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Relationship between the Molar Mass Distribution Width of Blocks and Chemical Heterogeneity of a Diblock Copolymer: Comparison between Theory and Experiment

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ABSTRACT: A modified anionic polymerization procedure has been developed, yielding a block copolymer with an intentionally broadened molar mass distribution of one or more blocks. Optimum conditions have been found which allow the P and Q parameters of the chemical heterogeneity of styrene/isoprene block copolymers to be measured by the light-scattering method with minimum error. Experimental values of these parameters for two diblock copolymers having a narrow and a broad molar mass distribution of the styrene and isoprene blocks were compared with the theoretical prediction; agreement was found within the limits of experimental error.

Introduction

Heterogeneity of a binary copolymer consisting of the constitutional units A and B is fully described by a two-dimensional distribution function of chemical composition and molar mass. The chemical heterogeneity is often characterized by experimentally available statistical moments of this function, the parameters P and Q. The parameter P is related to the mutual dependence of the chemical composition distribution and molar mass distribution, while the parameter Q characterizes the width of the chemical composition distribution.[1-4] The most suitable method for the determination of P and Q is light scattering.

Characterization of Copolymers by Light Scattering. Generally, light scattering from dilute copolymer solutions gives—instead of the true mass-average molar mass M_w^C—only an apparent value M^{ap}, for which two equivalent equations[1,2] may be written

$$M^{ap} = (\nu_A\nu_B/\nu_C^2)M_w^C + [\nu_A(\nu_A - \nu_B)/\nu_C^2]xM_w^A + [\nu_B(\nu_B - \nu_A)/\nu_C^2](1 - x)M_w^B \quad (1)$$

$$M^{ap} = M_w^C + [2(\nu_A - \nu_B)/\nu_C]P + [(\nu_A - \nu_B)/\nu_C]^2Q \quad (2)$$

where M_w^A and M_w^B are the mass-average molar masses of components A and B of the copolymer; ν_A, ν_B, and ν_C are the refractive index increments of the parent homopolymers A and B and of the copolymer, respectively, for which the relation

$$\nu_C = x\nu_A + (1 - x)\nu_B \quad (3)$$

is valid; here x is the average chemical composition of the sample expressed as the mass fraction of component A.

Relations between P, Q, M_w^A, M_w^B, and M_w^C read

$$2P = (1 - x)(M_w^C - M_w^B) - x(M_w^C - M_w^A) \quad (4)$$

$$Q = x(1 - x)(M_w^A + M_w^B - M_w^C) \quad (5)$$

The triads of the sought parameters M_w^C, P, Q or M_w^C, M_w^A, M_w^B can be obtained for the investigated copolymer by solving a system of at least three equations of type (1) or (2). It can be shown[4] that of all the triads of experimental points having coordinates $[M^{ap}, (\nu_A - \nu_B)/\nu_C]$ the stablest solution of the system is obtained by using the three points for which the following three conditions are successively fulfilled: (i) $|\nu_A|$ and $|\nu_B|$ large, sign ν_A = sign ν_B; (ii) $|\nu_A|$ large, $\nu_B = 0$; (iii) $\nu_A = 0$, $|\nu_B|$ large. Obviously, reliability of the determination of parameters M_w^C, P, and Q or M_w^C, M_w^A, and M_w^B increases with increasing number of experimental points.

In the processing of light-scattering data, M^{ap} is obtained by means of the relation

$$M^{ap} = (\Delta R_\theta/K'\nu_C^2c)_{c\to0,\theta\to0} \quad (6)$$

in which ΔR_θ is the excess Rayleigh ratio measured at the angle θ at the polymer concentration c, $K' = (2\pi^2n_0^2)/(\lambda_0^4N_A)$ is the optical constant, n_0 is the refractive index of the solvent, λ_0 is the wavelength of incident light in vacuum, and N_A is the Avogadro constant. By combining eq 1, 3, and 6 and by putting $\nu_A = 0$, we obtain a relation allowing M_w^B to be determined directly:

$$M_w^B = (1 - x)[\Delta R_\theta/K'\nu_B^2(1 - x)^2c]_{c\to0,\theta\to0} \quad (7)$$

Similarly, by putting $\nu_B = 0$, we obtain

$$M_w^A = x[\Delta R_\theta/K'\nu_A^2x^2c]_{c\to0,\theta\to0} \quad (8)$$

The expressions in brackets in eq 7 and 8 are apparent molar masses of the copolymer measured under the conditions $\nu_C = (1 - x)\nu_B$ and $\nu_C = x\nu_A$, respectively.

In addition to the procedure just described, Q may be obtained, in principle, by light scattering also in a single measurement:[4] If expression 6 is substituted into eq 2 and both sides of this equation are multiplied by ν_C^2, then for $\nu_C \to 0$ we obtain

$$Q = (\nu_A - \nu_B)^{-2}[\Delta R_\theta/K'c]_{c\to0,\theta\to0} \quad (9)$$

Hence, formally, the expression in brackets equals M^{ap} for $\nu_C = 1$.

Chemical Heterogeneity of Block Copolymers. Block copolymers, prepared by the anionic living polymerization, in most cases have relatively narrow molar mass distributions of blocks, and until recently their chemical heterogeneity has therefore been regarded as negligible. It has been shown, however, both theoretically[5-7] and experimentally,[6,8,9] that block copolymers possess a nonnegligible chemical heterogeneity, even if they do not contain any homopolymer. For most cases important in practice, it can be generally stated that, with respect to the extent of chemical heterogeneity, the common block copolymers lie between mixtures of homopolymers and statistical copolymers of similar chemical composition. Assuming the so-called random coupling of blocks[5-7,10] (i.e., assuming that propagation of the second block is not affected by the length of the first block which has initiated this propagation), relations have been derived[7] between the molar mass distribution width of blocks on the one hand and parameters of chemical heterogeneity on the other; these relations can be recast for a diblock copolymer to

$$a_C = x^2(a_A - 1) + (1 - x)^2(a_B - 1) + 1 \quad (10)$$

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$$P/M_w = [-x^3(a_A + a_B - 2) + x^2(a_A + 2a_B - 3) - x(a_B - 1)]/D \qquad (11)$$

