

Heterogeneity Parameters by Light Scattering for Statistical Copolymers Incorporating Long Side-Chain Comonomers

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Synopsis

Heterogeneity parameters were obtained by light scattering for a series of statistical copolymers incorporating long side-chain comonomers, by employing the method of Bushuk and Benoit. These copolymers were selected to exhibit varied compositional drift as required by copolymerization theory. The magnitude of the parameters found agreed qualitatively with the heterogeneity expected from the drift in composition with conversion. This was calculated using the treatment of Skeist, as modified by Kruse. However, values greater than the limit of unity were found in two instances for the heterogeneity index, Q/Q_{\max} , which relates the compositional drift constant Q to the maximum value obtained for mixtures of homopolymers. These anomalies were attributed to the insensitivity of the method for heterogeneous copolymers having small differences in the refractive increments of their respective homopolymers. The magnitude and sign of P , which reflects molecular weight effects on composition, was questionable because of experimental error. Both effects appear to be general deficiencies of the method, which limit its practical use. For solvents with high values of dn/dc (≈ 0.1), the observed weight-average molecular weight approached the true value.

INTRODUCTION

It is well known¹ that the intensity of light scattered by copolymers increases anomalously at low values of the refractive increment. Consequently, the observed weight-average molecular weights increase as refractive increment is lowered in a series of solvents. This was first attributed² to the distribution of the values of dn/dc with the variable composition present in both the instantaneously formed copolymer,³ and as composition drifts with conversion.⁴ The phenomenon was first treated theoretically by Stockmayer⁵ from a consideration of azeotropic copolymers. This theory was later extended by Bushuk and Benoit⁶ to provide a convenient means of determining heterogeneity in copolymers. The latter work provided parameters characterizing compositional drift resulting from both molecular weight distribution and reactivity differences between the comonomers, as well as yielding the true weight-average molecular weight of the copolymer, and of the components of the copoly-

mer. Experimental data obtained by the method have, so far, been limited essentially to copolymers of styrene and methyl methacrylate, but these included statistical copolymers,⁶⁻⁸ graft copolymers,⁹⁻¹¹ block copolymers^{6,7,12,13} and mixtures of homopolymers.^{6,7} Other systems studied were a styrene-acrylonitrile azeotropic copolymer¹⁴ and a statistical ethyl acrylate-methyl methacrylate copolymer.¹⁵ Both showed little heterogeneity by the method.

In this work the effect of increasing compositional heterogeneity and broad molecular weight distribution was evaluated by the method for a series of statistical copolymers containing long side-chain comonomers. Copolymers employed were *n*-octadecyl acrylate with, respectively, styrene, *n*-butyl acrylate, and vinyl acetate and *N*-*n*-octadecylacrylamide with, respectively, vinylidene chloride and acrylonitrile. Because Price-Alfrey parameters were available for both of the long side-chain comonomers^{16,17} the drift in composition with conversion could be computed.⁴ Batch copolymerization to high conversions and branching through the side-chain were expected to cause extensive molecular weight broadening. These factors, coupled with variation in the refractive increment differences between the homopolymer pairs, were expected to impose a severe test of the practical utility of the method.

EXPERIMENTAL

Preparation of the Long Side-Chain Monomers

N-*n*-Octadecylacrylamide was prepared as described.¹⁸ *n*-Octadecyl acrylate was obtained under special purchase from Monomer-Polymer Corporation and its physical properties have been described.¹⁹ The amide and ester were, respectively, 98.5% and 95% pure by gas-liquid chromatography. The ester was 99% pure by ester number; its impurities appeared to be the lower homologs, principally C₁₆. Other vinyl monomers were the purest available commercially and were distilled just before use.

