Glass transition and crystallization of poly(vinyl alcohol)-*g*-poly(methyl methacrylate) graft copolymers

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The glass transition behaviour, microphase separation morphology and crystallization of poly(vinyl alcohol)-*g*-poly(methyl methacrylate) graft copolymers (PVA-*g*-PMMA) were studied. A lamellar microphase separation morphology was formed, even for a copolymer containing only 28 wt% PVA. An unusual glass transition behaviour of the copolymer was found: the glass transition temperature (T_g) of PMMA microphase did not move towards the lower T_g of PVA, but increased markedly to as much as 20 K higher than the T_g of the PMMA homopolymer. The crystallization of the PVA microphase of the copolymer was also investigated.

(Keywords: glass transition; crystallization; graft copolymer)

Introduction

The microphase separation morphology, glass transition behaviour and crystallization of block and graft copolymers have been studied extensively[1–16]. Relatively speaking, a greater number of experimental and theoretical publications have been about amorphous block and graft copolymers[1–5], especially amorphous block copolymers. The dependence of microphase separation morphology on copolymer composition is usually very different for crystalline block and graft copolymers than for amorphous copolymers, owing to the crystallization of their crystallizable blocks[15]. Because of this influence, the glass transition behaviour of the amorphous microphases of crystalline–amorphous copolymers could also be different from the amorphous block and graft copolymer[7]. In the present work, the unusual glass transition behaviour, microphase separation morphology and crystallization of a series of poly(vinyl alcohol)-*g*-poly(methyl methacrylate) graft copolymers (PVA-*g*-PMMA) were studied.

Experimental

Graft copolymerization of methyl methacrylate onto poly(vinyl alcohol). Graft copolymerization of other monomers onto poly(vinyl alcohol) (PVA) has been studied by our group and by several other groups[17–21]. The graft copolymerization of methyl methacrylate (MMA) onto PVA was investigated by Ide[18] and Iwakura and Imai[20]. The synthesis of our PVA-*g*-PMMA copolymers was based on their methods, and was almost identical to the method we used previously for the preparation of poly(vinyl alcohol)-*g*-poly(acrylic acid) graft copolymers (PVA-*g*-PAA)[21]. A summary of the synthesis is given below.

PVA (degree of polymerization = 1750, fully hydrolysed) was extracted with acetone and dried in vacuum before use. MMA was purified by reduced-pressure distillation. The graft polymerization of MMA onto PVA was carried out in a 500 ml three-necked flask equipped with a mechanical stirrer and a condenser. PVA (3.0 g) was first dissolved in 90 ml of doubly distilled water at 360 K; after the solution was cooled to room temperature, and a certain amount of MMA monomer was added to it, the mixture was purged with nitrogen for 30 min and equilibrated to 308 K in a thermostat. Then 10 ml of initiator solution (0.02 M ceric ammonium nitrate in 0.4 M HNO_3) purged with nitrogen was introduced to the mixture to start the polymerization; the reactions were performed under a slight positive pressure of nitrogen for 2 h and finally terminated by pouring the product into a large amount of alcohol.

Purification and characterization of the graft copolymers. The unwanted PMMA homopolymer was extracted from the products in a Soxhlet extractor with acetone for 24 h; the unreacted PVA was extracted from the products with water/n-propanol (v/v = 75/25) mixed solvent for 48 h. The weight fractions of PMMA in the purified graft copolymers were obtained from proton n.m.r. measurements of the corresponding acetated poly(vinyl acetate)-*g*-PMMA in $CDCl_3$, based on the area ratio of a peak at 3.60 ppm ($-OH_3$ protons of PMMA units) and a peak at 4.89 ppm attributed to the methine proton of poly(vinyl acetate) units. The PMMA branches were isolated from the PVA-*g*-PMMA graft copolymers by oxidative degradation of the PVA backbone with concentrated nitric acid[19], and the number average molecular weight of the grafted PMMA was measured by membrane osmometry. The main characterization results of the purified graft copolymers are given in *Table 1*.