$$Q/M_w = (x^4 - 2x^3 + x^2)(a_A + a_B - 2)/D \qquad (12)$$

where $D = x^2(a_A + a_B - 2) - 2x(a_B - 1) + a_B$; a_A, a_B, and a_C are the mass to number-average molar mass ratios, M_w/M_n, for block A, block B, and the diblock copolymer, respectively. Equations 10–12 have a general validity irrespective of the type of molar mass distribution of blocks; it follows from these equations that the a_A and a_B values only little higher than unity lead to relatively high Q/M_w values. Thus, e.g., for $a_A = a_B = 1.1$, which is an acceptable result of an anionic synthesis, and for $x = 0.5$, we obtain according to eq 12 the value of Q/M_w as high as 0.012, i.e., a value which statistical copolymers reach, in most cases, at high degree of conversion only.[11] For $a_A = a_B = 1.2$ and the same x we have $Q/M_w = 0.023$, which is a value so high that it usually can readily be measured by the light-scattering method.[12]

The anionic synthesis of a block copolymer can be arranged in such a way that a portion of the solution of a living polymer block of type A is removed from the reactor and isolated before the monomer B is added (cf., e.g., ref 13). This gives us a homopolymer precursor, the molecular parameters of which can be measured directly and are identical with those of the copolymer block polymerized first. In this case, of the quantities a_A, a_C, and a_B only the first two are experimentally available, while a_B can be calculated by using eq 10.

An attempt at an experimental verification of the theoretical prediction according to eq 10–12 is the main goal of this study. In order to minimize the relative errors of determination of a_A, a_C, P/M_w, and Q/M_w, it was necessary to develop such a modification of the anionic synthesis which—somewhat paradoxically—would allow us to prepare a block copolymer with broad molar mass distributions of both blocks, containing no homopolymer(s). The monomer pair styrene/isoprene was chosen for the present study; for the sake of comparison, in addition to the diblock copolymer with broad molar mass distributions of blocks, a diblock copolymer with narrow molar mass distributions of blocks was also prepared. Another goal of the study was to compare the results of determination of Q by measuring a number of solutions in various solvents (eq 2) with those obtained by measurements in a single solvent, isorefractive with the copolymer (eq 9).

Experimental Section

Syntheses. Two diblock copolymers of styrene and isoprene were synthesized, denoted as SI-n and SI-w, the former with a narrow and the latter with a broad molar mass distributions of blocks. Oligomeric (α-methylstyryl)lithium,[14] prepared at 25 °C in situ from *n*-butyllithium and α-methylstyrene was used as the initiator ("seed") and a mixture of benzene and diethyl ether [6/1–8/1 (v/v)] was used as a solvent. Styrene was always polymerized first. Strictly speaking, the copolymer molecules thus prepared consist in fact of three blocks, because they contain a short block of α-methylstyrene, but in view of the fact that the average degree of polymerization of styrene in this case is at least a hundred times higher than that of α-methylstyrene, the presence of these chemically similar short blocks was neglected. In the synthesis of both SI-n and SI-w, polystyrene precursors were isolated and denoted as S-n and S-w, respectively. Purification and drying of solvents and reaction components, as well as isolation and purification of polymeric products, were carried out by employing a procedure reported earlier,[14] with the exception of styrene which was dried in the final step by di-*n*-butylmagnesium.[15] All procedures were carried out by using a standard high-vacuum technique and break-seal ampules.[15,16] Both copolymers were stabilized with 2,6-di-*tert*-butyl-*p*-cresol (*t*-BC). Detailed descriptions of the polymerization procedures as well as the sketch of reactors are available upon request.

With only minor changes, the precursor S-n and copolymer SI-n were synthesized according to a procedure described earlier.[14]

The precursor S-w and copolymer SI-w were prepared by employing a modified method: After the initiating "seed" was formed, the larger part of the solution was poured from the reactor into a joined side tube, and only after that styrene was added to the solution which remained in the reactor. During the propagation of styrene the initiator solution was being continuously returned to the reactor from the side vessel; in this way, chains initiated at the onset of polymerization were longer than those initiated later, which broadened the molar mass distribution of the polystyrene block. To prevent the formation of homopolymer (polyisoprene) admixtures in the copolymer, continuous addition of the initiator had to be finished before the conversion of styrene was complete. After the styrene monomer had been consumed, the smaller part of the solution of living polystyrene was poured into the side tube, sealed off from the reactor, and terminated and the polystyrene precursor was isolated. The larger portion of the remaining poly(styryllithium) solution was again poured into another side tube, isoprene was then added to the remaining mixture in the reactor, and during its propagation the removed part of poly(styryllithium) solution was being continuously returned to the reactor; this brought about broadening of the molar mass distribution of the isoprene block. In order not to give rise to any polystyrene homopolymer, the readdition of initiating chains of the living polystyrene to propagating isoprene blocks had again to be completed before all isoprene had polymerized. On reaching the full degree of isoprene conversion, the living chains of the diblock copolymer were terminated and the product was isolated.

As the reference polyisoprene for refractive index increment measurements, the PIP-1 sample, also stabilized with *t*-BC, was used; its synthesis and characteristics have been given in ref 14 and its microstructure (content of the individual annelation structures) roughly agrees with that of polyisoprene blocks of the copolymers under study.

Solvents for Optical Measurements. The solvents were either used as received or rectified prior to use. Their purity was checked by gas chromatography. In the following list, we give in parentheses the solvent codes used throughout the text, the manufacturer, the estimated percentage of purity (uncorrected gas chromatography data), and the procedure used for purification, if any: bromoform (BF, Fluka, 99.0%; the presence of 1.0% ethanol, added by the manufacturer for stabilization, was verified by GC; ethanol was not removed), 1,1-diphenylethylene (DPE, Fluka, 98%), 1-chloronaphthalene (CN, Fluka, 99.8%), 1,2-dichloroethane (DCE, POC Gliwice, Poland, 99.9%), phenetole (PHE, Fluka, chromatographically pure after rectification), anisole (AS, Lachema, Czechoslovakia, 99.9% after repeated rectification), α-methylstyrene (AMS, Fluka, 99.5%), 1,2-dichlorobenzene (DCB, Laborchemie Apolda, GDR, 99.1%), 1,2,4-trichlorobenzene (TCB, Fluka, 98.9%).