Polymerization Procedure

The copolymers containing *n*-octadecyl acrylate were prepared as follows. The styrene series were copolymerized in bulk at 60°C and were initiated with 0.2 mole-% of azobisisobutyronitrile (AIBN); the vinyl acetate series were copolymerized in benzene in a mole ratio of one, based on total monomers, and were initiated with 0.4 mole-% of AIBN; the *n*-butyl acrylate series were copolymerized in benzene at 63°C at a mole ratio of solvent to monomer of four, based on total monomer and were initiated with 0.2 mole-% of AIBN and regulated with 0.1 mole-% of *n*-dodecyl mercaptan. The copolymers incorporating *N*-*n*-octadecylacrylamide were prepared as follows; the vinylidene chloride series, through a feed composition of 25 mole-% of amide, were copolymerized in dispersion at 60°C with the use of a 0.5% polyvinyl alcohol solution (2 ml/g based on total monomer) containing 1.5 wt-% powdered magnesium car-

bonate (based on water) as a dispersing agent. The initiator was 0.1 mole-% of benzoyl peroxide. The balance of the vinylidene chloride copolymers were copolymerized in *tert*-butanol, with a solvent to total monomer ratio of 3 and were initiated with 0.4 mole-% of benzoyl peroxide. The acrylonitrile copolymers were prepared and purified as described.¹⁸ All of the solution- and bulk-polymerized copolymers were isolated by precipitation in a nonsolvent and freed of monomer by repeated extractions. Hot methanol was used for all of the copolymers, except the vinyl acetate rich copolymers, which were extracted at room temperature in either hexane or hexane-methanol mixtures. Samples were freed of solvent by evaporation from thin layers, usually in vacuum at <50°C. The purification of the dispersion copolymer has been described.¹⁹

Refractive Increments and Light-Scattering Molecular Weights

Solvents used for light scattering were of the purest available commercially and were distilled before use through an efficient column. All refractive increment measurements were made at $30 \pm 1^\circ\text{C}$ with the use of a Brice-Phoenix differential refractometer which had been modified electronically by Dr. Brice for facile read-out of the solvent and solution values. A small glass correction factor calibrating the divided measuring cells, also provided by Dr. Brice, was applied to the readings. The light source was the 5360 Å mercury line. Each polymer or copolymer was measured at two of the concentrations to be used for the measurement of molecular weight, and the average quotient was taken as dn/dc . Deviations were always small. The same procedure was followed for the homopolymers and copolymers used in Table I. The value found for NBS broad molecular weight polystyrene in toluene at 30°C was 0.114; the literature value in this solvent was 0.109–0.111 at $25\text{--}30^\circ\text{C}$.²⁰ A compilation of refractive increment values is available²⁰ for comparison with other values in Table I.

Light-scattering measurements were made with a Sofica light-scattering photometer, Model Number 701. The light source was the green mercury line at 5360 Å, and the calibration standard was pure dust-free benzene. All measurements were made at $30 \pm 1^\circ\text{C}$. Sample concentrations c were diluted to 0.75 c , 0.50 c , 0.33 c , and 0.25 c . The initial concentration was increased as scattering intensity decreased and ranged from 2.0 g/l when dn/dc was 0.1 to 0.2, to 15 g/l when dn/dc was 0.01 or less. Curvature of the virial slope was not found. Solvents and solutions were dedusted by filtering each concentration through a Millipore filter assembly directly into the solution cells, which were protected by slotted dust shields. Filter designation GSWP 0.22 μ was used with most solvents; when these were soluble (with tetrahydrofuran and *n*-butyl acetate) filter designation NRWP 1 μ , was used. With the latter porosity, however, some dust or microgel was present as evidenced by a marked downward drift of the Zimm plot at low angles. The data were treated by the method of Zimm²¹

