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Enthalpy-enhanced microphase separation in homopolymer/block copolymer blends

Adeyinka Adedeji, Steven D. Hudson and Alex M. Jamieson*
Department of Macromolecular Science, Case Western Research University, Cleveland, OH 44106, USA
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A recent analysis of the enthalpy-driven swelling of a polymer brush by a compatible homopolymer leads to a simple swelling criterion that delineates the entropic and the enthalpic contributions. We consider the implications of this model for the formation of microphase in binary blends of a symmetric diblock copolymer (A-b-B) for which each block has a degree of polymerization (DP) $= N$ and a homopolymer (A, B or X) which has $\mathrm{DP} = P$. The model suggests that, in A/A-b-B and B/A-b-B blends, microphase formation will occur only if $N/P > 1$. However, in X/A-b-B blends, where there is an exothermic interaction between X and A or B, the enthalpic swelling can enable microphase formation even if $N/P < 1$. We present morphological observations which are qualitatively consistent with these predictions. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

Numerous theoretical and experimental studies have been described of solubilization of block copolymer segments by homopolymers, where the homopolymer is of similar chemistry as one of the block copolymer segments (i.e. A/A-b-B, isochemical blends). The theoretical results indicate that solubilization occurs only when the molecular weight of the homopolymer, P, is equal to or lower than that of the compatible block copolymer segment, N (i.e. $N/P \geq 1$)[1–12]. This prediction is qualitatively consistent with various experimental observations[1–10]. In such isochemical blends, the solubilization is entropically controlled, and the molecular weights of the constituent polymers are the primary variables to manipulate the blend morphology. In addition, the molecular weights of the constituent polymers also determine the viscosity and the mechanical properties of the blends, so that generally some compromise of morphology, viscosity and mechanical properties is made. The requirement $N/P > 1$ implies that the molecular weights of the homopolymers, P, which are the principle components of the blend should be relatively low. This implies that isochemical homopolymer/block copolymer blends may be mechanically weak, particularly if a low molecular weight block copolymer is used. On the other hand, a large value of N may lead to processing difficulties since the melt viscosity increases strongly with N^{13}.

Theoretical and experimental studies show that solubilization of a block copolymer segment by an homopolymer is enhanced when an exothermic interaction occurs between them (i.e. in X/A-b-B blends)[14–20]. Specifically, Lowenhaupt *et al.*[19] developed a theoretical analysis of phase separation in homopolymer/diblock copolymer blends which predicts that macrophase separation will occur in A/A-b-B blends when $N/P > 1$, but that in X/A-b-B blends even a small exothermic interaction between X and A will produce microphase separation when $N/P < 1$. Morphological evidence to support this prediction was presented[19]. Tucker *et al.*[14] reported experimental evidence to demonstrate that swelling or solubilization of a homopolymer in a block copolymer is enhanced in the presence of an exothermic interaction. These observations were shown[15] to be in agreement with a theoretical treatment[14] based on the Flory–Huggins model. The experimental approach employed differential scanning calorimetry (d.s.c.) to monitor the glass transition temperature (T_g) of the hard phase in blends of poly(phenylene oxide) (PPO) and a triblock homopolymer copolymer that had polystyrene (PS) end blocks and a random copolymer of ethylene and butylene as the mid-block. Brown *et al.*[16] used secondary ion mass spectrometry (s.i.m.s.) with quadrupole mass analysis and secondary ion mass detection to show that a favourable exothermic mixing of a block copolymer segment (PS) with a polymeric solvent (PPO) can cause a significant increase in swelling of a block copolymer brush. This result is in qualitative agreement with a theoretical analysis[16], that is an extension of an equilibrium model earlier employed by de Gennes[21] and Leibler[22] to describe the swelling of block copolymer chains grafted to a wall (referred to as a polymer brush) by a homopolymer of the same chemistry. Brown's modification was obtained in the limit of infinite homopolymer molecular weight. Subsequently, Braun *et al.*[17] extended this treatment to include finite homopolymer molecular weight. This model is particularly relevant to our present study and thus will be discussed in more detail below. Our aims in this paper are:

1) to present a simple swelling criterion that shows clearly the enhanced solubilization of a homopolymer of molecular weight P in a polymer brush of molecular weight N with which it has an exothermic interaction;

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* To whom correspondence should be addressed

2) to report new morphological data that support this theoretical prediction.