Light Scattering. Scattering measurements were performed with each solvent or solution at 25 °C on two Sofica 42000 instruments (angular range 30–150°, vertically polarized light), one of which was provided with a standard mercury lamp (wavelength of the spectral line used $\lambda_0 = 546$ nm), the other was equipped with a He–Ne laser ($\lambda_0 = 633$ nm); such doubling of experimental results was intended to rule out a possible systematic instrumental error. Both instruments were calibrated with benzene, the Rayleigh ratios for benzene standard used were taken as 22.53×10^{-6} cm^{-1} for 546 nm and 12.55×10^{-6} cm^{-1} for 633 nm.[17] Optical clarification of solutions was carried out either by direct ultracentrifugation in the scattering cells[18] or by pressure filtration through a sintered-glass bacterial filter (Jena G-5). In most cases, after completion of the scattering measurement with one of the instruments, each optically clarified solution (or solvent) was measured immediately with the other, except the mixed solvents, which were isorefractive with the sample for 546 and 633 nm at slightly different solvent compositions. Experimental data were treated by the Zimm method[19] with a positive or negative[20] value of the constant k in the kc term. The estimated experimental error of M^{ap} and M_w was calculated from the standard deviation

Table I
Results of Membrane Osmometry and ^{1}H NMR Spectroscopy[a]

sample	$10^{-3}M_n^A$		$10^{-3}M_n^C$		x		structure[c]		
	theor	exptl	theor	exptl	theor	exptl	1,2	3,4	1,4
S-n	101	110 ± 10			1				
SI-n	101	99[b] ± 12	176	170 ± 20	0.576	0.58 ± 0.02	0.05	0.62	0.33
S-w	101	100 ± 3			1				
SI-w	101	112[b] ± 11	203	223 ± 20	0.496	0.50 ± 0.02	0.09	0.59	0.32

[a] M_n^A and M_n^C are number-average molar masses (in g/mol) of polystyrene precursors (S-n, S-w) and of styrene–isoprene diblock copolymers (SI-n, SI-w), respectively, calculated from the feed (theor) and measured by membrane osmometry (exptl); x is the mean mass fraction of styrene in the samples calculated from the feed (theor) and measured by ^{1}H NMR spectroscopy (exptl). [b] Values calculated from experimental M_n^C and x values by using eq 13. [c] Mole fractions of the individual structures of the isoprene blocks (content of the 1,4-structure is a sum of 1,4-cis and 1,4-trans contents).

of the respective quantity $Kc/\Delta R_\theta$ extrapolated to polymer concentration $c = 0$ and angle of measurement $\theta = 0°$; this standard deviation was obtained by a two-dimensional regression of scattering data. The stabilizer, i.e., *t*-BC, present in the samples SI-n, SI-w, and PIP-1, does not show fluorescence and therefore does not interfere with the light-scattering measurements.

Refractometry. The refractive indices, $n_{0,D}$, of the solvents used were measured with Abbé's refractometer (C. Zeiss, Jena, GDR) for $\lambda_0 = 589$ nm and 25 °C.

Differential Refractometry. Specific refractive index increments, ν, of polymer solutions were determined for $\lambda_0 = 546$ and 633 nm at 25 °C with a Brice-Phoenix Model BP-2000-V differential refractometer, calibrated with aqueous KCl solutions. Experimental errors of ν were expressed as standard deviations of slopes of the $\Delta n - c$ dependences (where Δn is the measured difference between the refractive indices of solution and solvent) and obtained by a linear regression from, in most cases, five experimental points. These deviations were used in the calculation of standard deviations of $(\nu_A - \nu_B)/\nu_C$.

Equilibrium Dialysis. The osmotic equilibrium between the polymer solution and polymer-free mixed solvent was established in simple stainless-steel dialyzers[21] at 25 °C within ca. 24 h using Sartorius SM 11539 membranes.

Membrane Osmometry. Number-average molar masses, M_n, were measured in toluene, with an automatic membrane osmometer Knauer at 37 °C with Schleicher-Schuell SS-08 membranes and with an automatic membrane osmometer Wescan, Model 231, at 42.5 °C (membranes supplied by the producer). For the same sample both instruments gave M_n values differing by less than 10%. The presence of the stabilizer *t*-BC in the samples SI-n and SI-w did not interfere with the determination of M_n; it only prolonged the time of the establishment of equilibrium in some cases. The value of M_n and its estimated experimental error were calculated from the intercept and its standard deviation (obtained by regression of the π/c vs. c data, where π is the osmotic pressure).

NMR Spectroscopy. The ^{1}H NMR spectra of block copolymers SI-n and SI-w were recorded with a PS-100 (JEOL) spectrometer at 70 and 74 °C, respectively, at 100 MHz, with CCl_4 as solvent and hexamethyldisiloxane as internal standard. Copolymer composition was calculated from the ratio of integrated peaks of aromatic and nonaromatic protons. The proton signals of the isoprene component were assigned according to the reported data.[22] The microstructure of isoprene blocks was determined from integrated signals of olefinic protons.[14,22]

Results and Discussion

Syntheses. The M_n value of samples S-w and SI-w prepared by our modified method (cf. Experimental Section) is the same as that which would be obtained in a standard synthesis (when the monomer is added at once to the *entire* initiator) under otherwise identical conditions, because the number of macromolecules formed is always the same (irrespective of the polymerization regime) and equal to that of the initiating entities. The expected M_n^A, M_n^C, and x values (i.e., the number-average molar masses of the polystyrene block and of the whole copolymer and the mass fraction of styrene constitutional units, respectively), calculated from the mass balance of both polymerizations, are compared in Table I with experimental values, obtained by membrane osmometry and ^{1}H NMR. For the sake of completeness, Table I also gives the relative content of 1,2-, 3,4-, and 1,4-structures in isoprene blocks. Here and throughout the following text, the component A of the copolymer always means styrene, the component B means isoprene. The fraction x determined by NMR includes also a small portion of α-methylstyrene, in addition to styrene (cf. Experimental Section).

