Asymmetric composition profiles in block copolymer interphases: 1. Experimental evidence

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New mechanical property data, coupled with a new interpretation of data from the literature covering many instrumental techniques, show that microphase-separated block copolymers have interphase regions that are generally asymmetric (rich in one component). New theoretical methods are needed to account for this and to accommodate it in thermodynamic predictions.

(Keywords: block copolymer; interphase; interphase composition profile; interphase glass transition)

INTRODUCTION

It is conventional in thermodynamic and other analyses of microphase-separated block copolymers (types AB, ABA, etc.) to view the interphase region joining the two distinct microphases as possessing a *symmetric* composition profile, $\phi'_A(x)$, where ϕ'_A is the local volume fraction of the A-component. Here, we draw attention to an existing body of literature—from disparate sources, and utilizing various experimental techniques—which, taken as a whole, presents an impressive argument for the existence of *asymmetric* composition profiles across the interphase region. This is supported further by mechanical property evidence that is presented here for the first time.

For purposes of this discussion, a symmetric interphase composition profile is defined as one which results in a volume-fraction average of 0.5 for each component in the interphase ($\overline{\phi'_A} = \overline{\phi'_B} = 0.5$), and an asymmetric profile as one which results in $\overline{\phi'_A} \neq \overline{\phi'_B}$. *Figure 1* presents a schematic illustration of several hypothetical composition profiles and their resultant values of $\overline{\phi'_A}$.

MEASUREMENTS OF $\overline{\phi'_A}$

Direct measurement of the composition profile across the interphase has not been achieved. Assumptions about its shape are required when inferring the interphase thickness (≈ 3 nm) from small angle X-ray scattering[1] (SAXS) or small angle neutron scattering[2] (SANS), and only the simplest symmetric shapes are postulated for mathematical convenience. However, both direct and indirect methods have been utilized to measure $\overline{\phi'_A}$ and inferences can be drawn about $\phi'_A(x)$ from such a knowledge of $\overline{\phi'_A}$.

Direct measurements can be made of the surface composition of block copolymer samples. X-ray photoelectron spectroscopy (XPS) has been used with polystyrene–poly(ethylene oxide) diblocks[3] and triblocks[4]. The XPS results for PEO–PS–PEO[4] showed the existence of a mixed phase (where PS and PEO chains are in close proximity) whose average composition ranged, for various samples, from 62.5% PS–40% PS on a mer-molar basis ($\overline{w'_S} = 0.799$–0.614 on a weight basis, or $\overline{\phi'_S} = 0.811$–$0.631$ on a volume basis). These samples were all cast from the same solvent (chloroform) and the only variation from sample to sample was in molecular composition; molecular weights (in thousands) were 8.5–5.1–8.5 (styrene weight fraction $w_S \doteq 0.235$), 8.4–10.5–8.4 ($w_S = 0.385$), and 9.1–43.2–9.1 ($w_S = 0.703$).

While classical surface tension considerations[5] provide an explanation for the surface-averaged excesses of one component or another in a macroscopic sample, they cannot be directly applied here. The 'interfacial tension' between microphases in a block copolymer is poorly defined at best, and in any case the classical arguments do not imply an excess of one component in the microscopic interphase region. (Nor is there any reason to expect the interphase composition in the surface regions to differ from that in the interior of the sample.) Regardless of the origin of the micro-interphase asymmetries, the XPS measurements[4] clearly show that $\overline{\phi'_A} \neq \overline{\phi'_B}$ near the surface of samples.

It should be emphasized that the XPS technique is a direct measurement of composition. Since such direct measurements of composition are not possible for the interior regions, only indirect methods of evaluating $\overline{\phi'_A}$ are available for bulk samples. Nonetheless, the latter will also be shown below to support $\overline{\phi'_A} \neq 0.5$, in qualitative agreement with the XPS results for the surface.

