Evaluation of the Light-Scattering Technique for Determining Compositional Heterogeneity in Copolymers

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Synopsis

The Bushuk and Benoit theory of light scattering in copolymer systems has been evaluated for the case of a copolycarbonate of bisphenol A and poly(ethylene oxide) (1000) and for a blend of this compositionally homogeneous copolymer with a homopolymer of bisphenol A polycarbonate. The experimental conditions necessary for a successful light-scattering analysis and an estimate of the limiting sensitivity of the method are reported. The technique was disappointingly insensitive to the amount of low molecular weight homopolymer incorporated in the blend. This finding, in addition to recent reports in the literature, suggests the method has limited applicability.

INTRODUCTION

It is well known that in copolymer systems the weight-average molecular weight ($\bar{M}_w$) as determined by light scattering can vary substantially with the refractive index of the solvent. Bushuk and Benoit[1] have developed a theory which relates this phenomenon to compositional heterogeneity in copolymers. The technique has been used successfully in the case of styrene/methyl methacrylate copolymers.[2-4] Copolymers of styrene/isoprene,[5] styrene/acrylonitrile,[6] and styrene and a series of long side-chained acrylates[7] have been studied with varying degrees of success.

This paper will describe: (1) the experimental conditions necessary for a successful light-scattering analysis, (2) the limiting sensitivity of the technique for determining compositional heterogeneity, and (3) a relationship between the amount of a heterogeneous component and its molecular weight that can be detected by this light-scattering method. The results of the above studies are supported by very recent, independent investigations by Kratochvil et al.[8]

Bushuk and Benoit have described the compositional heterogeneity in copolymers, as determined by light-scattering studies, as follows:

$$\bar{M}_{ap} = \bar{M}_w + 2P\left(\frac{\nu_a - \nu_b}{\nu_0}\right) + Q\left(\frac{\nu_a - \nu_b}{\nu_0}\right)^2 \tag{1}$$

where $\bar{M}_{ap}$ is the apparent molecular weight; $\bar{M}_w$ is the true molecular weight; ν_a is the specific refractive index increment, hereafter referred to as

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the "refractive increment," of homopolymer A; ν_b is the specific refractive index increment of homopolymer B; and ν_0 is the specific refractive index increment of the copolymer. The quantity P describes the variation in chemical composition as a function of molecular weight, whereas Q is a measure of the total compositional heterogeneity in the copolymer system. In principle, $\bar{M}_w$, P, and Q can be determined by performing light-scattering measurements in three solvents. In practice, though, four to six such measurements must be performed owing to the high experimental error associated with light-scattering measurements at low values of the refractive increment.

Thus, the method would appear to be a powerful technique for the characterization of copolymers since one can obtain (1) the weight-average molecular weight, (2) the molecular weight dependence of the compositional heterogeneity (P), and (3) a measure of the gross compositional heterogeneity in the system (Q).

This analysis scheme has been applied to copolymers of styrene/methyl methacrylate,[2-4] styrene/isoprene,[5] styrene/acrylonitrile,[6] and styrene and a series of long side-chained acrylates.[7] The most successful studies of compositional heterogeneity occurred in those cases where $\nu_a - \nu_b$ was large, i.e., $\geqslant 0.06$.

The block polycarbonate copolymer (I), was chosen for study since (1)

I
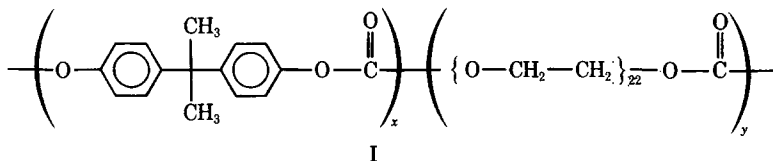
a number of similar copolymers having different degrees of blocking have been studied previously;[9] (2) the differences between the refractive increments of the homopolymers is large, i.e., $\nu_a - \nu_b \cong 0.10$; and (3) the copolymer is soluble in a wide variety of solvents.

EXPERIMENTAL

Materials

All reagent-grade solvents were freshly distilled before the light-scattering measurements were performed. Hygroscopic solvents were dried over a molecular sieve for several days before distillation.

