

Article

A Modulated Differential Scanning Calorimetry and Small-Angle X-ray Scattering Study of the Interfacial Region in Structured Latices

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A interface de latexes de poliestireno (PS)-poliacrilato de metila (PMA) foi investigada por calorimetria diferencial de varredura no modo modulado (DSC-modulado) e por espalhamento de raios-x de baixo ângulo (SAXS). A fração em massa da interface destes latexes foi estimada através do sinal do DSC-modulado, dC_p/dT . Foi encontrado o valor de 13% para latexes de PS-PMA (1:1 em massa) contendo PS reticulado com diferentes densidades de reticulação (0, 1, 3, 5 e 10 mol% de agente reticulante). O aumento da densidade de reticulação não alterou de forma significativa a fração da interface. O modelo *core-shell* foi usado na análise dos dados de SAXS. Os dados de DSC-modulado forneceram informações apenas sobre a fração em massa da interface, entretanto a combinação das técnicas DSC-modulado e SAXS forneceu informações adicionais sobre a morfologia dos latexes.

The interfacial structure of poly(styrene) (PS)-poly(methyl acrylate) (PMA) structured latices has been investigated by means of modulated-temperature differential scanning calorimetry (M-TDSC) and small-angle x-ray scattering (SAXS). The differential of heat capacity, dC_p/dT , signal from M-TDSC was used to quantify the weight fraction of interface in these latices. For PS-PMA (50:50 by weight) structured latices in which the PS component had different crosslink densities (0, 1, 3, 5 and 10 mol% of crosslinking agent), the weight fraction of interface was about 13%. With increasing crosslink density, the fraction of interface increased only slightly. A core-shell model has been used to analyse SAXS data for these PS-PMA latices. M-TDSC can only provide information about the weight fraction of interface, but the combination of M-TDSC and SAXS can provide much more information on the morphology of such structured latices.

Keywords: Latex, small-angle x-ray scattering, interface, modulated DSC

Introduction

Recently, we have carried out experimental investigations¹⁻⁶ on the morphology of polymer-polymer blends and interpenetrating polymer networks by means of modulated-temperature differential scanning calorimetry (M-TDSC). It has been shown⁴ that when the difference in glass transition temperatures is even as low as 10°C, the differential of heat capacity with respect to temperature, dC_p/dT , signal from M-TDSC can be used to characterise polymer-polymer miscibility. Weight fractions of less than 7% in multi-phase polymeric materials can also be determined³. In this paper, we want to extend the application to the characterisation of the morphology of structured latices and to examine whether M-TDSC can provide information on the morphology of such materials.

Here we investigate, by means of M-TDSC and small-angle x-ray scattering (SAXS), the interfacial structure of

structured latices whose cores are polystyrene (PS), with a shell of poly(methyl acrylate) (PMA). For the analysis of the SAXS data, a simple concentration gradient model for the interfacial structure was used.

Experimental

Latex preparation

The PS-PMA (50:50 by weight) structured latices were prepared by sequential emulsion polymerisation. Ammonium persulphate (AP), sodium dodecylbenzene-sulphonate (SDBS) and divinylbenzene (DVB) were obtained from Aldrich and were used as supplied. Methyl acrylate (MA) and styrene, also from Aldrich, were purified by passing through a column packed with inhibitor remover. The water used was deionized.

Stage I. Synthesis of the PS core. The reaction vessel, equipped with stirring, was kept in a water bath maintained

at 80°C. 250 mL water and 0.6 g SDBS were added and the vessel purged with nitrogen for 20 min. Then, 0.2g AP and 20g styrene were added and allowed to react for 30min. Thereafter, 80g styrene and 0.4g AP dissolved in 50ml water were pumped separately into the reaction vessel over a 3 h period. After the monomer addition was complete, the reaction was allowed to post-react for 1 h to ensure the completion of polymerization. The crosslinked PS latex with various DVB contents were prepared in the same way.

