Synthesis and characterization of narrowly distributed block copolymers from polystyrene and polymethylphenylsiloxane

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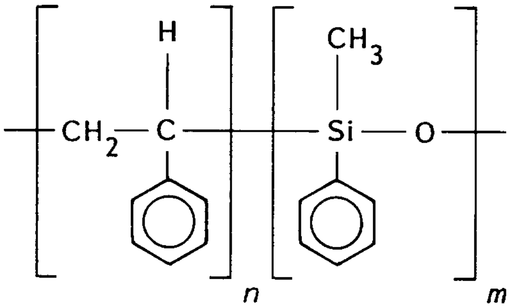
A reliable method for the anionic synthesis of block copolymers from polystyrene and polymethylphenylsiloxane is reported. Analysis of the block copolymers by h.p.l.c. proved the absence of homopolymer. The evaluation of g.p.c. measurements demonstrated that the copolymers exhibit a narrow molecular weight distribution ($M_w/M_n \leqslant 1.1$). Depending on molecular weight and composition the copolymers are homogeneous or undergo microphase separation.

(Keywords: synthesis; characterization; block copolymers)

INTRODUCTION

Block copolymers composed of polystyrene (PS) and siloxanes have been a long-standing subject of interest in polymer science because of the marked disparity in the glass transition of the two components[1,2]. Most of the work published up to now has been carried out using polydimethylsiloxane as the siloxane component. Here, the difference of the glass transition temperature (T_g) is ~230 K and both components are totally immiscible[3,4]. Block copolymers exhibiting at least partial miscibility would be very interesting if the one-phase region is accessible. Such materials would allow a comprehensive study of the phase behaviour of block copolymers and a comparison with recent experimental results.



PS-*b*-PMPS

In an earlier publication we have shown that polymethylphenylsiloxanes (PMPSs) with a narrow molecular weight distribution can be prepared by anionic polymerization of the cyclic trimers[5]. PMPS is miscible with PS within a certain range of temperature and molecular weights[6–8] and the respective phase diagrams have been studied by small-angle neutron scattering. This report is an extension of earlier studies[5] giving the preparation and characterization of block copolymers from PS and PMPS. Special emphasis is laid on the narrow molecular weight distribution of the blocks. Also, the resulting block copolymers are carefully analysed to ensure the absence of homopolymers which may profoundly affect subsequent measurements.

EXPERIMENTAL

Materials

The cyclic trimer of methylphenylsiloxane was prepared as described recently[5]. To avoid crystallinity[5] a mixture of *cis-* and *trans-*isomers was used in all the polymerizations. It was crystallized from n-hexane solution whereby first the *cis-* and then the *trans-*isomer crystallizes. The monomer was purified, the composition of *cis-* and *trans-*isomer analysed by ^{1}H n.m.r., and dried prior to use by distillation over CaH_2. Benzene and tetrahydrofuran (THF) were dried by refluxing with a Na/K alloy. Styrene (Reidel-de Haën, stabilized 99%) was treated with fluorenyllithium and distilled directly into ampoules. The fluorenyllithium was prepared by dissolving fluorene (1.6 g, Fluka, p.a., >99%) in benzene and treating with n-butyllithium solution (5 ml). Hexamethylphosphoric acid triamide (HMPT) (Merck-Schuchardt, p.a.) was distilled after refluxing with CaH_2. n-Butyllithium (1.6 M in n-hexane, Aldrich) was used as received. The activity of the solution was calculated from the ratio of the desired and the real molecular weight of a PS sample which turned out to be the most practical method of determination. Trimethylchlorosilane (Merck-Schuchardt, p.a.) was used as a terminating agent.

Methods

^{1}H n.m.r. spectra were recorded on a 300 MHz spectrometer (Bruker AC 300). G.p.c. was done at room temperature using THF as solvent with three columns (10^3, 10^5, 10^6 Å, Polymer Laboratories) covering the range of molecular weights between 10^3 g mol^{-1} and 10^6 g mol^{-1}. For data evaluation the Mark–Houwink

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relation was used for PMPS in THF at 25°C:

$$[\eta] = 0.0457 M_w^{0.784} \qquad (1)$$

This relation has been obtained using the PMPS samples synthesized previously[5]. Refractive index increments were determined using the method of Bodmann[9]. Thermal analysis (d.s.c.) was performed using a DSC7 (Perkin-Elmer). Membrane osmosis was done with a Knauer membrane osmometer. For vapour pressure osmometry, apparatus supplied by Corona Wescan was used.