The polycarbonate copolymer was prepared by reaction of bisphenol A and Carbowax 1000 with phosgene. Bisphenol A and Carbowax 1000 were dissolved in dichloromethane (200 ml) containing 60 g pyridine. A dichloromethane solution of phosgene ($\sim 1\%$ w/v) was added dropwise to effect the polymerization. The molecular weight was allowed to increase, and ca. 2 hr later the polymer was precipitated into a dilute solution of hydrochloric acid. The polymer was washed several times with dilute acid and distilled water to remove residual Carbowax 1000 and the pyri-

dinium hydrochloride. It was then dissolved in dichloromethane, precipitated once into a large excess of isopropanol, redissolved, and precipitated twice into a large excess of methanol. The weight fractions of the bisphenol A and ethylene oxide components are ~0.7 and ~0.3, respectively. Because of the large difference in monomer molecular weights, this corresponds to a molar ratio of ~0.25 and ~0.75, respectively.

The polycarbonate (Lexan 145) (PC) was commercially available (General Electric, Pittsfield, Massachusetts), as were the Carbowax 1000 (PEO) and Carbowax 20,000 (Analabs, New Haven, Connecticut). Carbowax 20,000 was used for the refractive increment determinations.

A blend of the block copolymer and polycarbonate homopolymer (1:1) was also prepared. The samples were dissolved in p-dioxane and freeze dried. The blend was further dried under vacuum at 120°C for 24 hr to remove residual solvent.

Light Scattering

Light-scattering measurements were performed at 23°C using a Bausch and Lomb instrument of the Sofica design. Scattering intensities were measured at 11 angles ranging from 30° to 150° using unpolarized light of wavelengths 436 nm and/or 546 nm. The instrument had been calibrated with the Cornell standard polystyrene and pure, dust-free benzene.[10] The observed scattering intensities were corrected for minor deviations from the predicted sine function by performing scattering measurements on dilute fluorescein solutions.

The polymer samples were dissolved in freshly distilled solvents and clarified by filtration through fine and/or ultrafine sintered glass filters. In some cases, Millipore filters (~1.0 to 0.2 μ) were used. The dissymmetry ratio of solvents or solutions (i_{45}/i_{135}) was generally 1.05 or less, indicating adequate clarification.

The refractive increment (dn/dc) of each solution was measured at 23°C before and after filtration. Concentration corrections were applied only in those cases where $dn/dc \geqslant 0.06$. These measurements were performed at 436 nm and/or 546 nm in a differential refractometer incorporating a Brice-Phoenix split cell. This cell is not suitable for liquids with refractive index greater than ~1.62. Therefore, dn/dc for bromoform and 1,1,2,2-tetrabromoethane was estimated from similar measurements in other solvents. In some cases, the value of dn/dc was taken from the data shown in Figure 1 and was used subsequently in the familiar light-scattering optical constant K and in the evaluation of $(\nu_a - \nu_b)/\nu_0$.

The scattering intensities of the clarified solutions were measured at 3–5 concentrations depending upon the value of ν_0. The reduced scattering intensities were extrapolated to zero angle and zero concentration by the method of Zimm[11] to obtain the weight-average molecular weight $\bar{M}_w$.

Gel Permeation Chromatography (GPC)