No attempt has been made to check whether or not a homopolymeric admixture is present in the copolymers; this would be revealed by fractionation according to chemical composition, which will be the topic of a forthcoming study.

According to Table I, the measured M_n and x values coincide within the limits of experimental errors with those estimated from the monomer and initiator feed. The tabulated experimental M_n^A values of the copolymers SI-n and SI-w obtained by using the equation

$$M_n^A = xM_n^C \qquad (13)$$

also agree with the measured M_n^A values of the precursors S-n and S-w; this agreement verifies the intrinsic consistency of osmometric data.

Choice of Solvents for Optical Measurements. The M^{ap} and ν values were measured by using both single and mixed binary solvents. Binary solvents were used, when exact isorefractivity with the copolymer or with its parent homopolymer components was mandatory; this is difficult to achieve with single solvents (in this study, it is only DPE which is isorefractive with polystyrene at 546 nm and 25 °C).

In a general case, however, the application of mixed solvents is complicated by the phenomenon of preferential sorption (cf., e.g., ref 23) of some components onto the polymer. In order to eliminate the effect of preferential sorption on M_w values (or, with copolymers, on M^{ap}) determined by the light-scattering method, the scattering data must be treated by using the refractive index increment ν_μ, measured at a constant chemical potentials of all diffusible components of the solvent, i.e., after the establishment of osmotic equilibrium between the polymer solution and the polymer-free mixed solvent, instead of the conventional refractive index increment ν_ϕ, measured at a constant composition of the mixed solvent.[4]

Common requirements to be observed in selecting both single and binary mixed solvents (Table II) were that these solvents (in the case of binary ones, both components simultaneously) should be thermodynamically good for the copolymer and both parent homopolymers and as nonvolatile and optically stable as possible.

Another criterion observed in the choice of single solvents was, in particular, suitable refractive index values n_0 (the method described in ref 12 was used): we tried to cover the broadest possible interval of the variable (ν_A –

Table II
Results of Light Scattering, Refractometry, and Differential Refractometry for 25 °C[a]

solvent	$10^{-3}M^{\mathrm{ap}}$			ν (λ_0 = 546 nm)			ν (λ_0 = 633 nm)		
	546 nm	633 nm	$n_{0,\mathrm{D}}$	S-w	SI-w	PIP-1	S-w	SI-w	PIP-1
BF	224 ± 19	225 ± 12	1.5881	0.023	−0.032	−0.086	0.022	−0.031	−0.084
DPE + 15% CN		239 ± 5	1.6101				−0.002	-0.052^b	-0.104^b
DPE	279 ± 8		1.6063	0.000_5	-0.053^b	-0.107^b	0.002		
CN	211 ± 10	207 ± 22	1.6302	−0.020	−0.082	−0.133	−0.016	−0.075	−0.122
DCE	325 ± 3	338 ± 6	1.4426	0.152	0.114	0.073	0.148	0.110	0.071
PHE + 14% AMS		371 ± 11	1.5098	0.090^b	0.046	−0.001	0.089^b	0.045^b	0.001
PHE + 10% AMS	374 ± 12		1.5085	0.091^b	0.045	0.000	0.090^b	0.047^b	0.002
AS	437 ± 10	514 ± 16	1.5150	0.086	0.039	−0.008	0.086	0.039	−0.007
AMS	632 ± 43	732 ± 30	1.5360	0.065	0.019	−0.032	0.067	0.020	−0.027
DCB + 10.6% CN		56	1.5580				0.046	0.002^b	
DCB + 9.3% CN	44		1.5570	0.047	0.001				

[a] M^{ap} is the apparent molar mass (in g/mol) of the copolymer SI-w, $n_{0,\mathrm{D}}$ is the refractive index of solvent at 25 °C and λ_0 = 589 nm, ν is the refractive index increment (in cm^3/g, 25 °C, λ_0 = 546 and/or 633 nm) for polystyrene S-w, copolymer SI-w, and polyisoprene PIP-1. In mixed solvents (composition in vol %) $\nu = \nu_\phi \approx \nu_\mu$ (cf. text). [b] Values obtained by interpolation according to Figures 1a,b.

Table III
Refractive Index Increments (in cm³/g) of Samples SI-n, SI-w, and PIP-1 at 546 nm and 25 °C

polymer	mixed solvent	$\nu_\phi{}^a$	$\nu_\mu{}^b$
SI-n	DCB with 50 vol % TCB	0.000	0.002
SI-w	DCB with 9.3 vol % CN	−0.001	0.000
SI-w	PHE with 10 vol % AMS	0.045	0.045
PIP-1	PHE with 10 vol % AMS	-0.000_5	-0.000_4

[a] Conditions of a constant composition of mixed solvent. [b] Conditions of a constant chemical potential of all diffusible components of solution. For the codes of solvents cf. Experimental Section.

$\nu_\mathrm{B})/\nu_\mathrm{C}$ while maintaining a tolerable accuracy of measurement of M^{ap} and to distribute equidistantly points in this interval.

When searching for a composition of a mixed solvent for which $\nu_{\mathrm{B},\mu} = 0$ (isorefractivity condition for polyisoprene) or $\nu_{\mathrm{C},\mu} = 0$ (isorefractivity condition for the whole copolymer), we measured $\nu_{\mathrm{B},\mu}$ or $\nu_{\mathrm{C},\mu}$ as a function of the solvent composition by means of standard dialysis experiments.[21,23] (An alternative procedure[4,24] consists of the search for a minimum of the dependence of excess scattering intensity on the mixed-solvent composition.)