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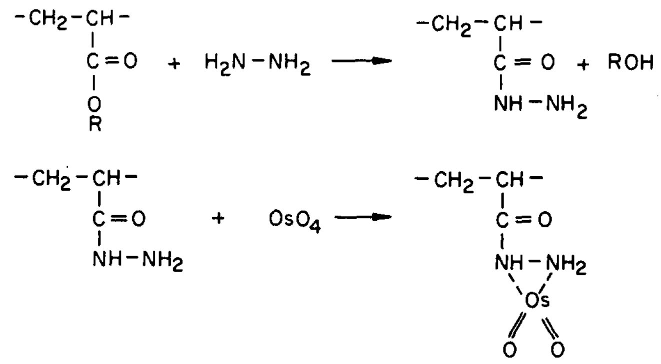
Table 1 Characteristics of the purified PVA-*g*-PMMA graft copolymers

Designation	Weight fraction PMMA	$\bar{M}_n$ (PMMA branch)	N^a (mmol/100 g PVA)
VM1	0.23	42 800	0.72
VM2	0.51	69 600	1.52
VM3	0.65	88 500	2.14
VM4	0.72	90 500	2.84

[a] Number of PMMA branch

D.s.c., WAXD and TEM studies. The samples used for these studies were prepared by evaporating the solvent of PVA-*g*-PMMA solution in dimethylsulfoxide (DMSO) at 403 K and then drying in vacuum. A differential scanning calorimeter (Perkin–Elmer DSC-2c) was used to study the crystallization of PVA-*g*-PMMA graft copolymers. The samples were tempered for 10 min at 523 K, cooled to 323 K at a rate of 10 K min^{-1}, and then heated to 523 K at a rate of 10 K min^{-1}. The wide-angle X-ray diffraction (WAXD) equipment (Philips PW-1700 automatic power diffractometer) was operated at 40 kV and 30 mA, with CuKα radiation filtered electronically, using a nickel film. The scans were obtained with a 0.05° step programme with a collection time of 10 s per step.

The microtomed sections of 60–100 nm thickness, used for transmission electron microscopy (TEM) observation, were prepared at room temperature using an LKB 8800-3 ultramicrotome equipped with a diamond knife. The staining method for acrylate-ester-containing polymer, reported by Kanig and Neff[22] and confirmed as effective by Misra *et al.*[23], was used in the present work. The staining principle is as follows: acrylate-ester-containing polymer was treated with hydrazine or hydroxylamine to form the hydrazide, then reduced with osmium tetroxide vapours in the absence of water (*Scheme 1*). The thin sections were deposited on 200 mesh stainless steel specimen substrates and exposed to hydrazine vapours by suspending them for 2 h over 85% aqueous hydrazine solution in a closed vessel at 318 K. The specimens were dried under vacuum for 15 h to remove all moisture and then exposed to osmium tetroxide (OsO_4) vapours in the absence of water, to stain the acrylate-ester-containing regions. A staining time of 5 min was sufficient to give satisfactory contrast. The stained specimens were examined in a Hitachi H-500 transmission electron microscope.



Scheme 1

Results and discussion

Microphase morphology of the copolymers. Microphase separated structure is an important structural feature of amorphous block and graft copolymers whose corresponding homopolymers are incompatible; it is also the structural feature of crystalline–amorphous block and graft copolymers owing to the added effect of crystallization, besides the driving force of the incompatibility of the two different blocks for some of these copolymers. TEM and small-angle X-ray scattering (SAXS) are two informative methods of studying this microphase structure. In the present work, the microphase morphology of PVA-*g*-PMMA graft copolymers was studied by TEM. The films of PVA/PMMA blends are all turbid in the melt, but the films of copolymer, obtained by slowly evaporating the solvent of the copolymer solutions in DMSO, are transparent, therefore the copolymers synthesized are graft copolymers with microphase separation structure.