Indirect techniques usually hinge upon measuring a relaxation temperature or effective glass transition temperature (T'_g) between T_g^A and T_g^B of the two block types and associated with interphase region. Positron annihilation techniques[6] have been used to measure transition events in a SBS triblock ($\bar{M}_n = 124\,000$; $\phi_S \approx 0.30$) cast from a variety of solvents. In addition to the two glass transitions for PB and PS (at -70 and 85°C), transitions were observed at either -14°C or 10°C, depending on casting solvent; these latter transitions were identified as corresponding to a mixed phase rich in PB and PS, respectively. If a linear mixing rule, similar to those used for random copolymers (i.e., for well-mixed binary systems), is used to characterize the effective T_g of the

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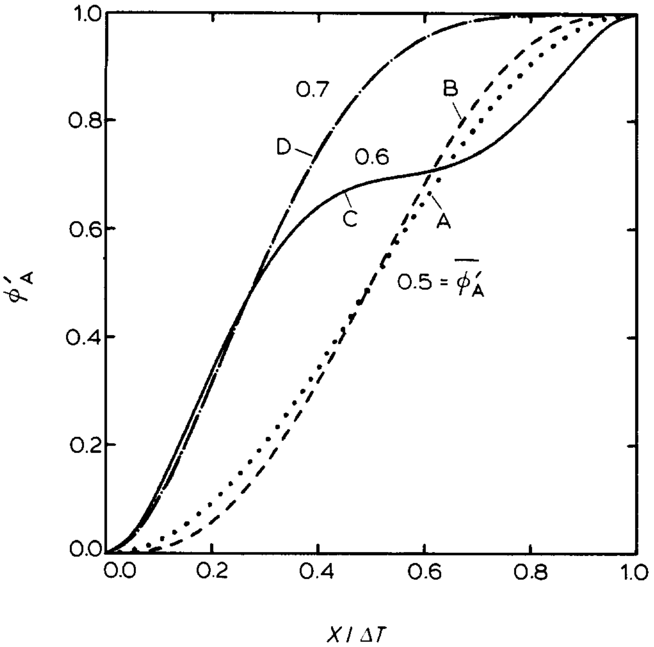

Figure 1 Hypothetical composition profiles for the interphase region (taken to be planar) in microphase-separated block copolymers; $\phi'_A(x)$ is the local volume fraction of component A and ΔT is the total interphase thickness. The curve A is symmetric ($\bar{\phi}'_A = 0.5$) and given by $\phi'_A = \sin^2 \pi x/2\Delta T$. The other curves are polynomials of the form $\phi'_A = a(x/AT)^2 + b(x/\Delta T)^3 + c(x/\Delta T)^4 + d(x/\Delta T)^5$ selected to show profiles of various kinds; their values of $\bar{\phi}'_A$ are 0.50, 0.60 and 0.70 for curves **B**, C and D, respectively. Note the great variety of shapes that can be represented and may be needed to conform with experimental results (see *Figure 2*)

interphase $[T'_g = \overline{w}'_S T^S_g + (1 - \overline{w}'_S) T^B_g]$, then the average weight fraction $\overline{w}'_S$ can be calculated from the T'_g, T^S_g and T^B_g obtained experimentally. This results in $\overline{w}'_S = 0.36$ for $T'_g = -14$°C and $\overline{w}'_S = 0.52$ for $T'_g = 10$°C. The Fox, or inverted, mixing rule $[1/T'_g = \overline{w}'_S/T^S_g + (1 - \overline{w}'_S)/T^B_g]$ yields $\overline{w}'_S = 0.50$ and 0.65 for $T'_g = -14$ and 10°C, respectively. Different mixing rules for T'_g would yield quantitatively different values, but in all cases at least one of the transitions would correspond to an interphase significantly rich in one component. (For PS and PB densities, $\bar{\phi}'_S$ and $\overline{w}'_S$ differ by only about 2%.)