Results of the measurements of ν_ϕ and ν_μ values at 546 nm and 25 °C for mixed solvents DCB with 50 vol % TCB (isorefractive with SI-n), DCB with 9.3 vol % CN (isorefractive with SI-w), and PHE with 10 vol % AMS (isorefractive with polyisoprene) are summarized in Table III (under the given conditions, a single solvent, i.e., DPE, is isorefractive with polystyrene). It can be seen in Table III that in two cases the differences $\nu_\phi - \nu_\mu$ are smaller than the generally accepted experimental error of determination of ν, while in the other cases they are almost zero. Hence we have that, in the mixed solvents used, the effect of preferential sorption can be neglected; consequently, for the light-scattering data treatment, the ν_μ values can be replaced, without affecting the accuracy, with the ν_ϕ values given for SI-w in Table II.

Heterogeneity of the Sample SI-w. The copolymer SI-w with a broad molar mass distribution of both blocks was characterized in detail by differential refractometry and light scattering.

In Figure 1 the refractive index increments ν_ϕ ($\approx \nu_\mu$) of the copolymer SI-w and of both parent homopolymers S-w and PIP-1 measured at 25 °C and both wavelengths are plotted against the refractive indices of all single and mixed solvents used; $n_{0,\mathrm{D}}$ values were measured for the same temperature but for the wavelength λ_0 = 589 nm (D line of the sodium spectrum). As the wavelengths for which the ν and n_0 values have been determined do not coincide, it is not possible to calculate any physically meaningful parameters from intercepts and slopes of the straight lines obtained; from the practical viewpoint, however, these dependences are useful, because they make possible a relatively reliable and exact interpolation of the ν_ϕ values or allow a single isorefractive solvent to be found. Moreover, the fact that in Figure 1 the experimental points very adequately fit the regression straight lines indicates that the ν_ϕ data are internally consistent and no solvent effect is observed.

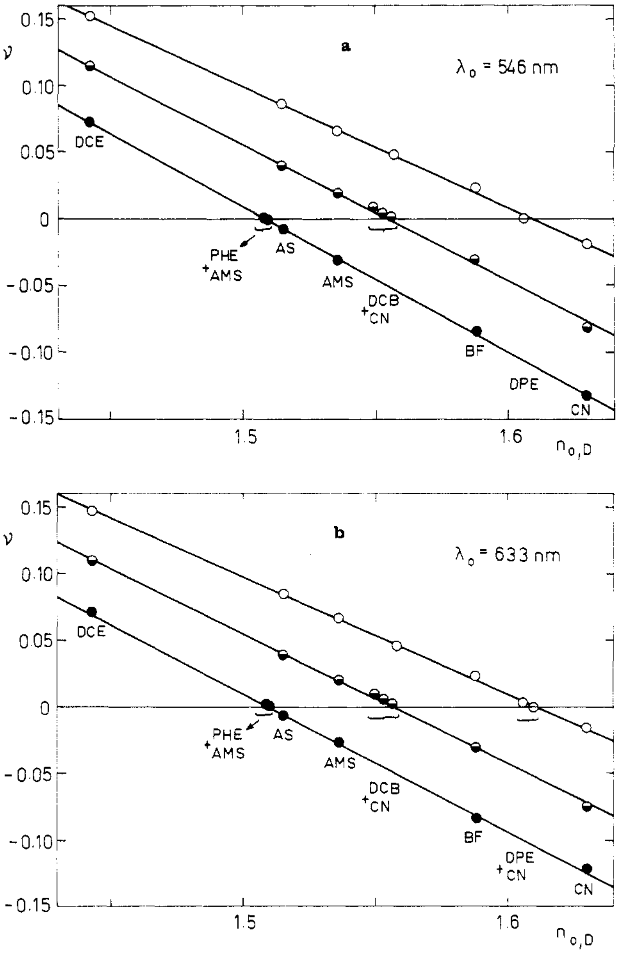

Figure 1. Plot of the specific refractive index increment ν (in cm^3/g) measured at 25 °C at two wavelengths (a, 546 nm; b, 633 nm) against the refractive index of the solvent, $n_{0,\mathrm{D}}$ (25 °C, 589 nm): (○) polystyrene; (⊖) copolymer SI-w; (●) polyisoprene. Straight lines correspond to linear regression. For codes used for the solvents see Experimental Section.

Table IV
Results of the Chemical Heterogeneity Measurements of the Styrene–Isoprene Diblock Copolymer SI-w[a]

						$10^{-3}M_w^A$					$10^{-3}M_w^B$		
	eq 2			eq 9, $10^{-3}Q$[b]			eq 8[b]		precursor S-w[b]			eq 7[b]	
	$10^{-3}M_w^C$	$10^{-3}P$	$10^{-3}Q$	546	633	eq 4 and 5	546	633	546	633	eq 4, 5	546	633
av values	292	22	7	11	14	204	187	186	179	184	116	139	119
std dev	18	3	2	2	2	13	6	6	2	2	13	4	2

[a] M_w^A, M_w^B, and M_w^C are mass-average molar masses (in g/mol) of block A, block B, and the whole copolymer, respectively, P and Q are parameters of chemical heterogeneity. [b] λ_0 (nm).

Table V
Calculated a_B Values and a Comparison between Measured and Calculated P/M_w^C and Q/M_w^C for Styrene–Isoprene Diblock Copolymers SI-n and SI-w[a]

	input data				P/M_w^C		Q/M_w^C	
sample	a_C	a_A	x	a_B calcd	exptl	calcd	exptl	calcd
SI-n av value	1.08	1.1	0.58	1.2_4		−0.01	0.006	0.02
std dev	0.06	0.1	0.02	0.4		0.04		0.02
SI-w av value	1.3	1.84	0.50	1.4	0.08	0.04	0.038	0.06
std dev	0.1	0.07	0.02	0.6	0.01	0.06	0.007	0.02

[a] Calculations were carried out by using eq 10–12 with the input data a_C, a_A, and x. Quantities a_A, a_B, and a_C are M_w/M_n values of block A, block B, and the whole copolymer, respectively; P and Q are parameters of chemical heterogeneity; M_w and M_n are mass- and number-average molar masses (in g/mol), respectively.