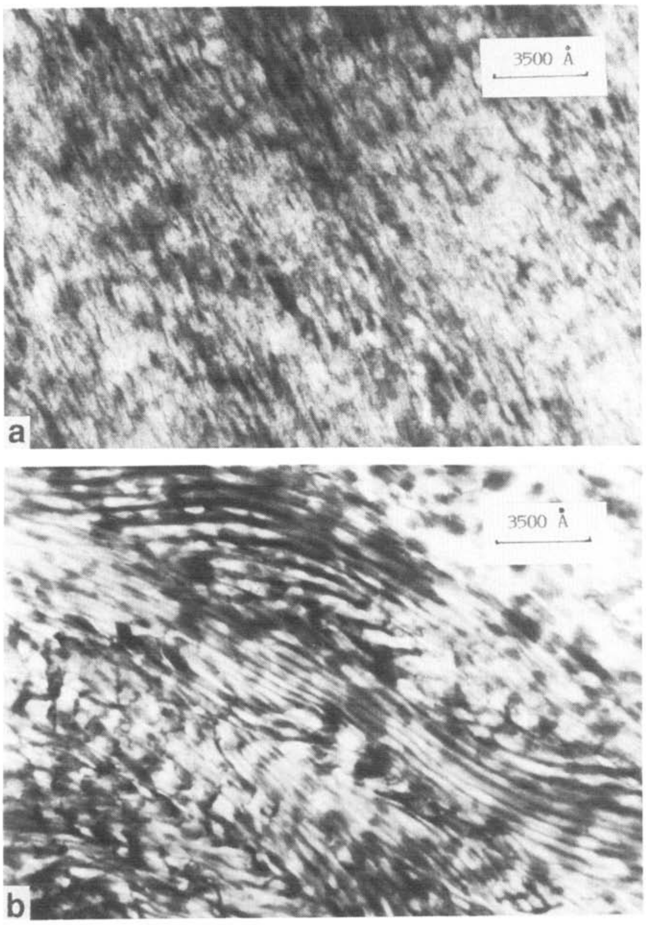


Figure 1 Transmission electron micrographs of osmium-tetroxide-stained microtomed sections of PVA-*g*-PMMA graft copolymers: (a) VM1 and (b) VM4

Figure 1 provides direct evidence for the microphase morphology of two such copolymers. According to the principle of sample staining, as described in the Experimental section, the black microdomains consist of PMMA blocks, and the white ones are PVA microphases. As shown in *Figure 1*, the microphase morphology of the graft copolymers is always lamellar, whether they contain 23 or 72 wt% MMA. This is because of the crystallization of the PVA block. The lamellar interfaces of the copolymer containing 23 wt% MMA are unclear, but they are very sharp for the copolymer containing 72 wt% MMA, indicating that a strong phase-separated structure was formed for the latter. In addition, the average distance between the lamellae of the copolymer with 72 wt% MMA is about 40 nm, and is larger than that of the copolymer containing 23 wt% MMA, as shown in *Figure 1*.

Unusual glass transition behaviour of PMMA microdomains. Amorphous block copolymers usually form microphase separated structure when the degree of incompatibility of the two different blocks is high enough[1]; amorphous graft copolymers behave in the same way. The two different microdomains have their own glass transition temperatures (T_gs). The T_gs are usually dependent on the molecular weights of the corresponding blocks, the copolymer composition and the thermal stress field[7], which is caused by the unequal coefficients of thermal expansion of the two phases. Generally speaking, the T_g of the 'hard phase' is lower than that of its corresponding homopolymer of the same molecular weight, and the T_g of the 'soft phase' is higher than that of its corresponding homopolymer of the same molecular weight. For the case of crystalline–amorphous block and graft copolymers, the dependence of microphase morphology on copolymer composition is usually different from the case of totally amorphous copolymers. The T_gs of the microphases also have something to do with the added effects of crystallization and the thermal stress field, arising from the presence of the crystallites of the crystalline microphase.

In the present work, the glass transition behaviour of PMMA microphases of PVA-*g*-PMMA copolymers was studied using differential scanning calorimetry. Since the T_g of PVA homopolymer (about 348 K) is apparently lower than that of PMMA homopolymer (usually about 378 K), the T_gs of PMMA microphases of the PVA-*g*-PMMA copolymers were expected to be lower than that of PMMA homopolymer. However, as shown in *Figure 2*, the T_gs of PMMA microphases are unexpectedly much higher than that of PMMA homopolymer. In addition, the T_g of PMMA microphase is strongly dependent on copolymer composition: it increases with increasing PMMA weight fraction when the weight fraction is less than 0.65 and decreases with further increase in the weight fraction. The maximum T_g of the PMMA microdomain is about 20 K higher than PMMA homopolymer. This T_g change is not common in block and graft copolymers. However, some reports about unusual T_g changes in block and graft copolymers are found in the literature, such as the unusual T_g behaviour of dimethylsiloxane (DMS) microphases in styrene–dimethylsiloxane block copolymers (PS-*b*-PDMS) reported by Wang and Krause[7]. They found that the T_gs of amorphous DMS microphases in PS-*b*-PDMS diblock copolymers containing $\leqslant 28$ wt% DMS were 6 K lower than the T_g (145 K) of slightly crystalline PDMS. This T_g lowering was caused by thermal stress effects, as confirmed by their theoretical calculations. The reason why the T_gs of PMMA microphases of PVA-*g*-PMMA copolymers are much higher than that of PMMA homopolymer is probably because the melting temperature (T_m) of PVA crystalline microdomains is much higher than the T_g of PMMA microdomains, and hence the crystalline microdomains play the role of hard domains when the temperature is above the T_g of PMMA; the thermal stress effects, arising from the crystallization of PVA backbone, presumably also result in the increase in the T_g of PMMA microphases.