A gel permeation chromatograph employing an R-4 differential refractometer (Waters Associates, Framingham, Massachusetts) and a Beckman
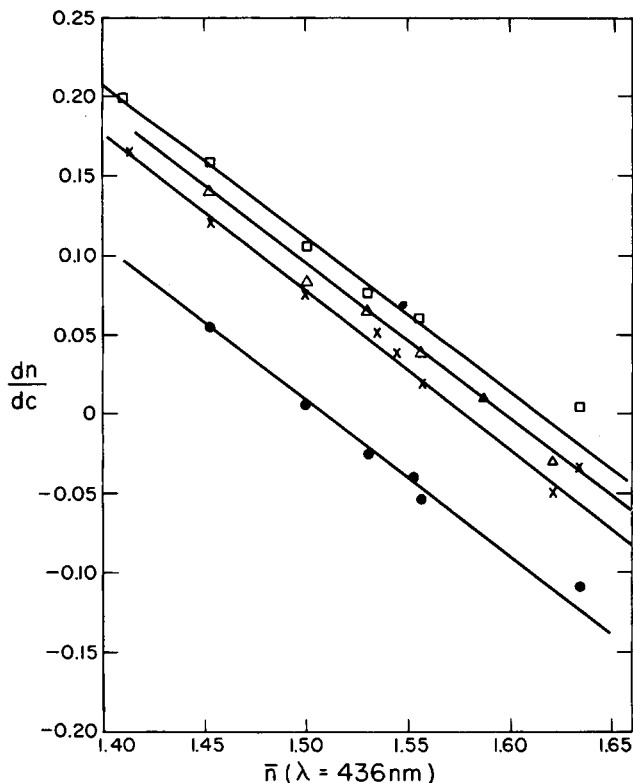
Fig. 1. Variation of refractive index increment with refractive index of solvent medium at λ = 436 nm: (—□—) polycarbonate; (—●—) poly(ethylene oxide); (—✕—) block copolymer; (—△—) blend.

DBG spectrophotometer were used as described previously.[12]   Four Styragel columns of 10^6-, 10^5-, 10^4-, and 10^3-Å porosity (nominal) were used. Tetrahydrofuran (THF) was used as the eluting solvent at 23°C at a flow rate of 1.0 ml/min.

RESULTS

Light Scattering of a Block Copolymer

The refractive increments of the polycarbonate (ν_a), poly(ethylene oxide) (ν_b), and the block copolymer (ν_0) are shown in Table I.   The quantity $\nu_a - \nu_b$ is constant, being 0.102 ± 0.002 and 0.091 ± 0.003 at 436 and 546 nm, respectively.

Figure 1 shows the linear dependence of the refractive increment of these materials as a function of the refractive index of the solvent (λ = 436 nm). It is apparent that the values obtained in bromoform are systematically in error by about 0.020 ± 0.005 as a result of the optical characteristics of the Brice-Phoenix cell.   Therefore, the values of the refractive increment were

TABLE I
Refractive Index Increment Measurements[a]

Solvent	Refractive increment		
	PC (ν_a)	PEO (ν_b)	Block copolymer (ν_0)
Bromoform	0.004 (0.004)	−0.108 (−0.090)	−0.033 (0.030)
Chlorobenzene	not soluble	−0.039 (−0.030)	0.039 (0.039)
Chloroform	0.157 (0.147)	0.054 (0.053)	0.121 (0.113)
1,2-Dibromoethane	0.054 (0.050)	−0.048 (−0.044)	0.018
Pyridine	0.077 (0.073)	−0.026 (−0.018)	0.052
1,1,2,2-Tetrachloroethane	0.106 (0.094)	0.006 (0.007)	0.088
Tetrahydrofuran	0.198 (0.186)	not soluble	0.153 (0.144)
Aniline	—	—	−0.053

[a] Values in parentheses are for λ = 546 nm; all other data were determined at λ = 436 nm.

TABLE II
Apparent Molecular Weight of Block Copolymer

Solvent	$\bar{M}_{ap}$		$(\nu_a - \nu_b)/\nu_0$[a]
	λ = 436 nm	λ = 546 nm	
Chloroform	95,600	95,700	0.85 (0.83)
	92,900	85,100	
Chlorobenzene	99,500	94,000	2.5 (2.5)
1,2-Dibromoethane	120,000	—	6.55
Bromoform	88,100	98,000	
	90,000	110,000	−1.79 (−1.77)

[a] Values in parentheses measured at λ = 546 nm.

extrapolated from Figure 1 when studies were performed in bromoform or 1,1,2,2-tetrabromoethane.