Intermediate transitions have been observed in other studies, one example of which[7] utilized d.s.c. to measure all T_g transitions in a series of polystyrene–polyisoprene triblocks (SIS). At low molecular weight ($\leqslant 19\,000$), or at low PI content coupled with intermediate molecular weight ($w_I \leqslant 0.20$; $\bar{M}_n \leqslant 31\,000$), only one T_g was observed. Electron micrographs here did not reveal any microphase separation; thus, this T_g was akin to that of a random copolymer for the entire bulk sample. Other samples with high $\bar{M}_n$ or w_I had observable microphase separation, and d.s.c. revealed either two or three transitions. The three samples with three transitions were intermediate in $\bar{M}_n$ (≈ 25–$30\,000$) and w_I (≈ 26–30%), and the transition at intermediate temperatures was identified as that of the interphase, T'_g. Higher molecular weight samples ($\bar{M}_n \geqslant 44\,000$) or higher-$w_I$ samples ($\geqslant 40\%$) had only T^I_g and T^S_g observable by d.s.c.

The values of T'_g measured in the three samples cited above correspond to values of $\overline{w}'_S$ significantly greater than 0.50. Using the experimental[7] values for T^I_g and T^S_g and the two mixing rules given above results in values for $\overline{w}'_S$ of 0.745–0.841 (linear mixing rule) or 0.828–0.894 (inverted mixing rule) for the different copolymers. These interphase values are not only rich in one component, they are also greater in magnitude than the overall PS content of the block copolymers.

Similar T'_g results have been obtained using e.s.r. spin-probe techniques[8] for a series of block copolymers having PS as the high-T_g component and either PB, PI, hydrogenated PB or PI, or polydimethylsiloxane (PDMS) as the low-T_g component. Block architecture was also varied (AB, ABA and radial $(AB)_4$), as were molecular weight and overall composition ($16\,050 \leqslant \bar{M}_n \leqslant 140\,000$; $0.15 \leqslant w_s \leqslant 0.75$). In almost all cases two glass transitions were found, one corresponding to the low-T_g component and another occurring at 33–114°C below T^∞_g for PS. This second T_g was identified as the glass transition of the interphase, T'_g. In a preliminary presentation of this discussion[9], the results for only SB and SBS copolymers were used to calculate $\overline{w}'_S$. *Table 1* presents a more complete listing of these calculations for all the copolymers in ref. 8 which had a T'_g identified. Computations utilized experimental values[8] for T_g of the rubbery components, but T^S_g was not measured and thus was calculated from: $T^S_g = T^\infty_g - k/\bar{M}_S$, where $\bar{M}_S$ is the PS block weight. [Constants used[10] are: $T^\infty_g = 373$ K, with $k = 2 \times 10^5$ for $\bar{M}_S > 10^4$ and 8×10^4 for $\bar{M}_S < 10^4$.] Sample 23 had poly(t-butylstyrene) as the high-T_g component, for which $T_g^{TBS} = 403$ K was used.

Calculated values of $\overline{w}'_S$ (or $\overline{w}'_{TBS}$) in *Table 1* are presented for each of the mixing rules used before; the ranges found are $0.435 \leqslant \overline{w}'_S \leqslant 0.952$ (linear) and $0.277 \leqslant \overline{w}'_S \leqslant 0.894$ (inverse). While the quantitative details of this calculation depend upon the T^S_g value and the choice of mixing rule, the vast majority of the samples appear to have an interphase that is very rich in one component—to the extent that the selection of a different mixing rule could not alter the qualitative nature of the results. Furthermore, if T^S_g for the PS block was actually lower than was computed here (as suggested by observations that T_g for the higher-T_g copolymer block is generally lower than for a homopolymer of the same molecular weight), then the true $\overline{w}'_S$ would have to be even higher than shown in *Table 1* in order to account for the measured T'_g.