Stage II. Preparation of PS/PMA structured latices. The reaction vessel, containing 70 mL water, was maintained at 72°C. To this 100mL PS latex (25wt% solid content) was added and purged with nitrogen while being stirred. Then, 25g MA and a solution of AP (0.3g in 30mL water) were pumped into the reaction vessel over a 2 h period. After the MA monomer addition was complete, the reaction was allowed to post-react for 1 h to ensure the completion of polymerization. The resulting latex had a core/shell ratio of 50/50 by weight.

Latex film preparation

Latex films were prepared by casting the latices and evaporating the water under ambient conditions. They were then dried under vacuum conditions for at least 2 weeks at room temperature.

Table 1. Codes for the PS-PMA structured latices.

Code	PS/PMA (wt.%)	DVB (mol%)
Latex1	50/50	0
Latex2	50/50	1
Latex3	50/50	3
Latex4	50/50	5
Latex5	50/50	10

M-TDSC

The study of the interfacial structure of core-shell latex particles presented in this paper was carried out with dried latex films. A TA Instruments M-TDSC 2920 calorimeter was used. An oscillation amplitude of 1.0 °C, an oscillation period of 60 seconds and a heating rate of 3 °C min⁻¹ were used. Temperature and cell constant were calibrated using an empty pan (20mg) and a standard indium sample (10mg) (TA-Instruments), and the baseline was established by running an empty pan (20mg). In order to reduce the heat transfer delay, an average sample mass of 6 mg was used. Nitrogen, at a flow rate of 35mL min⁻¹, was used as purge gas. The heat capacity and differential of heat capacity can be obtained directly.

SAXS measurements

SAXS measurements were undertaken on beamline 8.2 at the EPSRC SRS facility in the Daresbury Laboratory, Warrington, UK. The camera was equipped with a multiwire quadrant detector located approximately 1.0 m from the sample position. A vacuum chamber was placed between the sample and the detector in order to reduce air scattering and absorption. SAXS samples, approximately 0.5 - 0.9 mm thick, were prepared by casting. The scattering pattern from an oriented specimen of collagen was used to calibrate the SAXS detector. The experimental data were corrected for background scattering, for sample thickness and transmission, and for the positional alinearity of the detector.

Results and Discussion

M-TDSC analysis

Figures 1(a) to 1(e) show the dCp/dT versus temperature data for latex1 to latex 5, and for the PS latices with the corresponding crosslink densities physically blended with the PMA latex. The dCp/dT signals for these structured latices are distinctly different from those of the PS latices physically blended with the PMA latex. A decrease of the increment of heat capacity, ΔCp, at the glass transition temperature of both polymers was observed in these structured latices. ΔCp is proportional to the weight fraction of the component concerned⁴. This is based on the assumption that the different transition processes proceed independently of each other. Comparing the dCp/dT signals of the PS latices blended with PMA latex between the glass transitions of the pure PS and PMA phases, it was found that the values of the dCp/dT signal for these structured latices are larger than those of the physical blends. This indicates that there is a transition in this temperature range, which could be related to an interfacial layer⁶ between the two components. The weight fraction of this interfacial layer can be calculated⁶ from the experimentally determined “missing” amounts of the individual ΔCp values.

For an immiscible polymer blend, the total ΔCp is the sum of the ΔCp values of the two constituent polymers⁴.

$$\Delta C_p = \omega_{10} \Delta C_{p10} + \omega_{20} \Delta C_{p20} \quad (1)$$

ΔCp₁₀ and ΔCp₂₀ are the increments of heat capacity at Tg₁ and Tg₂, respectively, before mixing. ω₁₀ and ω₂₀ are the weight fractions of polymer 1 and polymer 2, respectively. When the system exhibits an interface, the following equation holds⁶.