TABLE I
Refractive Increments and Observed Molecular Weights

Experiment ^a	Solvent	ν_a	ν_b	ν	$M_{app} \times 10^{-5}$
1 (OA + BA)	Tetrahydrofuran	0.0651	0.0702	0.0634	3.681
	Hexane	0.0885	0.1096	0.0997	3.186
	Chlorobenzene	-0.0525	-0.0682	-0.0575	3.101
	Benzene	-0.0292	-0.0505	-0.0337	4.053
	Toluene	-0.0239	-0.0425	-0.0280	3.074
2 (OA + STY) ^b	Hexane	0.1972 ^d	0.1292	0.1588	10.31
	Tetrahydrofuran	0.1926	0.0898	0.1332	10.41
	Carbon tetrachloride	0.1518	0.0114	0.0714	10.31
	Benzene	0.1123	-0.0269	0.0253	15.44
	Chlorobenzene	0.0848	-0.0489	0.0007	638.0
3 (OA + STY) ^c	Hexane	0.1972 ^d	0.1292	0.1585	15.32
	Tetrahydrofuran	0.1926	0.0898	0.1016	17.41
	Chlorobenzene	0.0848	-0.0489	-0.0324	19.61
	Carbon tetrachloride	0.1518	0.0114	0.0409	21.53
4 (OM + VCL)	Hexane	0.1579 ^d	0.1168	0.1322	6.078
	Tetrahydrofuran	0.1263 ^d	0.0898	0.1028	6.031
	Cyclohexane	0.1145 ^d	0.0651	0.0797	6.901
	Toluene	0.0665 ^d	-0.0154	0.0135	14.72
	Benzene	0.0607 ^d	-0.0269	0.0059	73.53
5 (OM + AN)	Tetrahydrofuran	0.1244 ^d	0.0898	0.0961	2.767
	Chlorobenzene	0.0039 ^d	-0.0489	-0.0369	5.391
	Benzene	0.0072 ^d	-0.0269	-0.0193	5.883
	Toluene	0.0236 ^d	-0.0154	-0.0072	25.23
6 (OA + VA)	<i>n</i> -Butyl acetate	0.0716	0.0883	0.0812	5.755
	Tetrahydrofuran	0.0582	0.0723	0.0657	6.675
	Chlorobenzene	-0.0426	-0.0563	-0.0546	6.863
	Benzene	-0.0225	-0.0363	-0.0321	9.891
	Cyclohexanone	0.0083 ^d	0.0175	0.0140	18.33
7 (OM)	Hexane			0.1292	7.649
	Tetrahydrofuran			0.0898	6.986
	Cyclohexane			0.0651	6.333
	Chlorobenzene			0.0489	6.214
	Benzene			0.0269	6.367
	Toluene			0.0154	7.952

^a Letter combinations stand for the following: OM, *N*-*n*-octadecylacrylamide; OA, *n*-octadecyl acrylate; BA, *n*-butyl acrylate; STY, styrene; VCL, vinylidene chloride; AN, acrylonitrile; VA, vinyl acetate. The subscript *b* refers to the long side-chain copolymer.

^b Weight fraction, *n*-octadecyl acrylate, 0.594.

^c Weight fraction, *n*-octadecyl acrylate, 0.846.

^d Extrapolated by using regression coefficients obtained by least-square fitting of values of ν and w_b for soluble copolymers.

for measurements at angles ranging from 30° to 150° for all five concentrations.

Osmometric Molecular Weights

Osmometric molecular weights were usually run in toluene at 37°C on a Mechrolab osmometer 501, following the procedure described previously.¹⁸

Calculations by Computer

The parameters of eq. (1) were evaluated by an IBM 1130 computer using program designation IBM POLRG and were carried through a five-degree polynomial. An F test, applied to the analysis of variance, revealed that the second-degree polynomial was the most significant, as required by theory.⁶ The parameters of eq. (2) were evaluated by least-square fitting from a program calling subroutine SIMQ. A program solving the equation of Kruse²⁷ was written for insertion in a general calculation subroutine designated QREAD.