It should be noted that almost all samples examined by e.s.r. in this study displayed T'_g values, as compared to only three of the (phase-separated) samples in the d.s.c. study[7]. This suggests that the e.s.r. technique is much more sensitive to the interphase contribution. Similar comments have been made when comparing d.s.c.-derived T_g measurements to those of other techniques[11,12], and in general considerable care must be taken in the interpretation of thermal analysis[13]. At least one other d.s.c. study[12] has reported what may be a T'_g occurrence, but values of T'_g were not presented so no calculations of $\bar{\phi}'_A$ can be made.

Several researchers[14–16] have tentatively reported T'_g values obtained from mechanical property data. For an SBS triblock ($w_S = 0.32$; $\bar{M}_n = 86\,000$) cast from a variety of solvents, a temperature scan of dynamic loss modulus $E''(T)$ revealed[14] $T^B_g = -83$ to -73°C, $T^S_g = 95$ to 102°C, and $T'_g \simeq 50$°C. This last peak was identified as being associated with the interphase transition rather than with any secondary (β) polystryene loss mechanism. The

Table 1 Calculated compositions of interphase

Polymer	Architecture	$M_S \times 10^{-3}$	Glass temperatures (K) T_g^{S*}	T_g^{soft}	T_g'	$\overline{w'_S}$ Inverse	Linear
1	SB	22.0	364	184	272	0.654	0.489
2	SB	90.0	371	187	340	0.907	0.832
3	SB	90.5	371	195	333	0.874	0.784
4	SBS	16.5	361	188	272	0.644	0.486
5	SBS	13.0	358	183	339	0.941	0.891
6	SBS	7.0	362	185	287	0.727	0.576
7	SBS	21.0	364	198	323	0.849	0.753
8	SBS	21.1	364	194	308	0.793	0.671
9	SBS	22.3	364	187	329	0.888	0.802
10	SBS	18.7	362	188	337	0.920	0.856
11	SBS	19.9	363	190	339	0.922	0.861
12	SBS	44.3	368	185	323	0.859	0.754
13	SBS	45.4	369	188	303	0.774	0.635
14	SBS	17.05	361	194	263	0.567	0.413
16	S–DMS	16.6	361	155	259	0.704	0.505
17	S–DMS–S	8.6	364	155	316	0.887	0.770
18	S–DMS–S	12.8	357	150	335	0.952	0.894
19	DSM–S–DMS	7.7	363	191	320	0.851	0.750
20	S–HI	37.0	368	217	337	0.868	0.795
21	S–HB–S	7.5	362	203	331	0.880	0.805
22	S–HB–S	10.0	353–365	208	323	0.867–0.828	0.793–0.732
23	TBS–B–TBS	51.0	403	201	257	0.435	0.277
24	$(SB)_4$	18.0	362	185	300	0.784	0.650
25	$(SB)_4$	10.7	354–366	183	331	0.926–0.894	0.865–0.809

* Calculated

authors[14] pointed out that the interphase would have to be rich in PS; use of $T_g^S = 100°C$ and $T_g^B = -76°C$ yields $\overline{w'_S} = 0.716$ (linear) or $\overline{w'_S} = 0.827$ (inverse). Other results[15] for a similar copolymer (SBS; $w_S = 0.30$; $\overline{M}_n = 50\,000$) cast from four different solvents also show a middle transition for samples cast from two of the solvents. Both thermal analysis (d.s.c.) and mechanical analysis (tan δ vs. T) show an intermediate transition, although the temperatures differ slightly: d.s.c. has -88, -14 and 71°C for the three events, while the tan δ curve gives -70, $+10$ and 100°C. Identifying the middle event as a T_g' gives $\overline{w'_S} = 0.47$ (linear) and $\overline{w'_S} = 0.62$ (inverse) for both methods when the corresponding values of T_g^S and T_g^B are used.