The apparent molecular weight $\bar{M}_{ap}$ was then determined in chloroform, chlorobenzene, and bromoform. The observed $\bar{M}_{ap}$ values and values of the reduced refractive increment $\nu_a - \nu_b$ are listed in Table II. The experimental uncertainity in the $\bar{M}_{ap}$ determination approaches ±40% for the 1,2-dibromoethane data, the three sources of error being measurements of ν_0^2 (±20%), concentration of clarified light-scattering solutions (±5% to ±10%), and the precise measurement of the excess scattering of the dilute polymer solution and the attendant errors in the extrapolation to zero angle and zero concentration (±10% to ±15%). It is thus apparent that the $\bar{M}_{ap}$ values of greatest interest, at large values of $(\nu_a - \nu_b)/\nu_0$, are subject to the greatest experimental uncertainity. Since the $\bar{M}_{ap}$ does not vary significantly over the wide range of $(\nu_a - \nu_b)/\nu_0$, the copolymer can be said to be homogeneous in composition. Thus, any effects due to residual homopolymer of poly(ethylene oxide) or polycarbonate are within the experimental error of the technique. It is important to evaluate $\bar{M}_{ap}$ over a substantial range of the reduced refractive increment to describe accurately
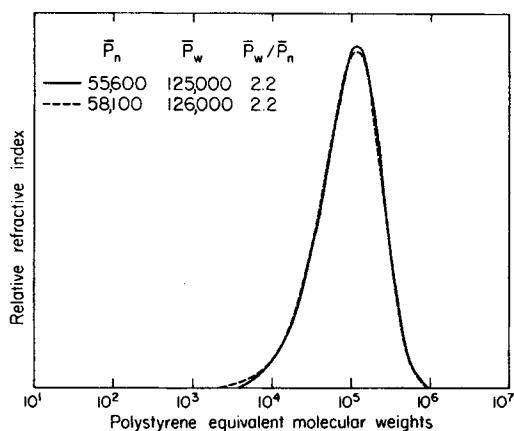
Fig. 2. GPC traces for block copolycarbonate of ethylene oxide and bisphenol A:
(———) refractometric data; (- - -) spectrophotometric data.

the parabolic function given in eq. (1). Such an analysis is simplified when the quantity $\nu_a - \nu_b$ is large, i.e., $\geqslant 0.06$.

GPC Studies

The molecular size distribution of the copolymer was determined by gel permeation chromatography (GPC). The apparent distribution curve is shown in Figure 2, wherein the refractometric data (solid line) and the spectrophotometric data (dashed line) are shown. The two traces are superposable, and variations of the molecular weight averages are within experimental error. The distribution is said to be apparent because most of the refractometric signal ($\sim 85\%$) is due to the polycarbonate components.

In Figure 2, we are actually comparing this refractometric signal with one (UV) that is entirely due to the polycarbonate portion of the copolymer. Although the GPC data are not conclusive evidence, they do support the light-scattering measurements to indicate that the composition of the copolymer is homogeneous, i.e., $P = Q = 0$.

Light Scattering of Polymer Blend

The light-scattering analysis of the block copolycarbonate is somewhat atypical, because the magnitude of $\nu_a - \nu_b$ is large. We believe that the case when $\nu_a - \nu_b \cong 0.02\text{-}0.05$ is more common. Therefore, a blend of a low molecular weight polycarbonate with this compositionally homogeneous copolycarbonate was prepared to investigate the sensitivity of the light-scattering analysis for determining compositional heterogeneity. The term ν_a still describes the refractive increment of the polycarbonate homopolymer; ν_b is the refractive increment of the compositionally homogeneous block copolycarbonate; ν_0 is the refractive increment of the blend. The

TABLE III
Light Scattering of Polymer Blend[a]

Solvent	$\bar{M}_{ap}$	ν_0	$(\nu_a - \nu_b)/\nu_0$
Chloroform	51,600 (52,300)	0.140 (0.131)	0.25 (0.23)
1,1,2,2-Tetrachloroethane	51,600 (50,000)	0.082 (0.072)	0.37 (0.37)[b]
Pyridine	67,000 (62,000)	0.066 (0.064)	0.53 (0.52)
1,2-Dibromoethane	100,000	0.039 (0.034)	0.90 (0.89)
Bromobenzene	177,000		2.92
	198,000	0.012	
1,1,2,2-Tetrabromoethane	70,000	-0.065[b]	-0.54[b]
Bromoform	135,000		
	200,000	-0.035[b]	-1.0
	250,000		
Aniline	—	-0.030	—

[a] Values in parentheses represent measurements at $\lambda = 546$ nm.
[b] ν_0 used in calculations of $\bar{M}_w$ and $(\nu_a - \nu_b)/\nu_0$ was estimated from Figure 1.

term $\nu_a - \nu_b$ now equals 0.035, which should allow us to adequately evaluate the light-scattering technique. The value of 0.035 was determined from the data in Figure 1 because the lines drawn for the homopolymer and homogeneous copolymer are essentially parallel and displaced from one another by this value (0.035 ml/g).