At this point, since the free energy of mixing will be minimized by maximizing the A-X contacts in an X/A-b-B blend, we note that this type of an enthalpically interactive block copolymer may improve interfacial adhesion in blends when P is much larger than N. Evidence to support this idea has been reported by Adedeji *et al.*[23]. In addition, Reimann *et al.*[24] have shown that an enthalpically interactive block copolymer has superior rheological properties and a higher tendency to entangle with the immiscible homopolymer matrices. Such observations suggest that blends of a low molecular weight block copolymer with high molecular weight homopolymers having good mechanical properties can be processed at a lower viscosity, compared to the isochemical counterparts.

Theory

First we note that de Gennes[21] obtained an expression for the thickness L of a polymer brush in a good solvent. Assuming that the brush consists of overlapping closely packed polymer coils of degree of polymerization N, grafted to a surface at distance D from one another such that $D = a\sigma^{-1/2}$, and the volume per grafted chain is LD^2 (where a is the monomer size and σ is the dimensionless areal density, then

$$L \cong Na\sigma^{1/3} \tag{1}$$

Thus, in this strong stretching regime, the brush thickness is proportional to N. This expression follows from arguments based on a Flory type of self-consistency, viz. when the polymer brush is exposed to a polymeric solvent described as mobile chains of lengths comparable to or smaller than that of the grafted chains (i.e. $N \leq P$), there are two contributions to the swelling of the grafted chains:

1) a translational entropic mixing between N and P chains;
2) the return conformational entropy or elastic term for the grafted brush which resists the swelling.

The Flory–Huggins entropy of mixing per lattice site is expressed as:

$$\Delta S_{\text{mix}} = \frac{1}{N}\phi_{\text{N}} \ln \phi_{\text{N}} + \frac{1}{P}\phi_{\text{P}} \ln \phi \tag{2}$$

where ϕ_{N} is the volume fraction of the brush, and ϕ_{P} is the volume fraction of the polymeric solvent in the brush. The first term of equation (2) is eliminated since a grafted chain or a block copolymer at an interface loses its translational degree of freedom. The second term is the translational entropy of the mobile homopolymer chains. When expressed per block copolymer chain at the interface, the free energy of mixing, F_{mix}, becomes[21]

$$\frac{F_{\text{mix}}}{kT} = \frac{LD^2}{a^3}\frac{1}{P}\phi_{\text{P}} \ln \phi \tag{3}$$

where $[LD^2/a^3]$ corresponds to the number of lattice sites per brush. In the following discussion, the reader should be mindful that this term is not valid when $P \gg N$, since in that case only segments of the homopolymer chains can be accommodated in the brush. In such case, segmental mixing entropy remains. Brown *et al.*[16] introduced an enthalpic term and expressed F_{mix} as

$$\frac{F_{\text{mix}}}{kT} = \frac{LD^2}{a^3}\frac{1}{P}\phi_{\text{P}} \ln \phi_{\text{P}} + \chi N\phi \tag{4}$$

The return entropy leads to an elastic free energy which can be expressed simply as[11]

$$\frac{F_{\text{el}}}{kT} = \frac{3}{2}\left[\frac{L^2}{L_0^2} + \frac{L_0^2}{L^2}\right] \tag{5}$$

where $L_0 = N^{-1/2}a$. Because equation (5) is approximate, the factor 3/2 is sometimes omitted. With the constraint that

$$\phi_{\text{N}} = 1 - \phi_{\text{P}} = \frac{Na^3}{LD^2} \tag{6}$$

minimization of $F_{\text{mix}} + F_{\text{el}}$ to obtain the brush thickness L leads to

$$\phi_{\text{N}} \ln(1 - \phi_{\text{N}}) + \phi_{\text{N}}^2 + \chi\phi_{\text{N}}^3 P = -2P\sigma^2[1 - (\phi_{\text{N}}^2/N\sigma^2)^2] \tag{7}$$

Equation (7) is equation (4) in ref. 16. On expanding $\ln(1 - \phi_{\text{N}})$ for a small value of ϕ_{N}, the following expression is obtained:

$$\left(\chi P - \frac{1}{2}\right)\phi_{\text{N}}^3 = -2P\sigma^2\left[1 - \left(\frac{L_0}{L}\right)^4\right] \tag{8}$$