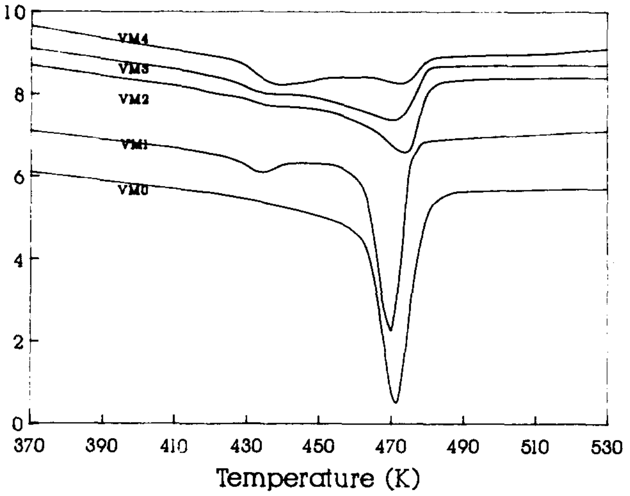


Figure 3 The crystalline temperature (T_c) of PVA-*g*-PMMA graft copolymers and PVA homopolymer during d.s.c. cooling

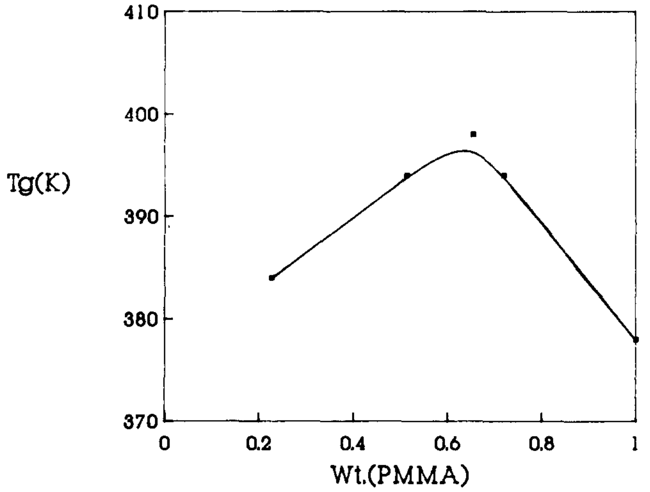


Figure 2 The glass transition temperature (T_g) of PVA-*g*-PMMA graft copolymers

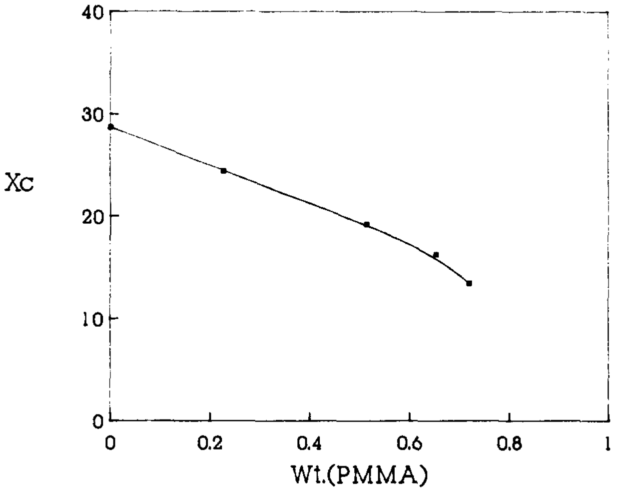


Figure 4 The crystallinity (X_c) of PVA-*g*-PMMA graft copolymers and PVA homopolymer during the d.s.c. cooling process in *Figure 3*