The implications resulting from calculations of $\overline{w'_S}$ or $\overline{\phi'_S}$ are not always believed by those who obtain them. The authors of one stress relaxation study[16] on SBS triblocks used a sequence of logic involving analysis of the magnitude of ΔH_a [$\equiv 2.303\ R\ \mathrm{d}(\log a_T)/\mathrm{d}(1/T)$, where a_T is the WLF temperature shift factor] and free volume considerations to deduce a $\overline{w'_S}$ of about 0.80. However, they doubted the reliability of that estimate and apparently rejected the possibility that an asymmetric interphase could exist.

MEASUREMENT OF $\phi'_A(x)$

More extensive investigations[17–20] into the relationship between interphase profile and viscoelastic properties utilize mechanical models to interpret experimental results for block copolymers. One group[17] investigated a series of SBS, BSB and SIS block copolymers, all with about 50% PS by weight (and with $17\,000 \leqslant \overline{M}_n \leqslant 136\,000$) and concluded that the interphase must be rich in PS. Experimental results for dynamic storage and loss moduli E' and E'' were compared to values predicted by a composite-type mechanical model. The model incorporated an orientation parameter relating the parallel and perpendicular contributions to the moduli, a composition profile across the interphase, and a volume fraction of interphase material predicted from Meier's thermodynamic model[21]. They found a better fit between the model predictions and the experiments when the mole-fraction profile across the interphase was assumed to be symmetric than when the volume fraction was symmetric. (Symmetry in mole fraction would imply $\overline{\phi'_S} \approx 0.64$ for the PS–PB system.)

Another composite model[18] used linear and sinusoidal ϕ'_A profiles (both symmetric) to mimic the dynamic behaviour for a series of block copolymers of the form ABC, where A is polystyrene, C is polyisoprene and B is a random copolymer of styrene and isoprene. This model was qualitatively successful in predicting many of the features of the storage modulus G' and tan δ as functions of temperature.

Both modelling attempts above[17,18] suffered from two major restrictions: only one or two composition profiles were considered, and the volume fraction of the interphase material was taken as a fixed value found from thermodynamic considerations[21] rather than being adjusted to fit the experimental data.

A more flexible model, developed independently[19,20], avoids these two constraints. In it, $G'(T)$ and $G''(T)$ for SBS triblocks are fitted quantitatively using a composite model somewhat different from the others and permitting substantially more microstructural information to be incorporated. The interphase profile itself is varied in great detail, while the volume fraction of the interphase is allowed to assume any consistent value. It is found that the $G'(T)$ results are most sensitive to the volume fraction of interphase material while the $G''(T)$ predictions are most sensitive to the detailed shape of $\phi'_A(x)$.

The model was matched[19,20] to the data with extreme precision for three SBS block copolymers ($w_S = 0.482$,