As three basic points $[M^{ap}, (\nu_A - \nu_B)/\nu_C]$ on parabola 2, those were selected for which the conditions $\nu_{A,\mu} = 0$ (mixed solvent DPE/CN), $\nu_{B,\mu} = 0$ (PHE/AMS), and $\nu_{C,\phi}$ high (single solvent DCE, cf. Introduction) are successively valid; four other points obtained by measurement in single solvents (Figure 2, Table II) have been added to these three points in order to increase reliability. Since both M^{ap} and $(\nu_A - \nu_B)/\nu_C$ were measured at 546 as well as at 633 nm, there is a total of 14 points at disposal for the quadratic regression according to eq 2. The standard deviations of the quantity $(\nu_A - \nu_B)/\nu_C$ shown in Figure 2 were calculated for each point from those of the quantities ν_A, ν_B, and ν_C (cf. error analysis, eq 14). The results of quadratic regression of data from Table II according to the system of equations (2), i.e., the M_w^C, P, and Q values, are given in Figure 2 and in the first three columns of Table IV.

An alternative independent method of determination of Q is a single light-scattering measurement under the condition $\nu_{C,\mu} = 0$ (which for SI-w can be fulfilled in the mixed solvent DCB/CN, cf. Tables II and III) followed by the treatment of the scattering data according to eq 9.

A comparison of Q values obtained by means of these two procedures (Table IV) shows that their difference is slightly larger than the experimental errors reported in this study; it seems, however, that the error is somewhat underrated here (for experimental errors cf. Experimental Section and further text).

Table IV also contains a comparison of M_w^A values obtained by (i) calculations using eq 4 and 5, the input data of which were M_w^C, P, and Q values from the first three columns of this table, (ii) measurement of M^{ap} of the copolymer SI-w under the condition $\nu_{B,\mu} \approx 0$ (eq 8), and (iii) measurement of M_w of the polystyrene precursor S-w. Similarly, in Table IV, we have a comparison of M_w^B values obtained by a calculation analogous to case (i) for M_w^A and by measuring M^{ap} of the copolymer SI-w under the condition $\nu_{A,\mu} \approx 0$ (eq 7). A good agreement ensues from this comparison for both M_w^A and M_w^B.

In Table V, in addition to the calculated a_B value which is not directly measurable, a comparison between the measured and calculated P/M_w^C and Q/M_w^C values is given: experimental values have been determined by using data in Table IV, with the arithmetic mean from values in the third to fifth columns of Table IV being substituted for Q, while the calculated values have been obtained by using eq 10–12, the input data of which were a_C, a_A, and x values in the first three columns of Table V; the values of a_C, a_A, and x have been determined by combining the data in Tables I and IV. It is obvious that the intervals of calculated and measured P/M_w^C and Q/M_w^C values delimited by the experimental error partly overlap each other.

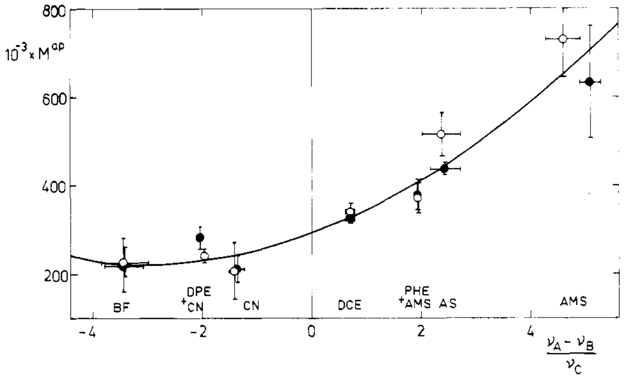

Figure 2. Dependence of the apparent molar mass M^{ap} (in g/mol) of the sample SI-w on $(\nu_A - \nu_B)/\nu_C$ according to eq 2, where ν_A, ν_B, and ν_C (in cm^3/g) are the specific refractive index increments of polystyrene, polyisoprene, and the copolymer SI-w, respectively. The points ● and ○ correspond to the two wavelengths of light used in the light scattering and differential refractometry, viz., 546 and 633 nm; for the sake of clarity, lengths of horizontal and vertical bars are sixfold values of the standard deviations of the two respective variables; solid line is a parabola calculated from all 14 points by the quadratic regression; for codes of the solvents used see Experimental Section.

An analysis reveals that the experimentally determined Q/M_w^C values for SI-w lie well within physically justified limits.

Heterogeneity of the Sample SI-n. For the copolymer SI-n with a narrow molar mass distribution of both blocks, only Q has been determined by the light-scattering measurement at $\lambda_0 = 546$ nm under the condition $\nu_{C,\mu} = 0$. A virtually isorefractive solvent is DCB with 50 vol % TCB (Table III). The scattering measurement in this case also gave, even for very high copolymer concentrations, only very low values of the excess Rayleigh ratio ΔR_θ (for the highest concentration used, 0.0196 g/cm^3, and the angle

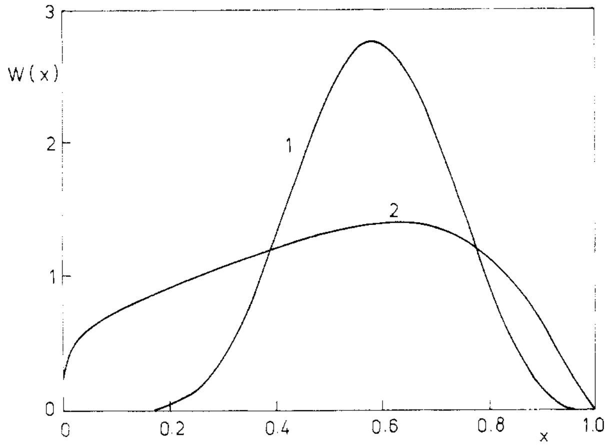

Figure 3. Differential mass distribution functions $W(x)$ of chemical composition x (mass fraction of styrene) of the individual chains of styrene–isoprene diblock copolymers SI-n (1) and SI-w (2) calculated by assuming the Schulz–Zimm molar mass distribution of both blocks.

of measurement 90°, the determined ΔR_θ value was as low as 12% of the Rayleigh ratio for a pure solvent), which indicates a relatively low chemical heterogeneity of the sample SI-n. The resulting considerable scatter of experimental points in the Zimm plot dramatically reduces the accuracy of extrapolation, so that the treatment of the scattering data in the sense of eq 9 gave only a semiquantitative estimate of Q (ca. 1200 g/mol) and did not allow the standard deviation to be determined. The Q value is so low that the apparent molar mass $M^{\mathrm{ap}} = 183 \times 10^3$ g/mol, determined for SI-n by the scattering measurement in DCE, where the refractive index increment is high ($\nu_\mathrm{C} = 0.126$ cm^3/g), is not affected by chemical heterogeneity and can be regarded as M_w^C. This allowed us to determine $Q/M_\mathrm{w}^\mathrm{C}$, which for SI-n is lower by almost an order of magnitude than for SI-w (Table V).

