm]	$\langle R_g \rangle_z$	$\langle R_g^2 \rangle_z^{1/2}$	$\langle 1/R_g \rangle_z^{-1}$	$\langle 1/R_h \rangle_z^{-1}$	w_h	w_g	ρ	ρ'
1	15.7	24.6	27.5	19.5	14.5	0.16	0.27	1.90	1.34
2	15.0	26.2	31.0	20.0	17.0	0.25	0.40	1.82	1.18
3	20.7	52.6	61.5	33.8	30.5	0.22	0.68	2.01	1.10
4	23.3	64.3	68.3	41.7	34.0	0.26	0.88	2.14	1.23
5	28.4	94.3	105.3	58.4	46.0	0.14	1.18	2.29	1.26
6	65.4	103.5	112.3	79.6	61.5	0.24	0.33	1.82	1.30

Table 3 Proportionality exponents in correlations of molecular weight and average size vs. branching index and of average sizes vs. molecular weight

This work	Exponent predicted by the FS theory ^{3,4,17,24-26}	
	Theta solvent	Good solvent
Branched system		
$\langle M \rangle_w \sim (1 - \gamma)^{-1.1}$	1.0	
$\langle 1/R_h \rangle_z \sim (1 - \gamma)^{0.53}$	0.5	
$\langle R_g \rangle_w \sim \langle M \rangle_w^{0.27}$		
$\langle 1/R_h \rangle_z^{-1} \sim \langle M \rangle_w^{0.44}$	0.44	0.5
$\langle 1/R_g \rangle_z^{-1} \sim \langle M \rangle_w^{0.49}$		
$\langle R_g \rangle_z \sim \langle M \rangle_w^{0.58}$	0.5	0.6
$\langle R_g^2 \rangle_z^{1/2} \sim \langle M \rangle_w^{0.58}$	0.5	0.6
Linear system		
$\langle R_g \rangle_z \sim \langle M \rangle_w^{0.58*}$	0.5	0.6
$\langle R_g \rangle_w \sim \langle M \rangle_w^{0.58}$	0.5	0.6

* $\langle M \rangle_w / \langle M \rangle_n \sim \text{const.}$

also for a description of our system in the pregelation stage. The slope of a double logarithmic plot of $\langle R_g^2 \rangle_z^{1/2}$ or $\langle R_g \rangle_z$ vs. $\langle M \rangle_w$ are found here to be nearly the same as for a linear polymer with the most probable distribution¹⁷ ($\langle M \rangle_w / \langle M \rangle_n \sim 2$), i.e. the influence of branching and polydispersity are just compensated as implied by the classical FS theory. The lower the size average ($\langle R_g^2 \rangle_z^{1/2} > \langle R_g \rangle_z > \langle 1/R_g \rangle_z^{-1} > \langle R_g \rangle_w$) used in the dependence on $\langle M \rangle_w$ is, the lower is the correlation exponent since the compensation effect of polydispersity decreases and finally disappears when $\langle R_g \rangle_w$ is used (i.e. only branching effect is manifested).

Due to low DLS sensitivity to polydispersity, the widths ω_h of the size distributions as given by equation (5) are lower than the corresponding ω_g values calculated from the SEC data (Table 2). The difference is the higher the wider the distribution is. This apparent narrowing of DLS size distributions results in a difference of power laws between inverse z -averages of R_g and R_h and $\langle M \rangle_w$ (Table 3). A decrease in the half-widths of the DLS distributions at critical branching was experimentally found also by others²⁵. Contrary to the ρ values, the observed decrease in ρ' values reflects the effect of branching when compared to the primary chain (Table 2). The absence of an expected systematic decrease in ρ' as γ approached unity in the case of broad samples was at least partially explained above. As branching does not considerably change the expansion properties of the coils, the observed effect cannot be expected to exceed much the experimental error. Why ρ' value in the case of sample 6 was so high (the highest molecular weight fraction prepared from sample 5) is unclear. On the other hand, a decrease in polydispersity of sample 6 (Table 2) is evident from the related ω_g and ρ values.

CONCLUSION

To our knowledge it is the first time the changes of the real size distributions during the pregelation period are presented instead of distorted molecular weight distributions which could be obtained owing to the SEC separation mechanism.

The insensitivity of correlation between z -average dimensions of unfractionated samples and their $\langle M \rangle_w$ (cf. Refs^{3,17,24}) to the degree of branching was experimentally confirmed. The correlation of weight average radius of gyration $\langle R_g \rangle_w$, accessible from SEC data, with $\langle M \rangle_w$ is proposed for characterization of branching because the interfering effect of sample polydispersity is eliminated.

Since the branching agent in copolymer macromolecules was very dilute, the excluded volume effect has been found to be very similar to that of a linear chain. Then one can hardly expect a pronounced change in segment density of the coil, i.e. relative increase in the hydrodynamic size when compared with the static one. Apart from only small

nonsystematic decrease in ρ' in slightly branched systems (ρ' values $\rightarrow 1,1$; cf. Table 2) the ratio of inverse z -average static and hydrodynamic size (parameter ρ') did not exhibit a reliable dependence on branching.

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