THEORY

The development of the theory has been described in detail elsewhere^{5-7,22,23} and has been treated in reviews.²⁴⁻²⁶ Consequently, only expressions pertinent to the present work will be discussed briefly here. Based on the assumption⁶ of linearity between the refractive increment and the weight fraction of copolymer composition, an expression yielding the heterogeneity parameters P and Q and the true weight-average molecular weight \bar{M}_w was derived and is given here as

$$M_{\text{app}} = \bar{M}_w + 2P(\nu_a - \nu_b/\nu) + Q(\nu_a - \nu_b/\nu)^2 \quad (1)$$

The weight-average molecular weights of the A and B component, M_a and M_b , respectively, are contained in the expression

$$M_{\text{app}} = (\nu_a\nu_b/\nu^2)\bar{M}_w + \nu_a(\nu_a - \nu_b)/\nu^2 w_a M_a + \nu_b(\nu_b - \nu_a)/\nu^2 w_b M_b \quad (2)$$

In both expressions M_{app} is the observed molecular weight, \bar{M}_w is the true molecular weight, ν_a is the refractive increment of homopolymer A, ν_b is the refractive increment of homopolymer B, ν is the refractive increment, and w_i is the weight fraction for the copolymer. P and Q are defined by

$$2P = 2\sum \gamma_i M_i \delta w_i = w_b(\bar{M}_w - M_b) - w_a(\bar{M}_w - M_a) \quad (3)$$

$$Q = \sum \gamma_i M_i \delta w_i^2 = (w_a)(w_b)(M_a + M_b - \bar{M}_w) \quad (4)$$

where γ_i and M_i are, respectively, the relative concentration and molecular weight of species having composition w_i , while δw_i is the deviation in composition of these molecules from the average one. Thus P expresses the molecular weight influence on compositional heterogeneity, while Q indicates compositional drift produced in accordance with the kinetics of propagation in copolymerization. Limits of P and Q are

$$-w_a \bar{M}_w \leq P \leq w_b \bar{M}_w \quad (1a)$$

$$0 \leq Q \leq \bar{M}_w [1 - (w_a w_b)] \quad (2a)$$

For comparing data, the terms P/\bar{M}_w and Q/\bar{M}_w are convenient. An especially useful quantity is Q/Q_{max} , where Q_{max} is the maximum value of the heterogeneity constant for a given system (i.e., the value obtained for a

mixture of two homopolymers) and is defined as $(w_a w_b) \bar{M}_w$. Q/Q_{\max} , which has the limits $0 \leq Q/Q_{\max} \leq 1$, is thus a useful index of compositional heterogeneity.

RESULTS AND DISCUSSION

The observed molecular weight, M_{app} and the values found for the refractive increment are listed in Table I. In this work the b subscript always refers to the long side-chain homopolymer. The copolymers used and their lettered designations, in the order given in Table I, are: 1, *n*-octadecyl acrylate, OA, *n*-butyl acrylate, BA; 2,3 *n*-octadecyl acrylate, styrene, STY; 4, *N*-*n*-octadecylacrylamide, OM, vinylidene chloride, VCL; 5, *N*-*n*-octadecylacrylamide, acrylonitrile, AN; 6, *n*-octadecyl acrylate, vinyl acetate, VA. Experiment 7 (OM) shows molecular weight data for the homopolymer, *N*-*n*-octadecylacrylamide, in the same solvents used for the copolymers. Further reference to these systems will be by experiment number only. Because neither poly(vinylidene chloride) or polyacrylonitrile is soluble in any of these solvents, values of refractive increment versus weight fraction for a series of five copolymers, carried to high conversion, were fitted as first-degree polynomials, with the intercept yielding ν_a . This procedure was required with one solvent each for experiment 3 (hexane) and experiment 6 (cyclohexanone). Increase in the magnitude of the slope of this relation, $\nu_b - \nu_a$, is in the direction of increasing accuracy. For these experiments the relative magnitude of $\nu_b - \nu_a$ was: vinyl acetate, 0.11; butyl acrylate, 0.14; acrylonitrile, 0.34, vinylidene chloride, 0.51; styrene, 1.0. As had been observed before,¹⁵ copolymers of similar structure had low relative values. The difference, $\nu_b - \nu_a$, was not constant for the solvent series of each experiment, as had been assumed for styrene and methyl methacrylate.¹³ Surprisingly, it varied from positive to negative for the butyl acrylate and vinyl acetate system. This may reflect the influence of the long side-chains on dn/dc in these two examples where the slopes are already low.