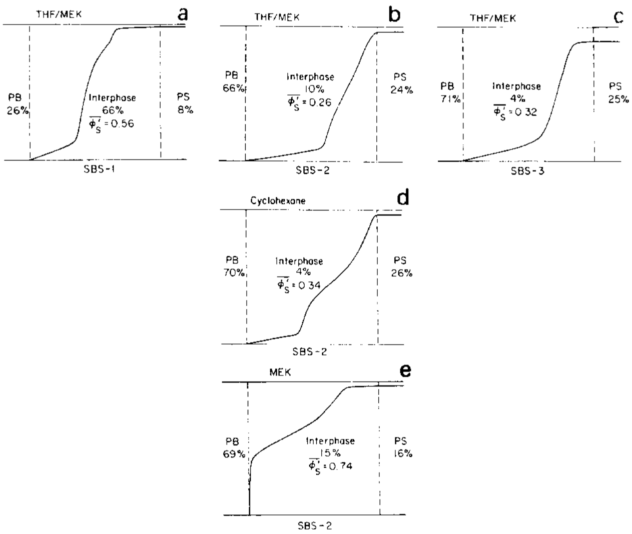

Figure 2 Shapes of interphase composition profiles $\phi'_S(x)$ inferred[19,20] from torsion pendulum data. Three SBS polymers are represented, and three solvents are used for sample casting. The effect of solvent is shown by (b), (d) and (e): tetrahydrofuran/methyl ethyl ketone (THF/MEK), cyclohexane, and MEK alone. The variation with copolymer properties is shown by (a), (b) and (c): SBS–1 has $w_S=0.482$ and $\bar{M}_n=58\,000$; SBS–2 has $w_S=0.293$, $\bar{M}_n=110\,000$; SBS–3 has $w_S=0.268$, $\bar{M}_n=49\,000$. The interphase positions are normalized by using the abscissa $x/\Delta T$, but ΔT may differ among the five cases. Values of $\overline{\phi'_S}$ are displayed for each, as are the volume percentages of the three regions (PB phase, PS phase, interphase)

$\bar{M}_n=58\,000$; $w_S=0.293$, $\bar{M}_n=110\,000$; $w_S=0.268$, $\bar{M}_n=49\,000$) cast from three solvents. Previously unreported results for microstructures inferred from this procedure are presented in *Figure 2*, which shows how the interphase varies with polymer composition (cast from the same solvent) or with the casting solvent (for the same polymer). The volume fraction of interphase ranges from 4%–66% of the total material, and $\overline{\phi'_S}$ ranges from 0.26–0.74 (and is never really close to 0.50). Examination of the $\phi'_A(x)$ indicates asymmetric behaviour (as must occur for $\overline{\phi'_S}\neq 0.50$) and several unusual or unexpected curve shapes. The magnitude of the asymmetries is sufficiently large to indicate that they are not artifacts of minute variations in the mathematical details of the model but instead represent a true phenomenological result. Reinforcement of the model's realism was recently provided[21] from its successful application to blends of SBS with PS and SBR random copolymer.

One important conclusion from all three mechanical models[17–20] is that intermediate loss peaks (a T'_g observation) are not needed to justify the presence of the interphase. The 'slice-by-slice' contribution of the interphase material accounts for the shape of the plateau region in $G'(T)$ or $G''(T)$. Hence an absence of a sharply discernable T'_g phenomenon in no way implies that the interphase is not present.

CONCLUSION

This communication has identified many isolated experimental observations, obtained with many different techniques (XPS, d.s.c., e.s.r. and viscoelastic mechanical property measurements), for a variety of block copolymer architectures (AB, ABA, BAB, ABC and star) and chemistries, all of which individually seem to support the existence of asymmetric interphase composition profiles. Taken as a whole, the evidence seems conclusive that such asymmetries exist and occur far more often than not.

Of course, the experimentally observed asymmetries may result from measurements on samples which may not be at, or even close to, a true thermodynamic equilibrium. The variation of bulk properties with casting solvent alone should be proof that some samples cannot be at equilibrium; otherwise, they would have the same properties, regardless of casting solvent. However, there is no obvious reason why the equilibrium profile shape should not change with copolymer composition, molecular weight or chemistry.

There is always a question[23] as to whether any glassy-state polymer approaches equilibrium. Such complications are expected to be even more severe in microphase-separated block copolymers[24]. One suggestion for evaluating possible nonequilibrium effects would be to perform experiments to measure $\overline{\phi'_A}$ or $\phi'_A(x)$ for block copolymers in the microphase-separated melt state, where greater molecular motion would presumably allow a closer approach to equilibrium. We are aware of no such experiments to date.