The approximation $M^{\mathrm{ap}} \approx M_\mathrm{w}^\mathrm{C}$ for SI-n in DCE can be justified by a simple calculation; the result shows that the expression $(M^{\mathrm{ap}} - M_\mathrm{w}^\mathrm{C})/M_\mathrm{w}^\mathrm{C}$ cannot exceed ca. 10% in the given case, which is a generally accepted error of determination of M_w by the light-scattering method.

For the polystyrene precursor S-n, $M_\mathrm{w}^\mathrm{A} = (122 \pm 2) \times 10^3$ g/mol was determined by light scattering (546 nm, 25 °C, DCE); M_w^C for SI-n has already been given above, and M_n^A and M_n^C for S-n and SI-n, respectively, are given in Table I. From these values, a_C and a_A were computed, which along with the composition x are input data for the calculation using eq 10–12 (Table V). A comparison between theory and experiment in the case of the sample SI-n is possible only for $Q/M_\mathrm{w}^\mathrm{C}$: its measured value lies in the interval delimited by the standard deviation of the calculated value (Table V).

Also for the SI-n copolymer, experimental $Q/M_\mathrm{w}^\mathrm{C}$ values are physically admissible.

Distribution Function of Chemical Composition. For the sake of illustration, the differential mass distribution functions of chemical composition of the samples SI-n and SI-w (Figure 3) were calculated from a_A, a_B (Table V), M_n^A, x (second and sixth columns of Table I), and M_n^B (the relation $M_\mathrm{n}^\mathrm{A} + M_\mathrm{n}^\mathrm{B} = M_\mathrm{n}^\mathrm{C}$). A method described in ref 7 was used, based on the assumption that both copolymer blocks have the Schulz–Zimm molar mass distribution. A comparison of these distribution functions with experimental ones obtained by the fractionation according to chemical composition will be dealt with in a forthcoming study.

Error Analysis. The majority of data in Tables I–V and Figure 2 are given with an estimated experimental error. All these errors are standard deviations, determined either directly from primary data or—in the case of derived quantities—by calculation from primary data deviations; in this calculation, the well-known relation for the standard deviation s_f of the function $f = f(y_1, y_2, ..., y_n)$ of n variables was used

$$s_\mathrm{f} = [\sum_{i=1}^{n} (\partial f/\partial y_i)^2 s_{y,i}^{\ 2}]^{1/2} \tag{14}$$

where $s_{y,i}$ is the standard deviation of the variable y_i. The quantity x is the only exception: its standard deviation was not determined but was estimated to be 0.02 on the basis of the generally accepted accuracy of the NMR method.

Since one of the main objectives of this study was an experimental verification of the validity of eq 10–12, derived in ref 7, calculation of the standard deviations of $P/M_\mathrm{w}^\mathrm{C}$, $Q/M_\mathrm{w}^\mathrm{C}$, and a_B from the mean values and standard deviations of a_C, a_A, and x was of key importance. The respective partial derivatives in the sense of eq 14 needed for the calculation are not given in this study due to their space requirements and can be supplied upon request. The results of these calculations are summarized in Table V. It appears that although the calculated mean $P/M_\mathrm{w}^\mathrm{C}$ and $Q/M_\mathrm{w}^\mathrm{C}$ values fit in adequately well with the experiment, the results of the calculations are to be taken with caution, because (especially with the sample SI-n) the relative errors of these quantities, obtained as the ratio of the standard deviation to average value, are rather high, due to low average values. In other words, the calculated quantities $P/M_\mathrm{w}^\mathrm{C}$, $Q/M_\mathrm{w}^\mathrm{C}$, and a_B are very sensitive to the accuracy of determination of the a_C, a_A, and x values. Both quantities in $M_\mathrm{w}/M_\mathrm{n}$ should be measured with greater accuracy than that allowed by the combination of light scattering and membrane osmometry. As expected, from the error analysis it follows that the requirement to the accuracy of determination of both quantities in $M_\mathrm{w}/M_\mathrm{n}$ increases with decreasing value of this ratio. Since in a general case neither gel permeation chromatography nor precipitation fractionation can provide direct information on the a_C value of the block copolymer (shape of the elution curve and the result of fractionation are affected by superimposed molar mass and chemical composition distributions), a sufficiently accurate determination of a_C remains an open methodical problem.

Conclusions

(i) Using the suggested modification of anionic polymerization, it was possible to broaden considerably the molar mass distributions of both blocks and to raise pronouncedly the chemical heterogeneity of the styrene–isoprene copolymer, which could thus be measured with an acceptable accuracy by light scattering.

(ii) The results of determination of the parameter Q of a copolymer with a broad molar mass distribution of both blocks obtained by light-scattering measurements in several solvents (eq 2) are close to those obtained by a single measurement in an isorefractive solvent (eq 9).

(iii) The values of the parameters P and Q of the diblock copolymer of styrene and isoprene with a broad molar-mass distribution of both blocks agree within the limits of experimental error with those predicted by theory.[7] For a copolymer prepared by the standard anionic synthesis, this agreement was verified and confirmed only for the parameter Q.

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Registry No. (S)(I) (block copolymer), 105729-79-1.