Assuming strong stretching $(L_0/L)^4 \ll 1$, and infinite molecular weight of the homopolymer $-\chi P \gg 1$, the thickness of an enthalpically swollen brush is obtained:

$$L \cong (-\chi/2)^{1/3} Na\sigma^{1/3} \tag{9}$$

When equation (9) [equation (5) in ref. 16)] is compared with equation (1) the difference is the new $(-\chi/2)^{1/3}$ term which increases swelling when there is an exothermic interaction ($\chi < 0$). However equation (9) omits the entropic contribution to swelling when $P < N$ in isochemical and exothermic blends, and hence predicts that for an athermal solvent ($\chi = 0$), as considered by de Gennes, there will be no swelling, irrespective of the value of P. Manipulation of equation (9) to correct for this deficiency is straightforward. By simply considering that P is finite but that the stretching is still large ($(L_0/L)^4 \ll 1$), equation (8) becomes

$$\left(\chi P - \frac{1}{2}\right)\left[\frac{Na^3}{LD^2}\right]^3 = -2P\sigma^2 \tag{10}$$

and simplifying further

$$L \cong \left[\frac{N}{4P} - \frac{N\chi}{2}\right]^{1/3} a(\sigma N^2)^{1/3} \tag{11}$$

This result is essentially identical to that derived by Braun *et al.*[17]. Equation (11), may be expressed more compactly as

$$\left(\frac{L}{L_{\text{ref}}}\right)^3 \cong \frac{N}{P} - 2N\chi \tag{12}$$

where $L_{\text{ref}} = [a^3\sigma/4]^{1/3}N^{2/3}$ is the brush length of the neat block copolymer. Equation (12) indicates that when the homopolymer molecular weight P is larger than that of the block copolymer brush, a favourable enthalpic interaction is necessary for swelling to occur, and that the enthalpic swelling is further enhanced by increasing the block copolymer molecular weight N relative to P.

Evidence to support the synergistic effects of N/P ratio and negative χ on swelling of a block copolymer brush has been obtained directly by Brown *et al.*[16] and indirectly in our laboratory by monitoring changes in interfacial curvature of the disperse phase in polymer blends containing block copolymers[25–27]. Here we focus on the implications of equation (12) for microphase vs macrophase formation in homopolymer block copolymer blends. Specifically, in blends A/A-b-B or X/A-b-B, microphase vs macrophase formation should be determined by the ability of the homopolymer A or X to solubilize the compatible block copolymer segment (A), provided we are in a thermodynamic 'window' defined by the repulsive interactions: $N\chi_{AB}$ or $N\chi_{XB}$ where $N = (P^{1/2} + N_B^{1/2})^2/PN_B$, where P and N_B are the degrees of polymerization A or X, and the B copolymer blocks, respectively. These quantities have to be large enough that we are above the critical micellar concentration, but not so large that macrophase separation occurs initially in the solvent casting process used to prepare blend samples for microscopic analysis. In this 'window' therefore, equation (12) indicates that microphase formation can occur when $\chi_{AX} < 0$ even if $N/P < 1$. Morphological evidence consistent with this prediction has been reported previously by Lowenhaupt *et al.*[19], who showed that in a blend of PS-b-PMMA/SAN where SAN, a random azeotropic copolymer of styrene and acrylonitrile, mixes exothermically with poly(methyl methacrylate) (PMMA), microphase separation occurs when $N/P < 1$. In this paper we present evidence that a similar effect occurs in blends of PS-b-PMMA/PVC, where PVC is polyvinyl chloride which also mixes exothermically with PMMA.

Equation (12), like that reported by Braun *et al.*[17], clearly shows that a negative χ is an additional driving force for the brush to swell, which may complement or dominate the entropic contribution. When the solubilization is athermal (zero χ), equation (12) indicates that the brush thickness decreases with increasing P. This prediction is consistent with that of Meier[12] and with the observations of Tucker and Paul[14] that the amount of a homopolymer that solubilizes in a block copolymer brush decreases to a very small level as the ratio P/N approaches unity. It should be stressed that equation (12) assumes that the polymeric solvent chain can be fully accommodated in the brush. When $P > N$, P in equation (12) should be replaced by N since the length of the solvent segment that is partly accommodated in the brush cannot be greater than N. One should note further that equation (12) indicates that the molecular weights of both homopolymer and brush are important, whereas Tucker *et al.*[14,15] deduce that brush swelling is only dependent on the molecular weight of the brush.