Even lacking results for $\overline{\phi'_A}$ in melts, the preponderance of evidence for asymmetries in the solid state suggests a need for fundamental investigations into the thermodynamics of block copolymer systems using a model wherein such asymmetric composition profiles can be accommodated. One theory[25] for block copolymers in solution allows 'unsymmetric' interphase profiles in the sense that the solvent fractions in the two homogeneous phases are not equal, and hence the calculated $\phi'_A(x)\neq 1-\phi'_B(x)$. Our recent thermodynamic model[26] allows any mathematically defined composition profile to be employed; model predictions for asymmetric profiles are discussed in the following companion paper[27] and elsewhere[28]. Since many physical properties of block copolymers have been found[26] or proposed[29] to depend strongly on the nature of the interphase profile, variations in the degree of asymmetry are expected to have significant impact on model predictions.

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REFERENCES

1 Hashimoto, T. *et al. Macromolecules* 1981, **14**, 844; 1981, **14**, 1196; 1980, **13**, 1660; 1980, **13**, 1237 and references therein
2 Richards, R. W. and Thomason, J. L. *Macromolecules* 1983, **16**, 982; *Polymer* 1983, **24**, 1089; 1983, **24**, 275; 1981, **22**, 581
3 Thomas, H. R. and O'Malley, J. J. *Macromolecules* 1979, **12**, 323
4 O'Malley, J. J., Thomas, H. R. and Lee, G. M. *Macromolecules* 1979, **12**, 996
5 Gaines, G. L., Jr. *Macromolecules* 1981, **14**, 208
6 Djermouni, B. and Ache, H. J. *Macromolecules* 1980, **13**, 168
7 Meyer, G. C. and Widmaier, J. M. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 389
8 Kumler, P. L., Keinath, S. E. and Boyer, R. F. *Polym. Eng. Sci.* 1977, **17**, 613
9 Henderson, C. P. and Williams, M. C., presented at IUPAC MACRO 82, Amherst, Mass., USA, July 1982

10 Boyer, R. F. *Macromolecules* 1974, **7**, 142
11 Lu, Z., Krause, S. and Iskander, M. *Macromolecules* 1982, **15**, 367
12 Krause, S., Lu, Z. and Iskander, M. *Macromolecules* 1982, **15**, 1076
13 Gaur, U. and Wunderlich, B. *Macromolecules* 1980, **13**, 1618
14 Beamish, A., Goldberg, R. A. and Hourston, D. J. *Polymer* 1977, **18**, 49
15 Miyamoto, T., Kodama, K. and Shibayama, K. *J. Polym. Sci., Part A-2* 1970, **8**, 2095
16 Kamykowski, G. W., Ferry, J. D. and Fetters, L. J. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 2125
17 Kraus, G. and Rollmann, K. W. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1133
18 Annighöfer, F. and Gronski, W. *Colloid Polym. Sci.* 1983, **261**, 15; see also Stadler, R. and Gronski, W. *Colloid Polym. Sci.* 1983, **261**, 215
19 Diamant, J. Ph.D. Thesis, Univ. of California, Berkeley, 1982
20 Diamant, J., Soong, D. S. and Williams, M. C. in 'Contemporary Topics in Polymer Science', (Eds. W. J. Bailey and T. Tsurata), Vol. 4, Plenum Press, New York, 1984
21 Diamant, J., Soong, D. S. and Williams, M. C. *Polym. Eng. Sci.* 1982, **22**, 673
22 Meier, D. J. *Am. Chem. Soc. Polym. Prepr.* 1974, **15**(1), 171
23 Roe, R.-J. *Macromolecules* 1981, **14**, 1586
24 Shibayama, M., Hashimoto, T. and Kawai, H. *Macromolecules* 1983, **16**, 1434
25 Noolandi, J. and Hong, K. M. *Macromolecules* 1983, **16**, 1443
26 Henderson, C. P. and Williams, M. C. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 1001
27 Henderson, C. P. and Williams, M. C. *Polymer* 1985, **26**, 2026
28 Henderson, C. P. Ph.D. Thesis, Univ. of California, Berkeley, CA, USA, 1984
29 Henderson, C. P. and Williams, M. C. *J. Polym. Sci., Polym. Lett. Edn.* 1979, **17**, 257