To analyse the resulting block copolymers for residual homopolymer, gradient h.p.l.c. runs on a Hyperchrome LiChrosorb SI 100 column (250 mm/4 mm/5 μm) were performed. The polymer was dissolved in dichloromethane (0.5%) and analysed using a mixture of dichloromethane and n-heptane (50/50 v/v, changed to 70/30 within 10 min). These conditions ensured complete separation of both homopolymers and allowed the analysis of the copolymers with an accuracy better than 1% (see below). Wide-angle X-ray scattering (WAXS) was performed using a Siemens D-500 goniometer with CuKα radiation.

Polymerization

All polymerizations were carried out in benzene as described previously[5]. HMPT served as a promoter and the initiator was n-butyllithium. To determine the conditions a number of kinetic experiments were performed where small samples were taken with strict exclusion of air and oxygen. After terminating the polymerization by addition of trimethylchlorosilane the content of polymer could be determined by g.p.c. analysis. These runs showed that the optimal monomer concentration was ~80 g l^{-1} and the chosen concentrations of initiator were <1 g l^{-1}. To assess the influence of the promoter, kinetic runs were performed with monomer concentration of 0.2 mol l^{-1} and an initiator concentration of 0.0013 mol l^{-1}. The concentration of the promoter HMPT was varied between 0.007 mol l^{-1} and 0.12 mol l^{-1}.

For the synthesis of the copolymers, oligostyryl anions were first prepared from styrene (5 g) and 1.6 M n-butyllithium (5 g) dissolved in benzene. (Toluene could not be used as a solvent since it suffered from attack by the styryl anions.) The resulting oligostyryl anions had an average length of 8 to 12 monomer units. Subsequently, benzene (150 ml) was distilled into the flask under strict exclusion of moisture and oxygen. Then at room temperature styrene (10 g) dissolved in benzene (20 ml) was added and subsequently the amount of initiator solution had to be adjusted to yield the desired molecular weight of the PS block. After ~3 h the polymerization was complete. Separate experiments showed that the resulting PS had a rather narrow molecular weight distribution (M_w/M_n = 1.03–1.12). The characterization of the PS block part could be done by removing a small amount of the PS anions from the polymerization flask while maintaining the exclusion of air and oxygen. The styryl anions were terminated by methanol separately.

The molecular weights determined are listed in *Table 1*. To these living styrene anions THF (10 ml) was added and subsequently the cyclic trimer (2 g) was dissolved in benzene (6 ml). The trimer slowly reacted with the styryl anions and the extent of reaction could be easily followed by the disappearance of the red colour. In some experiments the polymerization was interrupted after this step to ensure, by analysis of the polymer, that no broadening of the molecular weight distribution had taken place. After 2 h the remainder of the trimer was added. Subsequently a 16% solution of the promoter HMPT (5 ml) in benzene was added to the mixture.

Table 1

Sample	M_n (PS part)[a] (g mol^{-1})	M (calc.)[b] (g mol^{-1})	M_n (osm.)[c] (g mol^{-1})	M_{Cp} (g.p.c.)[d] (g mol^{-1})	W_{PS}[e] (calc.)	$W_{PS}\left(\frac{\partial n}{\partial c}\right)$[f]	W_{PS}[g] (n.m.r.)	*Cis*-isomer[h] (%)	W_m[i]	$\frac{M_w}{M_n}$[j]	Sample homogeneity[k] (d.s.c.)
Cp 47/11	6000	10 000	10 500*	11 400	0.50	0.47	0.49	65	0.36	1.12	+
Cp 68/24	16 400	25 000	23 700*	24 300	0.70	0.68	0.69	38	0.54	1.10	+
Cp 51/32	20 500	30 000	32 000	31 600	0.50	0.51	0.53	35	0.56	1.10	–
Cp 80/42	35 300	40 000	42 000	44 000	0.80	0.80	0.76	38	0.56	1.05	+
Cp 87/57	47 600	60 000	56 800	56 100	0.90	0.87	0.87	42	0.52	1.03	+
Cp 74/57	38 000	60 000	56 500	52 200	0.80	0.74	0.75	42	0.50	1.03	–
Cp 70/56	39 600	60 000	56 000	54 000	0.70	0.70	0.65	42	0.52	1.04	–
Cp 63/54	29 000	60 000	54 400	59 000	0.60	0.63	0.61	42	0.49	1.05	–
Cp 57/55	27 200	60 000	55 400	51 000	0.50	0.57	0.48	35	0.60	1.06	–
Cp 21/59	20 300	50 000	59 000	59 200	0.30	0.21	0.23	35	0.58	1.05	–
Cp 52/64	37 000	70 000	63 800	61 700	0.50	0.48	0.43	38	0.52	1.06	–