Experimental results and discussion

Mixtures of PMMA with PMMA-b-PS are chosen as the isochemical blends, and a mixture of PVC with PMMA-b-PS as the exothermic blend. The characteristics of the materials used are listed below.

1) PMMA(24) is a PMMA homopolymer of $M_w = 23\,800\,\mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.07$, purchased from Polysciences, Inc.
2) PMMA(107) is a PMMA homopolymer of $M_w = 107\,000\,\mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.10$, purchased from Polysciences, Inc.
3) PVC(120) is a polydisperse homopolymer of inherent viscosity = 0.65 and $M_w = 120\,000\,\mathrm{g\,mol^{-1}}$, purchased from Scientific Polymer Products, Inc.
4) B(65) is a PMMA-b-PS of $M_w = 65\,500$ (32 500/33 000, respectively) and $M_w/M_n = 1.06$, purchased from Polysciences, Inc.

Methyl ethyl ketone (MEK) is known as a good solvent that leads to molecularly homogeneous mixtures of PMMA and PVC[28], and is thus chosen as the solvent. Stock solution of each polymer was made in MEK solvent at 1 g per 100 ml concentration. Three binary blends were made with 60 vol% of B(65) and 40 vol% of PMMA(24), PMMA(107) or PVC(120). The solvent was slowly removed over a period of 21 days at room temperature. Final traces of the solvent were removed by drying at 70°C for 1 day at atmospheric pressure, and then for 1 day under vacuum. Central portions of the cast films (~0.4 mm thick) were sectioned, using a Microstar diamond knife and a RMC Inc. MT–7000 microtome machine, in a direction normal to the surface to obtain ultra-thin films (~60 nm thick). The PMMA(24)/B(65) and the PMMA(107)/B(65) samples were sectioned at room temperature, and the PVC(120)/B(65) sample was cryogenically sectioned at −70°C. The thin films were subsequently exposed to RuO_4 vapour for 45 min in an enclosed chamber containing approximately 0.15% aqueous solution of RuO_4. The PS component in the specimen is stained with the RuO_4 and therefore appears dark when imaged in bright field by mass–thickness contrast (using a JEOL JEM-100SX, transmission electron microscope (TEM), at an accelerating voltage of 100 kV).

The micrographs of PMMA(107)/B(65), PMMA(24)/B(65) and PVC(120)/B(65) blends are displayed in *Figures 1, 2* and *3*, respectively. Clearly microphase separation has occurred in the blends containing PMMA(24) (*Figure 2*) and in that of PVC(12) (*Figure 3*), whereas the PMMA(107)/B(65) blend has generated macrophase separation (*Figure 1*). There is poor solubilization of the B(65) block copolymer by the PMMA(107) homopolymer, as evidenced by the macrophase morphology shown in *Figures 1a* and *1b*. In *Figure 1b* (higher magnification), the macrodomains occupied by the block copolymer show a wormlike internal microstructure, indicative that microphase separation has occurred subsequent to macrophase separation. Solubilization is poor since the N/P ratio is 0.3, and there is no enthalpic contribution to solubilization of the PMMA(107) homopolymer in the PMMA brush, this leading to liquid–liquid macrophase separation. This result is consistent with observations made in previous studies by other investigators[1–10,12], and is also consistent with a small value obtained for the swelling criterion, equation (12). On increasing the entropic contribution by raising the N/P value from 0.3 to 1.37 (i.e. PMMA(24)/B(65) blend), uniformly distributed wormlike microstructures are formed as shown in *Figure 2*. This is again in agreement with equation (12) since $\chi = 0$, $N/P > 1$, and $L/L_{\mathrm{ref}} > 1$, predicting that the PMMA(24) homopolymer will be solubilized in the PMMA segment or brush.