$$\Delta C_p = \Delta C_{p1} + \Delta C_{p2} + \Delta C_{pi} \quad (2)$$

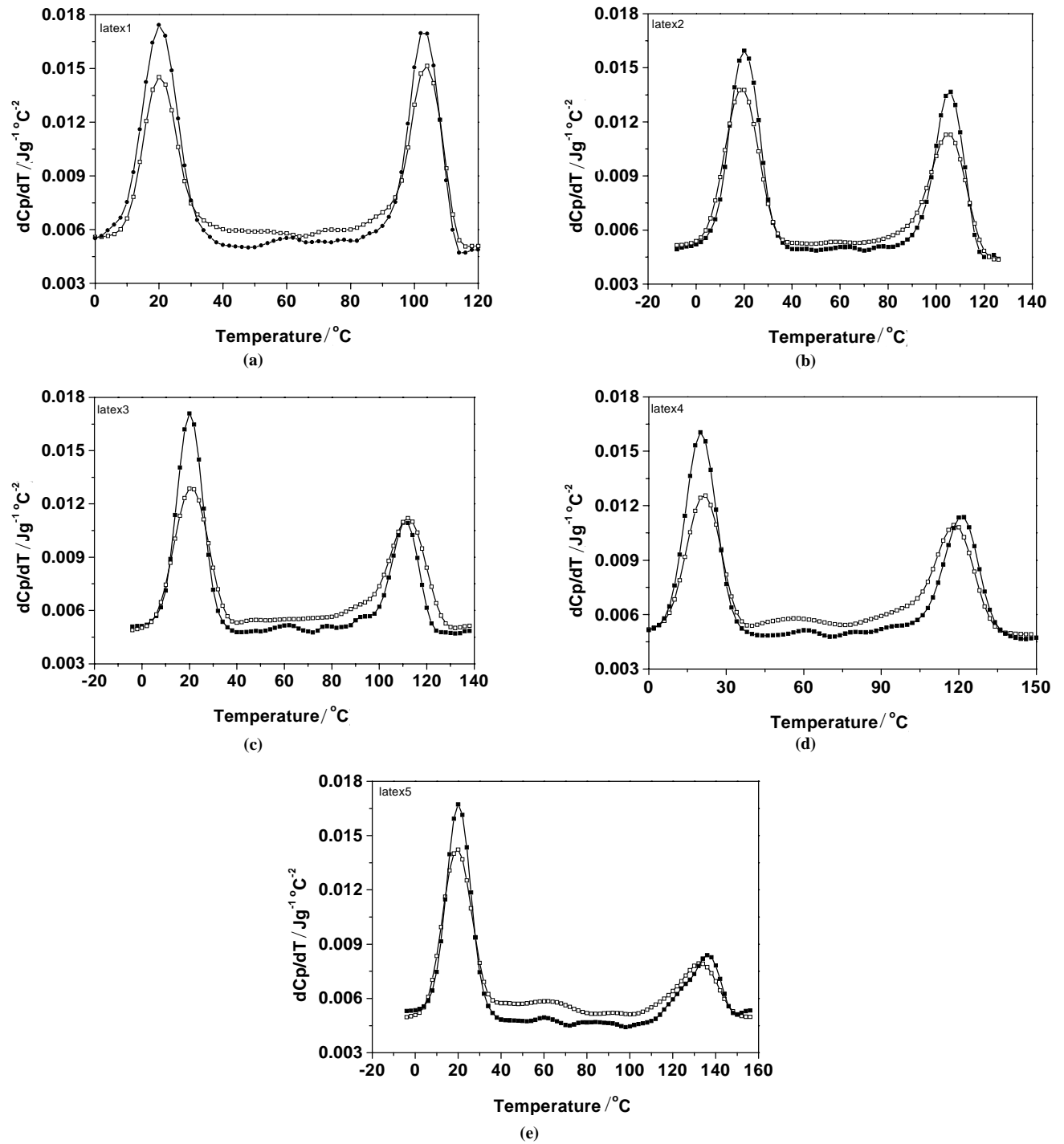


Figure 1. dC_p/dT versus temperature plots for the PS-PMA (50:50 by weight) structured latices. (a) latex 1, (b) latex 2, (c) latex 3, (d) latex 4 and (e) latex 5. \square : PS-PMA latices. \blacksquare : PS-PMA physical blends

$$\Delta C_{p1} = \omega_1 \Delta C_{p10} \quad (3)$$

$$\Delta C_{p2} = \omega_2 \Delta C_{p20} \quad (4)$$

ΔC_{p1} and ΔC_{p2} are the increments of heat capacity at T_{g1} and T_{g2} , respectively, after mixing. ΔC_{p1} is the increment of heat capacity of the interface in its glass transition region. ω_1 and ω_2 are the weight fractions of

polymer 1 and polymer 2, respectively, after mixing. The weight fractions, δ_1 and δ_2 , in the polymer1-polymer 2 interfacial regions can then be obtained⁶.