In Table II are listed the reactivity ratios r_a and r_b and the mole fractions of the long side-chain comonomers in, respectively, the feed f_{b0} , the initial copolymer, F_{b0} , and the final copolymer, F_b . This last value was estimated from the relation of Skeist⁴ and was read from plots using the simplified calculations of Kruse,²⁷ which were solved by computer. With the aid of these plots, the ratio of the experimental drift of F_b with conversion p compared to the maximum value at $p = 1.0$ was obtained as the ratio of areas in accordance with the relation

$$A/A_{\max} = n[F(n)] - \int_0^n f(p)dp/F(1) - \int_0^1 f(p)dp \quad (5)$$

The areas were measured from the plots with a planimeter and were given the designation A/A_{\max} . This ratio therefore, represents the extent of drift for each system. In similar fashion, A_{rel} (Table II) relates the hetero-

TABLE II
Reactivity Ratios and Calculated Initial and Final Copolymer Compositions

	Expt 1 (OA + BA)	Expt 2 (OA + STY)	Expt 3 (OA + STY)	Expt 4 (OM + VCL)	Expt 5 (OM + AN)	Expt 6 (OA + VA)
r_a	1.0	0.646	0.646	0.440	4.394	0.048
r_b	1.0	0.120	0.120	1.257	0.140	7.312
f_{b0}	0.350	0.300	0.600	0.250	0.350	0.400
F_{b0}	0.350	0.300	0.452	0.378	0.105	0.846
F_b^a	0.350	0.300	0.560	0.315	0.230	0.455
$F_b'^b$	0.157	0.320	0.638	0.357	0.380	0.340
w_b^b	0.320	0.594	0.846	0.649	0.789	0.660
Conversion, %	89.0	94.8	91.3	66.9	83.1	93.8
A/A_{\max}	0	0	0.635	0.342	0.415	0.830
A_{rel}	0	0	0.29	0.11	0.31	1.00

^a Calculated by the method of Kruse.²⁷

^b Calculated from the refractive increment data. w_b , calculated from the elementary analysis, was: expt 1, 0.574; expt 2, 0.567; expt 3, 0.827; expt 4, 0.642; expt 5, 0.783; expt 6, 0.701.

generosity of each experiment to the one having the greatest heterogeneity (experiment 6). F_b' and the corresponding weight fraction w_b were computed from the refractive increments of the homopolymers and copolymer. Similar values were obtained by elementary analysis. The values found for F_b' generally indicated greater compositional drift and more heterogeneity for the experiments than were estimated from the Kruse relation. However, large errors arise in determining copolymer compositions by elementary analyses.²⁸ Because error is also considerable in the Kruse relation, which depends on reactivity ratios,²⁸ these observed differences and apparent anomalies can be expected. Although composition estimates for copolymers by refractive increment probably involves less error than by the other methods, uncertainties in the determination can be large, arising mostly from impurities in the polymer and solvents.²⁹ This might be the cause of the low value of F_b' in experiment 1. In this case, however, the value of F_b' by elementary analysis seems to be correct. Reactivity ratios were calculated, the values for *N*-*n*-octadecylacrylamide, $Q = 0.66$, $e = 1.13$ being used,¹⁷ except for experiment 5 (see below) and for *n*-octadecyl acrylate, $Q = 0.43$, $e = 0.80$, as estimated from reference 16. Other values of Q and e were from Young.³⁰