In the PVC(120)/B(65) blend, the entropic contribution is unfavourable as in the PMMA/B(65) blend since $N/P = 0.27$. However, there is a contribution from the negative nature of χ, the favourable exothermic mixing between PVC and PMMA. PVC is known to be exothermically miscible with PMMA at all compositions[29–33] due to a hydrogen-bonding interaction between the PVC methine hydrogen and the carbonyl oxygen of

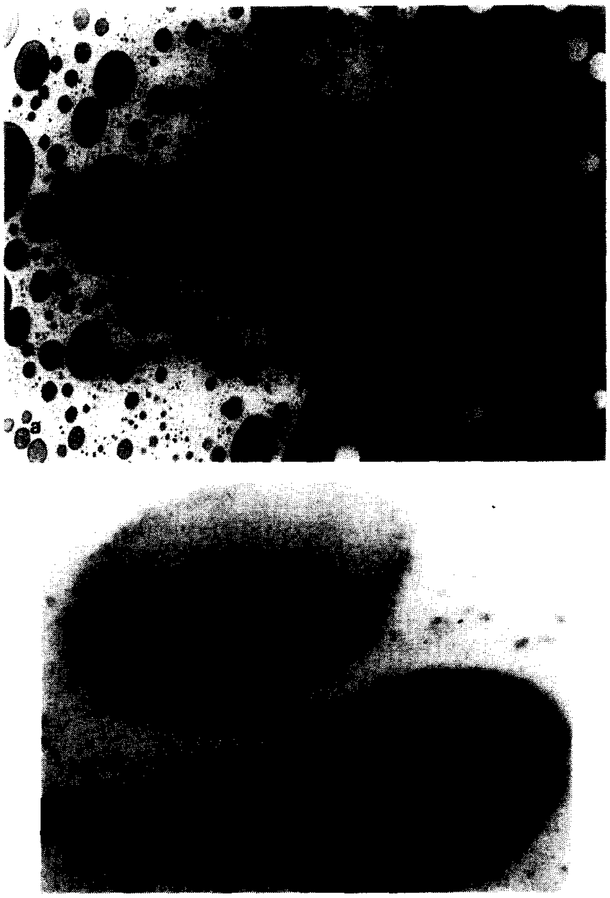

Figure 1 (a) Macrophase separated structure in a PMMA(107)/PMMA-b-PS(65) blend. Block copolymer rich domains appear dark. (b) Microphase separation within these domains is evident at higher magnification

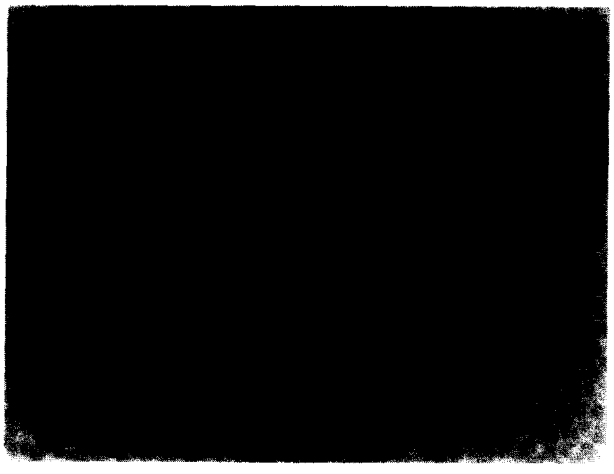

Figure 2 Wormlike microstructures formed in a PMMA(24)/PMMA-b-PS(65) blend indicating good solubilization when N/P is greater than unity in an isochemical blend

Figure 3 Wormlike microstructures formed in a PVC(120)/PMMA-b-PS(65) blend indicating excellent solubilization enhanced by the enthalpic mixing between PVC and the PMMA segment. The average size of the microstructure is smaller than that of the PMMA(24)/PMMA-b-PS(65) (see *Figure 2*), which suggests that the brush swelling in PVC(120)/PMMA-b-PS(65) is stronger in spite of the N/P value being merely 0.27

PMMA[33,34]. Thus, despite the unfavourable entropic effect in PVC(120)/B(65), it is predicted from equation (12) that PVC will be solubilized in the PMMA block copolymer segment, and hence that microphase formation can occur. Indeed, as evident in *Figure 3*, uniformly distributed wormlike microstructures are formed, similar to those in the PMMA(24)/B(65) blend. A significant difference should be noted, however. In *Figure 3*, the diameter of the microdomains is approximately half that of the isochemical blends (*Figure 2*). Exothermic interfacial mixing therefore maximizes swelling, increasing the microdomain surface to volume ratio, significantly influencing both the overall morphology and the interfacial structure.