The apparent molecular weight varies approximately fourfold (Table III) over the limited range of reduced refractive increment studied. The range of reduced refractive increment available for study is limited by $|\nu_a - \nu_b|$ since the denominator, ν_0, can be reduced only to $\sim$0.01–0.02 if meaningful light-scattering data are to be collected. Thus, in this study, we must evaluate a parabolic function near its minimum. Moreover, the observed $\bar{M}_{ap}$ values become increasingly uncertain as one performs measurements at larger values of $(\nu_a - \nu_b)/\nu_0$.

Evaluation of the Heterogeneity Parameters

Calculation of the P, Q, $\bar{M}_w$ terms in eq. (1) is commonly done by graphic or numerical analysis techniques.[12,13] The first method suffers from the inability to draw a truly parabolic function through a limited number of data points in a statistical manner. The second method analyzes j sets of $\bar{M}_{ap}$ and reduced refractive increment values, three at a time, to determine "averaged" $\bar{M}_w$, P, and Q. Inaccurate estimates[2] of these parameters have been reported because of an accumulation of errors in ν_0 and the uncertainties in $\bar{M}_{ap}$.

Computer techniques have been used to evaluate eq. (1) with some success; we have used a weighted, nonlinear regression analysis to calculate the heterogeneity parameters. The $\bar{M}_{ap}$ values are weighted according to our estimates of the experimental uncertainty. This analysis, however, may not yield a unique solution to eq. (1) if the light-scattering studies are performed over a narrow range of the reduced refractive increment and/or if the extent of the compositional heterogeneity is small.

TABLE IV
Compositional Heterogeneity Parameters

Parameter	Calculated [eqs. (1)–(4)]	Experimental
$\bar{M}_w$	6.2×10^4	7.6×10^4
P	-1.63×10^4	-2.6×10^4
Q	1.55×10^4	3.2×10^4
$Q/\bar{M}_w$	0.24	0.43
$P/\bar{M}_w$	-0.26	-0.34
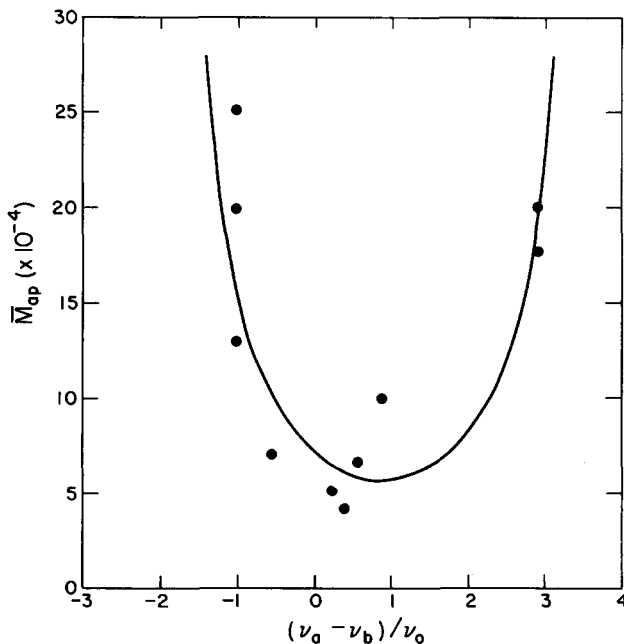
Fig. 3. Variation of apparent molecular weight with reduced refractive index increment for copolymer blend.