The parameters, evaluated by computer, for eqs. (1) and (2) are listed in order of increasing heterogeneity in Table III. Equation (1) describes a parabola in which the magnitude of Q indicates the degree of curvature, the slope at $v_a - v_b/v = 0$ indicates the value and sign of P , and the intercept is \bar{M}_w . Relative heterogeneity is best expressed as Q/\bar{M}_w , while the fraction of the maximum heterogeneity attainable (realizable for mixtures) is given as Q/Q_{\max} . Consequently, for comparison with the data in Table II it is convenient but only qualitatively proper to compare A_{rel} and Q/\bar{M}_w ,

TABLE III
Molecular Weights and Compositional Heterogeneity Parameters

	Expt 1 (OA + BA)	Expt 2 (OA + STY)	Expt 3 (OA + STY)	Expt 4 (OM + VCL)	Expt 5 (OM + AN)	Expt 6 (OA + VA)
$\bar{M}_w \times 10^{-5}$ [eq. (1)]	3.342	9.397	15.75	6.622	2.945	6.703
$\bar{M}_w \times 10^{-5}$ [eq. (2)]	3.248	11.29	14.69	6.445	2.863	5.135
$P \times 10^{-4}$	-1.03	4.88	5.13	-4.37	-3.29	56.28
$s_p \times 10^{-4}$	± 4.72	± 0.89	± 1.08	± 0.997	± 1.11	± 46.36
$Q \times 10^{-4}$	0	0.121	3.49	3.64	6.30	44.00
$s_q \times 10^{-4}$		± 0.009	± 0.83	± 0.13	± 0.39	± 10.79
P/\bar{M}_w		0.052	0.033	-0.066	-0.112	0.840
Q/\bar{M}_w	0	0.0013	0.022	0.055	0.214	6.57
$Q/Q_{\max} \times 10^{-5}$		2.307	2.176	1.522	0.500	1.405
Q/Q_{\max}	0	0.0053	0.160	0.239	1.26	31.3
$M_a \times 10^{-5}$	-1.823	4.252	6.114	2.549	2.976	114.1
$M_b \times 10^{-5}$	-1.991	7.078	9.609	5.440	3.698	48.18
$\bar{M}_n \times 10^{-5}$	1.017	3.609	3.813	1.722	1.232	1.076
\bar{M}_w/\bar{M}_n	3.29	2.60	3.99	3.85	2.39	6.23

with a value of one arbitrarily assigned to the latter parameter in experiment 6. Actually, if the limit of heterogeneity is assumed for experiment 6 [see relation (2a)], Q/\bar{M}_w is then approximately 0.78, yielding for experiments 1-5 relative values for Q/\bar{M}_w of respectively 0, 0, 0.03, 0.07, 0.27. The quantities A/A_{\max} and Q/Q_{\max} have different meanings, of course, and cannot be compared. In general, the values in Table III for Q , Q/\bar{M}_w and Q/Q_{\max} are in the expected order as required by their kinetic parameters r_a and r_b and are qualitatively in harmony with the calculated values of Table II. For example, in the two special cases of equal comonomer reactivity (experiment 1) and azeotropic feed composition (experiment 2) where both comonomers enter at equal rates, the values of the parameters are reasonable. Because these data seem to indicate that the reactivity ratios are correct, the value for Q/\bar{M}_w in experiment 3 seems to be too low. Both the extent of drift, A/A_{\max} , and the quantity A_{rel} indicate the presence of considerable heterogeneity. In contrast, in experiment 4 there is better correspondence between the constants of Tables II and III.