Conclusion

The theoretical expression obtained by Brown *et al.*[16] for enthalpy-driven swelling of a block copolymer brush in polymeric solvent of infinite molecular weight has been extended to the case when the homopolymer molecular weight is finite to obtain a simple swelling criterion that can be used to explain the contributions of configurational entropy and exothermic mixing to solubilization of a homopolymer in a block copolymer. This result is essentially identical to an expression previously developed by Braun *et al.*[17]. It is noted that, above the CMC of the block copolymer, this model suggests that exothermic mixing of the homopolymer and the compatible block copolymer segment can enable microphase separation even when $N/P < 1$. Morphological evidence to support this was obtained in blends of PVC with PS-b-PMMA. These confirm a major influence on both copolymer solubilization and interfacial structure.

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References

1 Thomas, E. L. and Winey, K. I. *Proc. ACS, Div. Polym. Mater. Sci. Eng.* 1990, **62**, 686
2 Winey, K. I., Thomas, E. L. and Fetters, L. J. *Macromolecules* 1991, **24**, 6182
3 Mayes, A. M. and Olvera de la Cruz, M. *Macromolecules* 1988, **21**, 2543
4 Kinning, D. J., Thomas, E. L. and Fetters, L. J. *J. Chem. Phys.* 1989, **90**, 5806
5 Kinning, D. J., Winey, K. I. and Thomas, E. L. *Macromolecules* 1988, **21**, 3502
6 Lowenhaupt, B. and Hellmann, G. P. *Polymer* 1991, **32**, 1065
7 Lowenhaupt, B. and Hellmann, G. P. *Coll. Polym. Sci.* 1990, **268**, 885

8 Tanaka, H., Hasegawa, H. and Hashimoto, T. *Macromolecules* 1991, **24**, 240

9 Koizumi, S., Hasegawa, H. and Hashimoto, T. *Makromol. Macromol. Symp.* 1992, **62**, 75

10 Jeon, K. J. and Roe, R. J. *Macromolecules* 1994, **27**, 2439

11 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca NY, 1979

12 Meier, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1977, **18**, 340

13 Dalvi, M. C., Eastman, C. E. and Lodge, T. P. *Phys. Rev. Lett.* 1993, **71**, 3383

14 Tucker, P. S., Barlow, J. W. and Paul, D. R. *Macromolecules* 1988, **21**, 2794

15 Tucker, P. S. and Paul, D. R. *Macromolecules* 1988, **21**, 2801

16 Brown, H. R., Char, K. and Deline, V. R. *Macromolecules* 1990, **23**, 3383

17 Braun, H., Rudolf, B. and Cantow, H. J. *Polym. Bull.* 1994, **32**, 241

18 Siqueira, D. F. and Nunes, S. P. *Polymer* 1994, **35**, 490

19 Lowenhaupt, B., Steurer, A., Hellmann, G. P. and Gallot, Y. *Macromolecules* 1994, **27**, 908

20 Vilgis, T. A. and Noolandi, J. *Macromolecules* 1990, **23**, 2941

21 de Gennes, P. G. *Macromolecules* 1980, **13**, 1069

22 Leibler, L. *Makromol. Chem., Macromol. Symp.* 1988, **16**, 1

23 Adedeji, A. and Jamieson, A. M. *Polymer* 1993, **34**, 5038

24 Reimann, R.-E., Braun, H., Weese, J. and Schneider, H. A. *New Polym. Mater.* 1994, **4**, 131

25 Adedeji, A. and Jamieson, A. M. *Macromolecules* 1994, **27**, 4018

26 Adedeji, A., Jamieson, A. M. and Hudson, S. D. *Macromolecules* 1995, **28**, 5255

27 Adedeji, A., Jamieson, A. M. and Hudson, S. D. *Polymer* 1995, **36**, 2753

28 Schmidt, J. J., Gardella Jr., J. A. and Salvati Jr., L. *Macromolecules* 1989, **22**, 4489

29 Walsh, D. J. and McKeown, J. G. *Polymer* 1980, **21**, 1330

30 Walsh, D. J. and McKeown, J. G. *Polymer* 1980, **21**, 1335

31 Walsh, D. J. and Cheng, G. L. *Polymer* 1982, **23**, 1965

32 Walsh, D. J. and Cheng, G. L. *Polymer* 1984, **25**, 495

33 Coleman, M. M. and Zarian, J. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 837

34 Kogler, G. and Mirau, P. A. *Macromolecules* 1992, **25**, 598