$$\delta_1 = \omega_{10} - \Delta C_{p1} / \Delta C_{p10} \quad (5)$$

$$\delta_2 = \omega_{20} - \Delta C_{p2} / \Delta C_{p20} \quad (6)$$

The weight fractions of interface in these PS-PMA structured lattices are shown in Figure 2. With increasing crosslink density in the PS component, the weight fraction of interface increases slightly. This observation will be discussed again later in this paper.

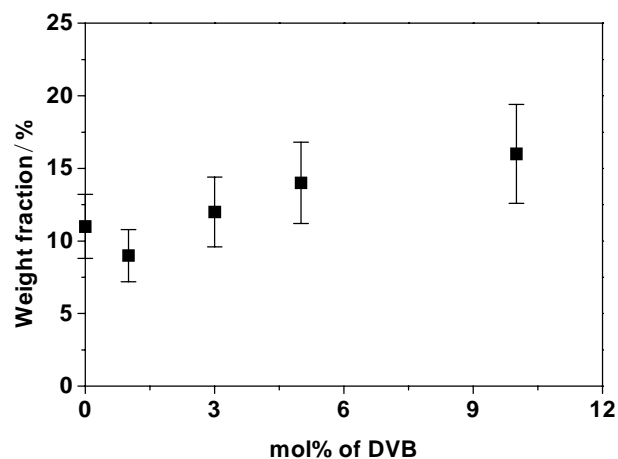


Figure 2. Weight fraction of interface vs. divinyl benzene content for the PS-PMA (50:50 by weight) films formed from the structured lattices.

SAXS analysis

In the following discussion, it is assumed that these PS-PMA film samples are prepared from core-shell particles, *i.e.* core, interface and shell phases are present with the shell fully covering the core. This is a very reasonable assumption given the relative hydrophilicities of the two polymers. As seen already, based on M-TDSC data, the interfacial thickness can now be calculated. To prove whether these PS-PMA structured lattices are indeed core-shell particles, SAXS was used to study their morphology. Figure 3 shows the scattered intensity vs. scattering vector q ($q = 4\pi/\lambda \sin\theta$) for the five PS-PMA samples λ is the scattering wave length (0.154 nm). θ is the scattering angle. However, it is not possible to determine whether they are core-shell lattices from the raw SAXS data alone. A model has to be used to predict this.

For monodisperse particles⁷ the scattering intensity is given by Eq.7.

$$I(q) = NF^2(q) \quad (7)$$

N is the number of particles per unit volume and $F(q)$ is the scattering amplitude. For spherically symmetrical particles with radius R , $F(q)$ is given by Eq. 8⁷.

$$F(q) = 4\pi \int_0^R [\rho(r) - \rho(r_0)] r^2 \sin(qr)/(qr) dr \quad (8)$$

where $\rho(r)$ is the local electron density in the particles and ρ_0 is the respective quantity for the dispersion medium.

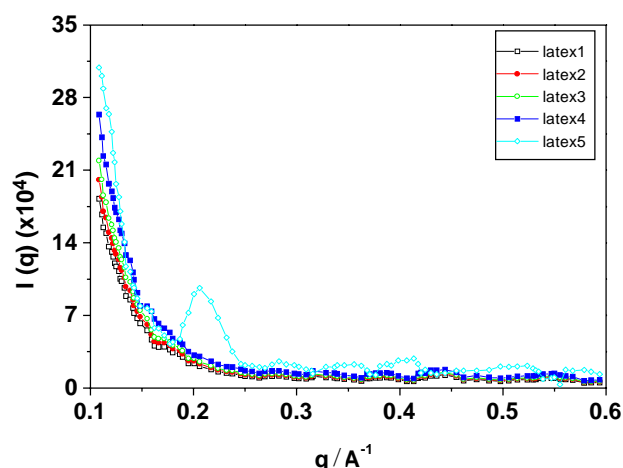


Figure 3. SAXS data for the PS-PMA films formed from the structured lattices.