[a] Molecular weight of the PS block part of the respective sample by g.p.c. analysis

[b] Molecular weight calculated from the conversion of PS and PMPS polymerization

[c] Total molecular weight detected with membrane or vapour pressure osmometry

[d] Molecular weight calculated on the basis of equation (3) in consideration of the polydispersity

[e] Weight fraction of PS calculated from the ratio of monomers D_3-MPS and styrene used in the respective polymerization

[f] Weight fraction calculated on the basis of equation (2)

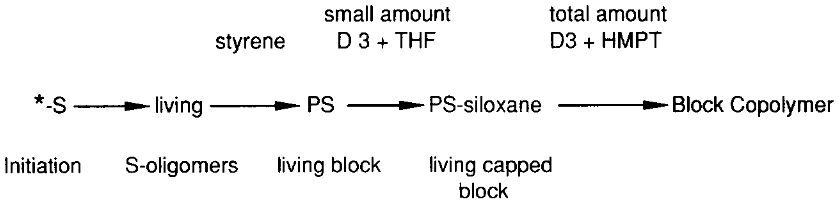
[g] Weight fraction of PS calculated from n.m.r. measurements

[h] Content used for the respective polymerization

[i] $W_m = W_{iso} + 0.5W_{hetero}$, where W_m is the *meso* dyads content of the PMPS part in the block copolymer

[j] Polydispersity

[k] As detected by d.s.c. measurements: +, homogeneous; –, inhomogeneous



Scheme 1 Diblock copolymerization

Polymerization of the second monomer was complete after 24 h. After this time the anions were terminated with trimethylchlorosilane. The polymer solution was diluted with toluene and washed carefully with distilled water. The copolymers were precipitated into methanol, filtered off and dried *in vacuo* (*Scheme 1*).

^{1}H n.m.r. analysis of the diblock copolymers was used to determine the molar fraction of PS in the sample and gave the contents of the *meso* dyad of the PMPS part.

^{1}H n.m.r. (CD_2Cl_2)[5] δ (ppm): 0.07 (S, $C\underline{H}_3$ syndiotactic); 0.13 (S, $C\underline{H}_3$ heterotactic); 0.17 (S, $C\underline{H}_3$ isotactic); 1.45 (area 1.3–1.7, $C\underline{H}_2$ of PS backbone); 1.85 (area 1.7–2.25, C$\underline{H}$ of PS backbone); 6.35–7.44 (m, Ar-$\underline{H}$ of PS and PMPS).

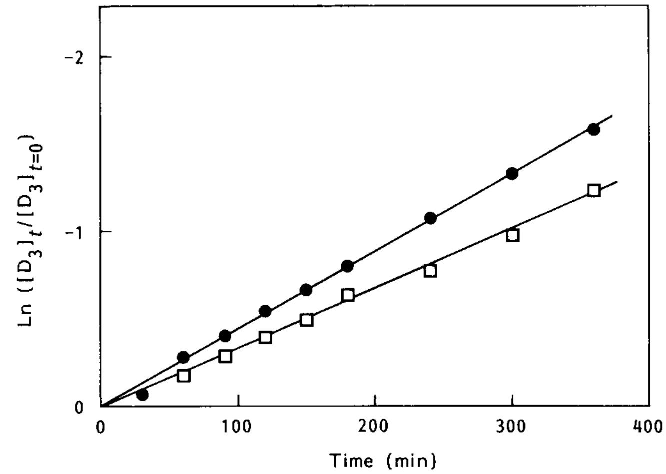


Figure 1 Logarithm of $[D_3]/[D_3]_0$ *versus* time (min) for the polymerization of PMPS. The concentration of the promoter HMPT is 7×10^{-3} mol l^{-1} (□) and 2.4×10^{-2} mol l^{-1} (●) at a constant concentration of $[D_3] = 0.2$ mol l^{-1} and initiator [n-BuLi] = 1.6×10^{-3} mol l^{-1}