The computer-drawn least-squares fit of eq. (1) is shown in Figure 3, and the $\bar{M}_w$, P, and Q terms obtained are shown in Table IV. Since the molecular weight and composition of the compounds in the blend are known, the dependence of $\bar{M}_{ap}$ on the reduced refractive increment can be derived (see Appendix).

The agreement of the heterogeneity parameters shown in Table IV is poor. This illustrates our inability to describe quantitatively the extent of compositional heterogeneity for the case $\nu_a - \nu_b \cong 0.03$. The tendency of the light-scattering technique to overestimate the amount of compositional heterogeneity[14] will be discussed later.

GPC Studies of Copolymer Blend

The molecular size distribution of the copolymer blend was obtained by GPC using dual detectors, as described earlier. The refractometric trace
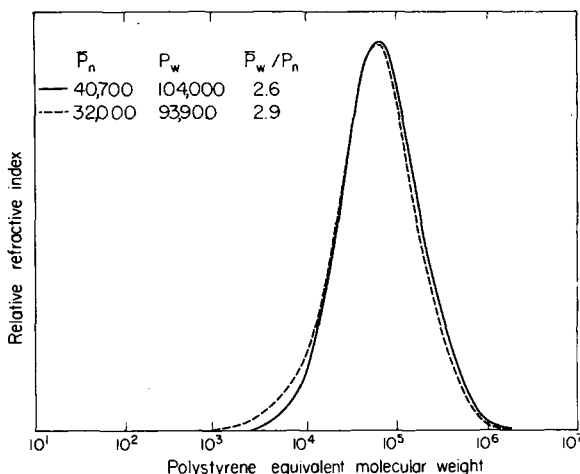
Fig. 4. GPC traces of copolycarbonate blend: (- - -) UV; (———) refractive.

shown in Figure 4 (solid line) has a narrower molecular weight distribution and larger polystyrene equivalent weight-average molecular weight ($\bar{P}_w$) than the spectrophotometric trace. Although these differences are rather small, we know them to be real because the composition of the components in the blend is known. Thus, in this limiting case, where the response of the differential refractometer (92% due to bisphenol A moiety) is compared to the UV spectrophotometric response (100% due to the bisphenol A moiety), we can yet barely discern compositional heterogeneity.

It was not believed warranted to quantitatively compute the values of the P and Q parameters from the GPC data as reported by Grubisic-Gallot et al.[15] because the differences between the two traces are so small. However, such an analysis would correctly show the sign of P to be negative.

DISCUSSION

The sensitivity of the light-scattering technique can be investigated further by examining the functionality of the parameter Q (see Appendix):

$$Q/M = \left(\frac{\bar{M}_a + \bar{M}_b}{\bar{M}_w} - 1\right) W_a W_b. \tag{2}$$

We believe that, owing to the experimental uncertainties, a value of $Q/M \cong 0.05$ is a somewhat arbitrary but reasonable lower limit for determining compositional heterogeneity in many copolymers. Figure 5 shows the relationship between the minimum weight fraction detectable by light scattering and the molecular weight of residual homopolymer in an otherwise compositionally homogeneous copolymer ($\bar{M}_a \cong 10^5$).

In this study, with $M_b = 2.6 \times 10^4$, as much as 15% polycarbonate homopolymer could be present and barely be detected. If we chose a lower limit of Q/M, say, 0.02, for determining the sensitivity of the technique,
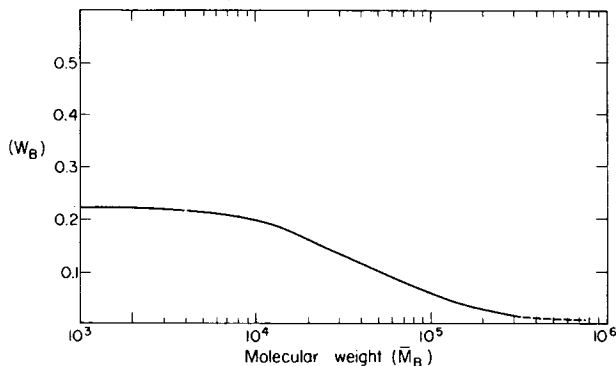
Fig. 5. Estimated limit of detection of homopolymer B in a compositionally homogeneous copolymer.