For the electron density of the PS-PMA core-shell particles, the model shown in Figure 4 was used. δ is the interfacial thickness. ρ_c and ρ_s are the electronic densities for core and shell, respectively. R_c is the core radius.

$F(q)$ can be rewritten as follows.

$$F(q) = 4\pi[\rho_c + (\rho_c - \rho_s)R_c/\delta] \int_0^{R_c - \delta/2} r \sin(qr)/(qr) dr + 4\pi(\rho_s - \rho_c)/\delta \int_0^{R_c + \delta} r^2 \sin(qr)/(qr) dr - 4\pi[\rho_s + (\rho_s - \rho_c)R_c/\delta] \int_0^{R_c - \delta/2} r \sin(qr)/(qr) dr \quad (9)$$

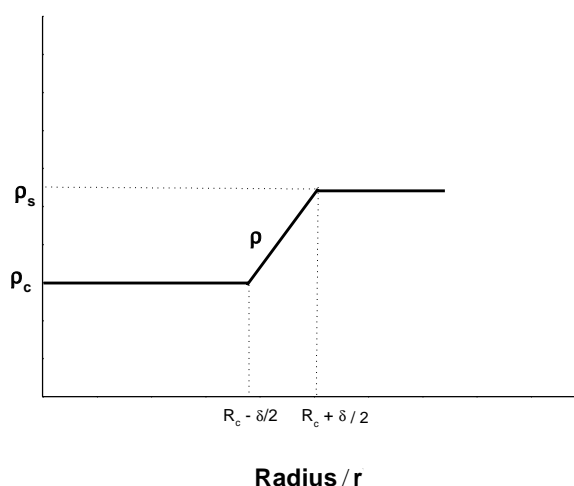


Figure 4. Model for a core-shell particle with an interface.

Figure 5 shows the calculated SAXS result for this model.

Here, 60 nm for R_c and 3 nm for δ were used. These values were obtained from the M-TDSC results by

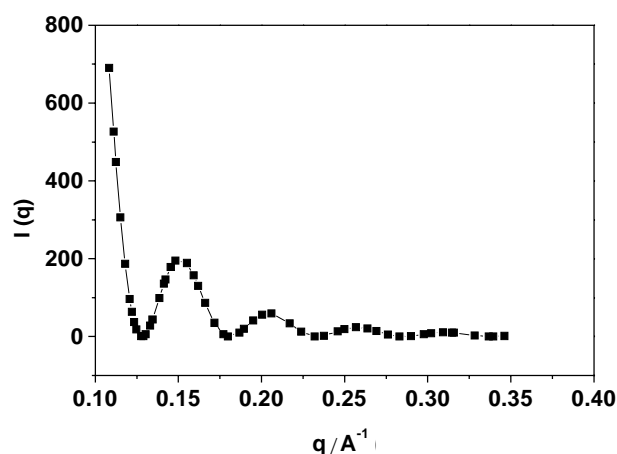


Figure 5. Model-predicted SAXS results

assuming that the PS-PMA structured latices are core-shell particles. Comparing the model and experimental results (see Figure 3), only the SAXS data for latex5 are similar to that predicted by the core-shell model. Obviously, the SAXS data can not be described by a core-shell model. This implies that these PS-PMA samples are not core-shell latices, except for latex 5. However, the interfacial values for the 5 samples were quite similar. It is clear that M-TDSC can only provide information on the weight fraction of interface in structured latices, but not on morphology.

Polymer latices have found widespread use for a multitude of applications⁸. Thus, characterisation of the interfacial structure of structured latices is an outstanding problem of considerable importance^{7,9-11, 16-18} with direct relevance for many applications and several methods such as x-ray scattering^{7,9,10}, high-resolution NMR spectroscopy¹¹⁻¹⁴ and fluorescence non-radiative energy transfer¹⁵⁻¹⁷ have been employed to probe the interfacial structure of core-shell latex particles.