References and Notes

(1) Benoît, H.; Froelich, D. In *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic: London, 1972; p 467.
(2) Eskin, V. Ye. *Rasseyaniye Sveta Rastvorami Polimerov*; Nauka: Moscow, 1973.
(3) Bushuk, W.; Benoît, H. *Can. J. Chem.* **1958**, *36*, 1616.
(4) Tuzar, Z.; Kratochvíl, P.; Straková, D. *Eur. Polym. J.* **1970**, *6*, 1113.
(5) Kotaka, T.; Donkai, N.; Min, T. I. *Bull. Inst. Chem. Res., Kyoto Univ.* **1974**, *52*, 332.
(6) Tanaka, T.; Omoto, M.; Donkai, N.; Inagaki, H. *J. Macromol. Sci., Phys.* **1980**, *B17*, 211.
(7) Stejskal, J.; Kratochvíl, P. *Polym. J.* **1982**, *14*, 603.
(8) Kuhn, R. *Makromol. Chem.* **1980**, *181*, 725.
(9) Dumelow, T.; Holding, S. R.; Maisey, L. J.; Dawkins, J. V. *Polymer* **1986**, *27*, 1170.
(10) Omoto, M.; Tanaka, T.; Kadokura, S.; Inagaki, H. *Polymer* **1979**, *20*, 129.
(11) Procházka, O.; Kratochvíl, P. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *22*, 501.
(12) Podešva, J. *Eur. Polym. J.* **1982**, *18*, 667.
(13) Ohnuma, H.; Kotaka, T.; Inagaki, H. *Polymer* **1969**, *10*, 501.
(14) Podešva, J.; Špaček, P.; Sikora, A.; Podol'skii, A. F. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3343.
(15) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(16) Fetters, L. J. *J. Res. Natl. Bur. Stand., Sect. A* **1966**, *70*, 421.
(17) Millaud, B.; Strazielle, C. *Makromol. Chem.* **1979**, *180*, 441.
(18) Mrkvičková-Vaculová, L.; Kratochvíl, P. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2015.
(19) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(20) van Wijk, R.; Staverman, A. J. *J. Polym. Sci., Polym. Phys. Chem.* **1966**, *4*, 1011.
(21) Tuzar, Z.; Kratochvíl, P. *Collect. Czech. Chem. Commun.* **1967**, *32*, 3358.
(22) Šimák, P.; Fahrbach, G. *Angew. Makromol. Chem.* **1970**, *12*, 73.
(23) Strazielle, C. In *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic: London, 1972; p 633.
(24) Kuhn, R. *Makromol. Chem.* **1984**, *185*, 1003.

Properties of Dimethylsiloxane Microphases in Phase-Separated Dimethylsiloxane Block Copolymers

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ABSTRACT: Differential scanning calorimetry after fast, 200 K min^{-1}, and slow, 10 K min^{-1}, cooling rates was used to study the glass-transition temperature, T_g, and the crystallization and melting of dimethylsiloxane, DMS, microphases in styrene–dimethylsiloxane (S–DMS) block copolymers. The T_g's of amorphous DMS microphases in S–DMS diblock copolymers containing $\leq$28 wt % DMS were 6 K lower than the T_g = 145 K of slightly crystalline PDMS. This T_g lowering was apparently caused by thermal stress effects, as confirmed by calculations. Under the conditions of these experiments, DMS blocks with molecular weights $\leq$3800 did not crystallize, while those with molecular weights $\geq$15 400 were semicrystalline. The degree of crystallinity of semicrystalline DMS microphases which had been cooled from above the crystallization temperature at 10 K min^{-1} and then reheated at 10 K min^{-1} averaged 10% higher in samples containing $\geq$71 wt % DMS than in those containing $\leq$53 wt % DMS. These results are probably connected with the surface-to-volume ratios of the microphases. Single melting peaks were observed in samples that had been cooled at 10 K min^{-1}, while double melting peaks were observed in samples that had been cooled at 200 K min^{-1}.

Introduction

In a previous publication from this laboratory,[1] glass-transition data obtained by using differential scanning calorimetry (DSC) on dimethylsiloxane (DMS) microphases in some styrene–dimethylsiloxane (S–DMS) diblock copolymers were reported and discussed. Most of the DMS microphases made up of blocks with number-average molecular weights above 3600 were semicrystalline, but crystallization and melting data were not reported in that work because of problems with base lines in the crystallization and melting region obtained by using the DuPont 990 thermal analyzer. The DMS glass transitions of the amorphous DMS microphases were broadened relative to those of polydimethylsiloxane (PDMS), while the heat capacity change at the glass transition, ΔC_p, was comparable to that of PDMS. The T_g's of five fully amorphous DMS microphases were reported; one of these was 2 deg less than that of PDMS while the rest were 4–10 K higher than that of PDMS. The results were discussed qualitatively in terms of the thermal stress field that exists in these samples below the T_g of the styrene (S) microphases. This thermal stress field is caused by the unequal coefficients of thermal expansion of the two phases below the S microphase T_g. The rubbery DMS microphase has a larger thermal expansion coefficient than the glassy S microphase. When the rubbery DMS microphases are inclusions in the glassy PS matrix, these DMS inclusions are under a greater dilatational stress as the temperature decreases farther below the S microphases T_g. This dilatational stress is equivalent to a pressure decrease and thus leads to a decrease in the T_g of the DMS inclusions in the S microphase. The same argument holds for any rubbery inclusion in a glassy matrix. As an example, the thermal stress field in both phases in rubber-modified plastics such as high-impact polystyrene (PS) was studied by Paterno and Sternstein[2] who found that the dilatational stresses in the rubber particles should and do lead to a small decrease in T_g of these particles. Their work also indicates that an increase of the T_g of a rubbery microphase should be expected when this phase comprises the matrix instead of the inclusion. The calculations of the expected T_g increase are not straightforward and have not yet been attempted. The rubbery matrix should be able to sustain a stress field up to a few diameters away from the glassy inclusions. This leads to a small increase of the T_g. Earlier work by Beck et al.[3] only estimated the thermal stresses on rubbery inclusions in glassy matrices.

In the present work, the use of a much more accurate and precise DSC than that used in the previous work allowed us not only to obtain significant information on the

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