~8% residual homopolymer could be just discerned. A number of other techniques, such as fractionation, turbidimetric titration, or density gradient ultracentrifugation, are more sensitive for the determination of compositional heterogeneity.[16]

Interestingly, Kratochvil et al.[3] could generally detect only 15–20% polybutadiene homopolymer in a similar light-scattering study of a styrene/butadiene/styrene block copolymer. Calculated values of $Q/M \cong 0.07$–0.09 were obtained when their experimental data were used in eq. (2). Optimization of all light-scattering parameters for minimum experimental error yields a limiting Q/M value of $\geqslant 0.02$ in their study.

Note that eq. (2) is rather general and describes the theoretical dependence of Q/M as a function of $W_a W_b$. The relationships shown in Figure 5 are valid for blends of two homopolymers or blends of a compositionally homogeneous copolymer with one of its homopolymers. Figure 5 further indicates that the light-scattering analysis can detect smaller amounts of residual homopolymer as the molecular weight of the homopolymer increases; that is, the sensitivity of the technique increases as the molecular weight of the heterogeneous component increases.

Bushuk and Benoit,[1] Krause,[2] and others[17,18] have applied this light-scattering analysis to various copolymers of styrene and methyl methacrylate. Experimental values of $Q/M \cong 0.24$ were found;[1,2,17,19] however, these values are considered to be too high, based upon the kinetics of the copolymerization.[7,8] A careful study by Krause[2] using whole copolymers and fractions indicates that the highest molecular weight components (~8 × 10^6) are rich (93%) in methyl methacrylate. The methacrylate content decreases smoothly to a minimum value of ~30% for the lower molecular weight species (~2.8 × 10^5).

One would expect, however, that copolymers of methyl methacrylate and styrene prepared at low to medium degrees of conversion would be more nearly homogeneous than those of Krause. Kratochvil[8] has prepared such copolymers with molecular weights of (1–4) × 10^5 and has been unable to

observe any compositional heterogeneity by the light-scattering method. Kratochvil[14] has recently reported on the practical considerations of determining compositional heterogeneity by the light-scattering technique. The utility of such an analysis is discussed in detail. It appears that careful fractionation and characterization of these copolymers would yield further insight into the utility and sensitivity of the light-scattering method for determining compositional heterogeneity.

It seems that the copolymers prepared by Krause at high conversion contained heterogeneous components, for which the light-scattering method has its greatest sensitivity (see Fig. 5).

CONCLUSIONS

The Bushuk and Benoit theory of light scattering in copolymers has been evaluated for a copolymer of poly(ethylene oxide) and polycarbonate. It is believed that, with sufficient care, one could quantitatively determine the heterogeneity parameters P, Q, etc., for the case $\nu_a - \nu_b \gtrless 0.06$ because light-scattering measurements could be performed over a wide range of $(\nu_a - \nu_b)/\nu_0$. For the more common case where $\nu_a - \nu_b \cong 0.03$, poorer estimates of the heterogeneity parameters may be obtained because of the limited range in which the parabolic function $\bar{M}_{ap}$, eq. (1), may be experimentally evaluated.

There may be greater utility in this method of estimating compositional heterogeneity if the light-scattering analysis is performed on a qualitative basis. One can determine the value of $\bar{M}_{ap}$ at large and small values of the reduced refractive increment. If these values differ by a factor of ~ 1.5, one can be reasonably sure that the system is heterogeneous. If the values differ by a factor of less than 1.5, some ambiguity exists; the copolymer may be homogeneous or the extent of compositional heterogeneity may be less than the sensitivity of the light-scattering method.

When the parameter P is small, as is generally assumed, the $\bar{M}_{ap}$ determined in a solvent wherein the copolymer has a high refractive increment ($\nu_0 \cong 0.15$) is a very good estimate of the true $\bar{M}_w$. If P is large, as is the case for this copolymer blend, a similar measurement of $\bar{M}_{ap}$ can deviate substantially ($\sim 15\%$) from the true $\bar{M}_w$.