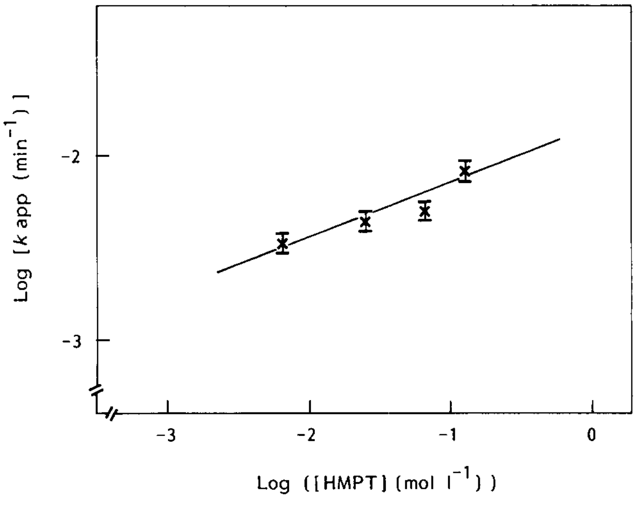


Figure 2 Dependence of k_{app} on the concentration of the promoter

RESULTS AND DISCUSSION

A prerequisite for the synthesis of well-defined block copolymers is the unperturbed anionic polymerization of both monomers. In the case of PS the optimal conditions are well known[10], whilst for PMPS this point still requires attention. As an example of the results of kinetic runs, *Figure 1* shows a plot of $\ln([D_3(t)]/[D_3(t = 0)])$ *versus* time. The strict linearity demonstrates that up to 90% conversion the reaction is of first order with respect to monomer concentration. This finding is in accord with results obtained by Andrianov *et al.*[11].

To avoid side reactions and to tune the reactivity of the anion, the promoter HMPT was added. To determine the influence of HMPT in more detail, kinetic runs were performed in which the concentration of promoter was varied between 0.007 mol l^{-1} and 0.12 mol l^{-1}. The rate constants displayed in *Figure 2* are only slightly dependent on the concentration of HMPT (apparent reaction order: 0.3) and the evaluation of the data strongly suggests that under the conditions chosen the polymerization proceeds without side reactions. Therefore, it is expected that the PMPS blocks will have a narrow molecular weight distribution.

Another test for an unperturbed anionic polymerization is the comparison between the measured molecular weights and the values calculated from the ratio of the monomer concentration to the initiator concentration (*Table 1*). For this comparison the number average molecular weights of selected samples have been determined by membrane osmometry. In all cases considered (see *Table 1*), the expected and the measured M_n coincide within experimental uncertainty.

A serious obstacle in the synthesis of block copolymers is the cross-step between the two blocks. Termination at this stage will lead to homo PS which is difficult to separate from the copolymer. Therefore all copolymers were analysed by h.p.l.c. *Figure 3* shows the resulting eluogram. It demonstrates that PS can be easily separated from the copolymer, since the retention time of PS samples with $M_w = 10\,000–200\,000$ g mol^{-1} in this gradient ranges from 12.3 to 14.8 min whereas the retention time of PMPS samples with $M_w = 9000–85\,000$ g mol^{-1} is 2.8–2.9 min. The retention time of the PMPS samples is close to the retention time of the injected solvent CH_2Cl_2 (2.8 min) which is denoted by 'inj.' in *Figure 3*. The respective retention times for the block copolymers are located between these values depending on their compositions. Therefore h.p.l.c. analysis allows the detection even of minute amounts of homopolymer[12,13]. The homopolymer content is found to be below the limits of detection for all the samples in