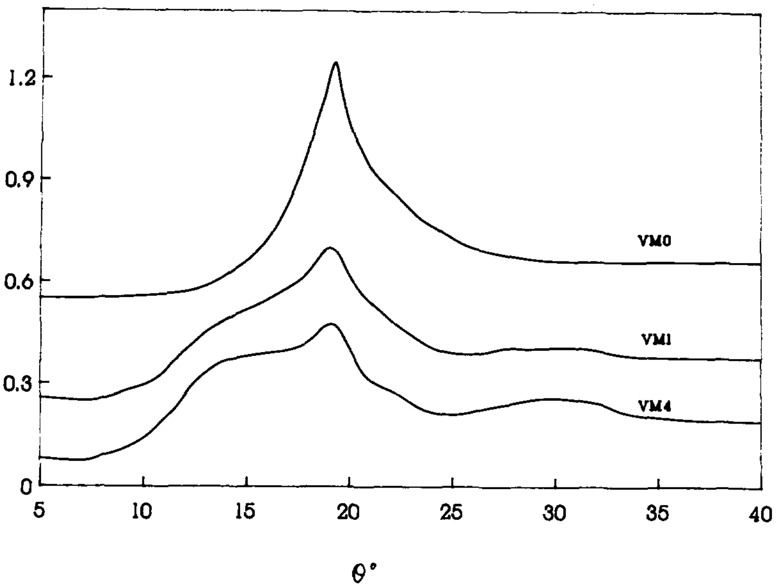


Figure 5 X-ray diffraction patterns of PVA homopolymer and PVA-*g*-PMMA graft copolymers VM1 and VM4

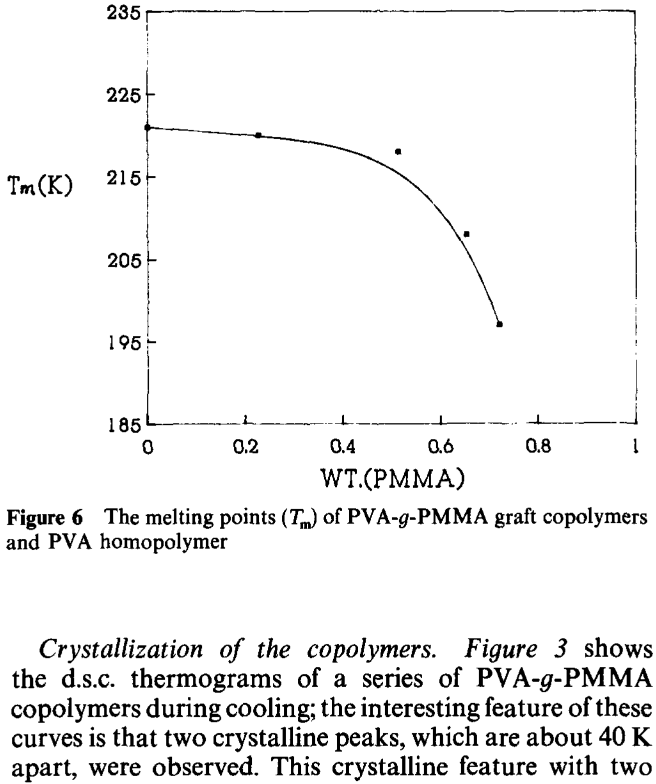


Figure 6 The melting points (T_m) of PVA-*g*-PMMA graft copolymers and PVA homopolymer

Crystallization of the copolymers. Figure 3 shows the d.s.c. thermograms of a series of PVA-*g*-PMMA copolymers during cooling; the interesting feature of these curves is that two crystalline peaks, which are about 40 K apart, were observed. This crystalline feature with two crystalline temperatures (T_cs) was first reported in a study on poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PS) diblock copolymer and PEO–PS–PEO triblock copolymer when the major component was PS[11], where two T_cs were about 60 K apart. The difference in this feature between PVA-*g*-PMMA graft and PEO/PS diblock or triblock copolymers is that the lower T_c is also observed for the graft copolymer, even when the weight fraction of the crystalline component of the copolymer is as high as 0.77. The two T_cs of amorphous–crystalline block and graft copolymers suggest that two nucleation mechanisms occur during their crystallization[11]. The higher T_c corresponds to heterogeneous nucleation, the same mechanism as in PVA homopolymer, and the lower one corresponds to the homogeneous nucleation of some dispersed small PVA microdomains. *Figure 3* also shows that the higher T_c of the copolymer is lower than the crystalline temperature of PVA homopolymer, but this difference does not change very much with the change in copolymer composition.