Two divergent Q and e parameters exist for the N - n -alkylacrylamides,^{17,31} leading to different predictions of reactivity and of homogeneity for the N - n -octadecylacrylamide-acrylonitrile system (experiment 5). The values r_a and r_b listed in Table II³¹ predict much heterogeneity, while the other¹⁷ values ($r_a = 0.836$, $r_b = 1.191$) indicate very little. Because Q/\bar{M}_w and especially Q/Q_{\max} were both large, the former values were considered to be correct and were listed. Some reservations exist however. The compositions of all copolymers of N - n -octadecylacrylamide with acrylonitrile have always been found at this laboratory to equal the monomer feed in either *tert*-butanol or benzene, where copolymerization occurs heterogeneously. Anomalies are known to exist which affect the kinetic

parameters of copolymerization under heterogeneous conditions,³² being especially severe with acrylonitrile copolymers. Conceivably heterogeneity could be present that was not reflected in the copolymer analysis.

The extreme heterogeneity found for the *n*-octadecyl acrylate-vinyl acetate system (experiment 6) is predictable from the reactivity ratios in view of A/A_{\max} . However, the ratio Q/Q_{\max} is far in excess of the theoretical limit of unity, for this system and, to some extent, for the previous one. For vinyl acetate this may be related to the small value of $\nu_b - \nu_a$ (Table I) coupled with the low value of ν used to calculate M_{app} in benzene and in cyclohexanone. By setting P equal to zero and using Q_{\max} , \bar{M}_w , and found values for the ratio $\nu_a - \nu_b/\nu$, values of M_{app} were calculated which were close to values found for the first three solvents in experiment 6, but which differed widely for the last two. Although this explanation may be an oversimplification, similar results were found for experiment 5.

The magnitude and sign of P reflects the shift in composition of the A or B species into the higher molecular weight fractions of the copolymers [eq. (3)]. In these systems, a negative value for the constant indicates a shift of the long side-chain monomers into the high molecular weight fractions; a positive value indicates the opposite. While specific trends in Table III may be rationalized, it is considered that the large error (values of s) in P make such rationalizations speculative. The errors in literature values of P and Q showed similar trends when all available data^{6,7,9,10,13} were recalculated by the computer methods used for this work. With statistical copolymers, the data indicated greater heterogeneity than would be expected from the respective reactivity ratios.

Values of \bar{M}_w from eq. (2) agree fairly closely with those of eq. (1) (Table III), while values of M_a and M_b , when inserted in eq. (3) yielded reasonable values of P . Credence is thus lent to the above remarks by the parameters of eq. (2).

SUMMARY AND CONCLUSIONS

In this work, several copolymers of increasing heterogeneity were prepared at high conversions from monomers selected to produce compositional drift in accordance with copolymerization theory. Molecular weight broadening was obtained by batch polymerization and through branching. It was shown that, in general, the heterogeneity index followed the kinetic predictions but that indices of heterogeneity higher than those theoretically possible were observed in two cases, one case being extreme. These facts, together with uncertainties with respect to the magnitude and sign of P , lead to the conclusion that experimental quantitation depends on the differences in value for the refractive increments of the two homopolymers. Insensitivity becomes particularly severe when $\nu_b - \nu_a$ is low and where ν_a and ν_b are of opposite sign. In this situation ν is extremely low, casting doubt on the validity of M_{app} . It is under these circumstances that M_{app}

attains its highest values and so exerts the greatest influence on Q and P . When the copolymer is homogeneous, the effect is negligible (experiment 1), but when heterogeneity is present (experiments 5 and 6) the effect is greatly magnified, leading to the anomalies observed. When $\nu_b - \nu_a$ is high and heterogeneity is low (experiment 2) the sign of ν_a and ν_b can be opposite and ν quite low while still yielding data leading to reasonable values of P and Q , even though in experiment 3 the value of Q seems low. Approximate values of \bar{M}_w can be obtained by using solvents giving high values of dn/dc , (≈ 0.1), for the copolymers. In this situation, the ratio of $\nu_a - \nu_b/\nu$ approaches zero where $M_{app} = \bar{M}_w$. Considerable data on a much wider variety of copolymer systems will be required to definitively characterize this light-scattering method.

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