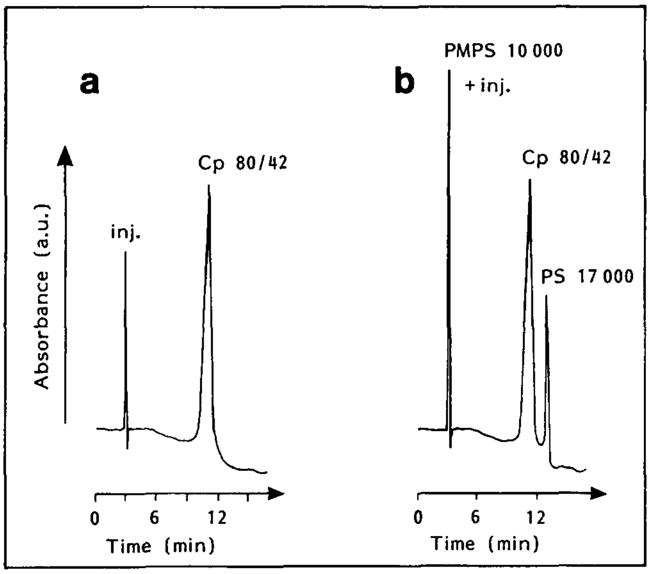


Figure 3 U.v. absorption *versus* retention time during gradient h.p.l.c. analysis: (a) Cp 80/42; (b) Cp 80/42 together with PMPS 10000 and PS 17000. The signal at 2.8 min is due to the injected solution of the samples

Table 1. This proves that the cross-step proceeded in a practically quantitative fashion.

Since the refractive index increments of the homo- and copolymers can be determined with great accuracy (PS, $dn/dc = 0.145\ \mathrm{cm^3\ g^{-1}}$; PMPS, $dn/dc = 0.204\ \mathrm{cm^3\ g^{-1}}$; both values measured at 436 nm at room temperature) the mass fraction of one component has been determined using the relation[14]:

$$\left(\frac{\delta n}{\delta c}\right)_{\mathrm{Cp}} = W_1\left(\frac{\delta n}{\delta c}\right)_1 + (1 - W_1)\left(\frac{\delta n}{\delta c}\right)_2 \qquad (2)$$

with W_1 denoting the mass fraction of homopolymer 1 in the block copolymer. The resulting weight fractions of PS are given in *Table 1*. They agree very well with the values calculated from the ratio of the monomers used for the polymerization (*Table 1*).

The monomer consists of *cis*- and *trans*-isomers which leads to polymers of different tacticities[5]. *Table 1* summarizes the *cis*-isomer content in the monomer used for the respective polymerization. The analysis of the copolymers obtained by ^{1}H n.m.r. gave a mass fraction of the PMPS part which agrees with the determination by (dn/dc) (see above) within experimental uncertainty (*Table 1*). The quantitative evaluation of the signal of the methyl protons furthermore allows the determination of the content of *meso* dyads (W_m) in the PMPS part. The respective data are collected in *Table 1* and agree with the values expected from previous findings[5]. Furthermore, the respective analysis of the homopolymer PMPS revealed that W_m does not depend on the degree of conversion. This supports the previous conjecture[5] that both cyclic isomers exhibit the same reactivity towards the living end. It is thus ensured that the PMPS part has the same content of *meso* dyads regardless of molecular weight. This fact is of particular importance in view of the fact that the microstructure of PMPS has a profound influence on the physical properties of this polymer[5].

The g.p.c. analysis of the PS part could be done separately and showed that the polydispersity is below 1.12 (see above)[15]. A similar broadening of the molecular weight distribution has been reported by Worsfold and Bywater[10]. The analysis of the block copolymers by g.p.c. can be evaluated in a first approximation by[14]:

$$\log M_{\mathrm{Cp}} = W_1 \log M_1 + (1 - W_1) \log M_2 \qquad (3)$$

where M_1 and M_2 are the molecular weights of homopolymers 1 and 2 at the same elution volume. The M_{Cp} thus obtained compares favourably with the respective values deduced from osmometry (*Table 1*).

The polydispersity obtained from this analysis (*Table 1*) shows that despite two polymerizations connected by one cross-step the molecular weight distribution is still very narrow. This fact together with the absence of homopolymer renders these block copolymers uniquely suitable for a thorough analysis of the phase behaviour.