The degree of crystallinity, X_c, of the copolymer decreases with increasing PMMA weight fraction of the copolymer, as shown in *Figures 4* and *5*. *Figure 4* gives the X_cs of the copolymers during the cooling process, and *Figure 5* shows the WAXD patterns of PVA homopolymer and two copolymer samples, which were all prepared by evaporating the solvent of the polymer solutions in DMSO at 403 K. Although two crystalline peaks were observed for all PVA-*g*-PMMA copolymers during the cooling process, just one melting point (T_m) was detected for each copolymer, and the T_m also decreased with increase of PMMA weight fraction of the copolymers, as shown in *Figure 6*. This implies that the larger the amorphous fraction of the copolymer, the less perfect is its crystal.

To summarize, the synthesized PVA-*g*-PMMA copolymers formed lamellar microphase separation morphology, even for a copolymer with only 28 wt% PVA. Their crystallization kinetic behaviour and glass transition behaviour are also very interesting. The T_g of PMMA microphase could be 20 K higher than that of PMMA homopolymer, presumably due to the effects of the much higher T_m of PVA microphase than the T_g of PMMA microphase, and the added thermal stress field arising from the crystallization of PVA backbone. Further work on these features is still in progress.

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References

1 Leibler, L. *Macromolecules* 1980, **13**, 1602
2 Thomas, E. L., Alward, D. B., Kinning, D. J., Martin, D. C., Handlin, D. L. and Fetters, L. J. *Macromolecules* 1986, **19**, 2197
3 Hasegawa, H., Tanaka, H., Yamasaki, K. and Hashimoto, T. *Macromolecules* 1987, **20**, 1651
4 Roe, R. J., Fishkis, M. and Chang, V. C. *Macromolecules* 1981, **14**, 1091

5 Jiang, M., Chao, X. and Yu, T. *Polymer* 1986, **27**, 1917

6 Takahashi, A. and Yamashita, Y. in 'Copolymer, Polyblends, and Composites', Advances in Chemistry Series no. 142, American Chemical Society, Washington, DC, 1975, p. 267

7 Wang, B. and Krause, S. *Macromolecules* 1987, **20**, 2201

8 Crystal, R. G., Erhardt, P. F. and O'Malley, J.J. in 'Block Copolymers' (Ed. S. L. Aggarwal), Plenum, New York, 1970, p. 179

9 O'Malley, J. J., Crystal, R. G. and Erhardt, P. F. in 'Block Copolymers' (Ed. S. L. Aggarwal), Plenum, New York, 1970, p. 163

10 Skoulios, A. E., Tsouladze, G. and Franta, E. *J. Polym. Sci. Part C* 1963, **4**, 507

11 O'Malley, J. J. *J. Polym. Sci., Polymer Symp.* 1977, **60**, 151

12 Gervais, M. and Gallot, B. *Macromol. Chem.* 1973, **171**, 157

13 Gervais, M. and Gallot, B. *Macromol. Chem.* 1977, **178**, 2071

14 Gervais, M., Gallot, B., Jerome, R. and Teyssie, P. *Macromol. Chem.* 1981, **182**, 989

15 Whitmore, M. D. and Noolandi, J. *Macromolecules* 1988, **21**, 1482

16 Heuschen, J., Jerome, R. and Teyssie, Ph. *J. Polym. Sci., Polym. Phys.* 1989, **B27**, 523

17 Mino, G. and Kaizerman, S. *J. Polym. Sci.* 1958, **31**, 242

18 Ide, F. *J. Chem. Soc. Jpn, Ind. Chem. Sect.* 1961, **64**, 1676

19 Staszewska, D. *Makromol. Chem.* 1975, **176**, 2481

20 Iwakura, Y. and Imai, Y. *Makromol. Chem.* 1966, **98**, 1

21 Fang, T. R., Ji, L. C., Yu, J. G., Wang, L. Y. and Xu, S. X. *Polym. Bull.* 1992, **29**, 71

22 Kanig, G. and Neff, H. *Colloid Polym. Sci.* 1975, **253**(1), 29

23 Misra, S. C., Pichot, C., El-Aasser, M. S. and Vanderhoff, J. W. *J. Polym. Sci., Polym. Lett. Edn* 1979, **17**, 567