In other SAXS studies of the interfacial structure in latices^{7,9,10}, it has been assumed that the interfacial structure is symmetrical. The result is that the SAXS data can be described approximately by a core-shell particle model^{7,9,10}. The deviation could result from the fact that the interfacial structure is asymmetric or because some proportion of the particles are not core-shell in type. Thus, according to SAXS data alone, it is not easy to calculate accurately the value of the weight fraction of interface in structured latices.

Now the results shown in Figure 2 will be reconsidered. The SAXS data show that these PS-PMA samples are not core-shell latices, except for latex 5, which has the highest core crosslink density. It is reasonable with increasing PS core crosslink density that the diffusion of the methacrylate monomer into the PS cores becomes more restricted. During emulsion polymerisation, some small

PMA phases may form inside the lower crosslink density PS core particles. This morphology may dominate in these samples. The core (PS)-shell (PMA) structure may dominate in latex 5 where a diffuse mixed layer now exists between the core and shell phases.

SAXS can provide information on whether or not a core-shell structure exists. The combination of M-TDSC and SAXS can provide much more information about the morphology of structured latices in that the weight fraction of interface in structured latices can, additionally, be obtained readily from M-TDSC. Thus, morphological parameters such as weight fraction and interface thickness in structured latices can be obtained from this combination of M-TDSC and SAXS techniques.

Conclusions

The dCp/dT versus temperature signal from M-TDSC permits the interfacial structure of structured latices to be studied. This yields precise information on the weight fraction of the interface in such particles. The study revealed the absence of a sharp boundary between the phases, but concluded a diffuse interface existed. SAXS data showed that these PS-PMA latices were not core-shell particles, except at high degrees of core crosslinking. Combining M-TDSC and SAXS data, the morphology of structured latices can be well characterised in that the weight fraction and thickness of interface and the morphology can be obtained.

References

1. Song, M.; Hourston, D. J.; Pollock, H. M.; Schafer, F. U.; Hammiche, A. *Thermochim. Acta* **1997**, *304/305*, 335.
2. Song, M.; Hammiche, A.; Pollock, H. M.; Hourston, D. J.; Reading, M. *Polymer* **1996**, *37*, 5661.
3. Hourston, D. J.; Song, M.; Hammiche, A.; Pollock, H. M.; Reading, M. *Polymer* **1997**, *38*, 1.
4. Song, M.; Hammiche, A.; Pollock, H. M.; Hourston, D. J.; Reading, M. *Polymer* **1995**, *36*, 3313.
5. Song, M.; Hourston, D. J.; Pollock, H. M.; Schafer, F. U.; Hammiche, A. *Thermochim. Acta* **1998**, *315*, 25.
6. Song, M.; Hourston, D. J.; Pollock, H. M.; Hammiche, A.; Reading, M. *Polymer* **1997**, *38*, 503.
7. Grunder, R.; Urban, G.; Ballauff, M. *Colloid Polym. Sci.* **1993**, *271*, 563.
8. Keddie, J. L. *Mater. Sci. Eng. (R)*, **1997/1998**, *R21*, 101.
9. Dingenouts, N.; Ballauff, M. *Acta Polym.* **1993**, *44*, 178.
10. Ballauff, M. *Macromol. Symp.* **1994**, *87*, 93.

11. Nzudie, D. T.; Delmotte, L.; Riess, G. *Makromol. Rapid Commun.* **1991**, *12*, 251.
12. Nzudie, D. T.; Delmotte, L.; Riess, G. *Macromol. Chem. Phys.* **1994**, *195*, 2723.
13. Nzudie, D. T. Ph.D Thesis, University of Uaaute Alsace, 1992.
14. Nelliappan, V.; El-Aasser, M. S.; Klein, A.; Daniels, E. S.; Roberts, L. E. *J. Appl. Polym. Sci.*, **1995**, *58*, 323.
15. Winnik, M.; A., Xu, H.; Satguru, R. *Macromol. Symp.* **1993**, *70/71*, 107.
16. Perez, H.; Lang, L. *Langmuir* **1996**, *12*, 3180.
17. Marion, P.; Beinert, G.; Juhue, D.; Lang, L. *Macromolecules* **1997**, *30*, 123.

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