The light-scattering technique has been shown to be disappointingly insensitive to low molecular weight, compositionally heterogeneous components in copolymers. Owing to the stringent requirements for a successful analysis, the technique cannot be recommended as a routine method for determining the extent of compositional heterogeneity in copolymers. These findings further suggest that the technique may not be well suited to the determination of residual A or AB in ABA-type copolymers.

Appendix

The molecular weight of the polycarbonate homopolymer used in the blend was determined by light scattering in chloroform. The viscosity-average molecular weight was computed from the published relationship[19]

$$[\eta]_{\text{THF}}{}^{25} = 3.99 \times 10^{-4}\ \bar{M}_v{}^{0.70}. \tag{A1}$$

Weight-average and viscosity-average molecular weights of 29,600 and 28,000, respectively, were thus obtained.

Since the molecular weights and composition of the components in the blend are known, one can calculate the dependence of $\bar{M}_{ap}$ on the quantity $(\nu_a - \nu_b)/\nu_0$. Yamakawa[20] has shown that the P and Q parameters can be calculated as follows:

$$P = \frac{1}{2}[(\bar{M}_a - \bar{M}_w)W_a + (\bar{M}_w - \bar{M}_b)W_b] \qquad (A2)$$

and

$$Q = (\bar{M}_a + \bar{M}_b - \bar{M}_w)W_aW_b \qquad (A3)$$

where $\bar{M}_a$ = molecular weight of the A component (9.5×10^4 in this study); $\bar{M}_b$ = molecular weight of the B component (2.96×10^4 in this study); $\bar{M}_w$ = molecular weight of the blend component (6.23×10^4 in this study); W_a = weight fraction of the A component (0.50 in this study); and W_b = weight fraction of the B component (0.50 in this study).

The Q term is always positive, and the quantity $Q/\bar{M}_w$ is a measure of the breadth of the parabola described by eq. (1). The P term can be positive or negative, depending upon the drift in chemical composition with molecular weight. It is negative in this study. The calculated values of $\bar{M}_w$, P, and Q are shown in Table IV in the text.

References

1. W. Bushuk and H. Benoit, *Can. J. Chem.*, **36**, 1616 (1958).
2. S. Krause, *J. Phys. Chem.*, **65**, 1618 (1961).
3. M. Leng and H. Benoit, *J. Chem. Phys.*, **58**, 480 (1961).
4. M. Leng and H. Benoit, *J. Polym. Sci.*, **57**, 263 (1962).
5. J. Prud'homme and S. Bywater, *Macromolecules*, **4**, 543 (1971).
6. Y. Shimura, I. Mita, and H. Kambe, *J. Polym. Sci. B*, **2**, 403 (1964).
7. E. F. Jordan, *J. Polym. Sci. A-1*, **6**, 2209 (1968).
8. P. Kratochvil, B. Sedlacek, D. Strokova, and Fz. Tuzar, *Makromol. Chem.*, **148**, 271 (1971).
9. S. H. Merrill and S. E. B. Petrie, *J. Polym. Sci. A*, **3**, 2189 (1965).
10. J. S. Tan and S. S. Potterton, unpublished results.
11. B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
12. A. L. Spatorico, O. E. Schupp, and A. S. Marshall, Ninth International Seminar on GPC, Miami, Florida, 1970.
13. J. R. Urwin and M. Girolamo, *Makromol. Chem.*, **142**, 161 (1971).
14. J. Vorlicek and P. Kratochvil, *J. Polym. Sci.*, **11**, 855 (1973).
15. Z. Grubisic-Gallot, M. Picot, Ph. Gramain, and H. Benoit, *J. Appl. Polym. Sci.*, **16**, 2931 (1972).
16. *Polymer Fractionation*, M. J. R. Çantow, Ed., Academic Press, New York, 1967, pp. 229, 281, 341–370.
17. T. Kataka, Y. Murakami, and H. Inagaki, *J. Phys. Chem.*, **72**, 829 (1968).
18. G. V. Schultz and A. Horback, *Makromol. Chem.*, **29**, 93 (1959).
19. I. A. Baranovskaya, A. D. Litmanovich, M. S. Protasova, and V. E. Eskin, *Vysokomol. Soedin.*, **7**, 509 (1965).
20. H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York, 1971.