In accordance with the findings of reference 8, there is no crystallinity of the materials as analysed by WAXS. The d.s.c. traces shown in *Figure 4* therefore only exhibit glass transitions. For comparison, traces of the respective homopolymers are included. From *Figure 4* it is obvious that Cp 51/32 and Cp 52/64 are microphase separated. Copolymer Cp 47/11 displays only a single broad transition. Further analysis by small angle X-ray scattering (SAXS) demonstrates the latter sample to be in the one-phase region[16]. The marked shift of the T_g of PS for the phase separated samples Cp 51/32 and Cp 52/64 leads to the conclusion that the phase boundary is not as sharp as in totally incompatible systems. A similar shift of the T_g of PS is found in studies of mixtures of the two homopolymers PS and PMPS[5]. A detailed investigation of the phase behaviour by SAXS will be given in a subsequent paper.

CONCLUSIONS

A reliable method for the synthesis of block copolymers of PS and PMPS has been given. The analysis of the block copolymers by h.p.l.c. demonstrated the absence of homopolymer. Also, the copolymers obtained exhibit a narrow molecular weight distribution. A d.s.c. analysis revealed partial compatibility of both components. Therefore the system is well-suited to study the phase behaviour of partially compatible block copolymers over a wide range of temperatures.

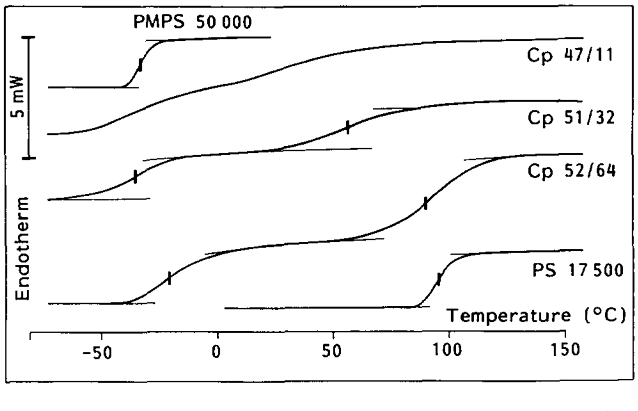


Figure 4 D.s.c. traces measured with a heating rate of 10 K min^{-1} for three block copolymers of approximately the same composition but varying molecular weight compared with the homopolymers PMPS and PS (cf. *Table 1*)

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REFERENCES

1 Kendrick, T. C., Parbhoo, B. M., White, J. W. in 'Comprehensive Polymer Science' (Eds G. Allen and J. C. Bevington), Pergamon Press, Oxford, 1989, p. 459
2 Yilgor, I. and McGrath, J. E. *Adv. Polym. Sci.* 1988, **86**, 1
3 Krause, S., Iskandar, M. and Iqbal, M. *Macromolecules* 1982, **15**, 105
4 Wang, B. and Krause, S. *Macromolecules* 1987, **20**, 2201
5 Momper, B., Wagner, Th., Maschke, U., Ballauff, M. and Fischer, E. W. *Polym. Commun.* 1990, **31**, 186
6 Shiomi, T., Hamada, F., Mihoichi, M., Nasako, T. and Nakajima, A. *Polymer* 1990, **31**, 448
7 Murschall, U., Fischer, E. W., Herkt-Maetzky, Ch. and Fytas, G. *J. Polym. Sci., Polym. Lett. Edn* 1986, **24**, 191
8 Nojima, S. and Nose, T. *Polym. J.* 1982, **14**, 269
9 Bodmann, O. *Chem. Ing. Technik* 1957, **29**, 465
10 Worsfold, D. J. and Bywater, S. *Can. J. Chem.* 1960, **38**, 1891
11 Andrianov, K. A., Temnikovskiij, V. A., Khananashvili, L. M. and Lyapina, N. A. *Vysokomol. Soyed.* 1972, **A14**, 2235
12 Mourey, Th. H. *J. Chromatogr.* 1986, **357**, 101
13 Danielewicz, M., Kubin, M. and Vozka, S. *J. Appl. Polym. Sci.* 1982, **27**, 3629
14 Riess, G., Hurtrez, G. and Bahadur, P. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. F. Mark, N. M. Bikales, Ch. G. Overberger, G. Menges and J. I. Kroschwitz), Vol. 2, John Wiley & Sons, New York, 1985, p. 325
15 Müller, A. H. E. in 'Comprehensive Polymer Science' (Eds G. Allen and J. C. Bevington), Vol. 3, Pergamon Press, Oxford, 1989, p. 387
16 Gerharz, B., Urban, G. and Fischer, E. W. in preparation