Polymerization in the presence of seeds. Part IV: Emulsion polymers containing inorganic filler particles

Wolf-Dieter Hergeth, Uwe-Jens Steinau, Hans-Joachim Bittrich, Gerald Simon and Klaus Schmutzler*
Department of Physics, 'Carl Schorlemmer' Technical University Leuna-Merseburg, Merseburg, DDR-4200, GDR
(Received 10 March 1988; accepted 11 July 1988)

Polymer composites containing quartz powder filler particles were produced by the emulsion polymerization technique. The distribution of the inorganic material was observed by electron microscopy. Ultrasonic velocity measurements, differential scanning calorimetry (d.s.c.) and nuclear magnetic resonance (n.m.r.) were used to investigate the properties of the polymer composites. Deviations from the properties of the pure polymers can be discussed in terms of a modified polymer shell around the filler particles. The thickness of this shell varies between approximately 2 nm and 9 nm.

(Keywords: polymer composites; fillers for plastics; quartz powder; poly(vinyl acetate); poly(methyl methacrylate))

INTRODUCTION

Investigations have shown that the emulsion polymerization of vinyl acetate is greatly influenced by the presence of inorganic quartz powder filler particles[1,2]. The experimental results indicate that the polymerization reaction takes place in a surface layer region of these fillers. This reaction locus is favoured because of the adsorption of monomer at the filler surfaces, which results in a very high monomer concentration in the vicinity of the particles compared with a limited concentration in the bulk dispersion medium. The inorganic filler particles, which are very strongly aggregated in the aqueous phase, disaggregate due to this surface layer polymerization[1,2].

The polymer which originates close to the surface is physically or chemically bound to this surface. Hence, the physical properties of such amorphous polymers are different from those of the bulk polymer. Because of the binding to the rigid surface, the molecular mobility of the attached polymer chains is hindered and their molecular conformation is changed. Additionally, the structure of the polymer in the vicinity of the surface should be altered from the amorphous to a higher ordered state as a consequence.

These deviations of physical properties from those of the amorphous bulk polymer decrease in relation to the distance from the particle surface. Hence, the filler particle, the amorphous polymer and the altered shell polymer contribute to the bulk properties of the whole polymer–filler system. Therefore, it is necessary to determine the thickness of the modified polymer shell around the particles in order to estimate the corresponding polymer volume fraction and to understand the macroscopic properties of the system.

The aim of this paper is to present results concerning the determination of the shell thickness by ultrasonic velocity measurements, differential scanning calorimetry (d.s.c.) and nuclear magnetic resonance (n.m.r.) in the case of amorphous poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) polymerized in the presence of small sized quartz particles.

EXPERIMENTAL

The polymerizations were carried out without any soap in a half-litre reactor (stirring rate 250/min). The doubly distilled water and the quartz powder were poured into the reaction vessel and heated, under constant stirring, to the reaction temperature (70°C). The aqueous solution of initiator (7×10^{-3} mol dm^{-3} $K_2S_2O_8$) was added to

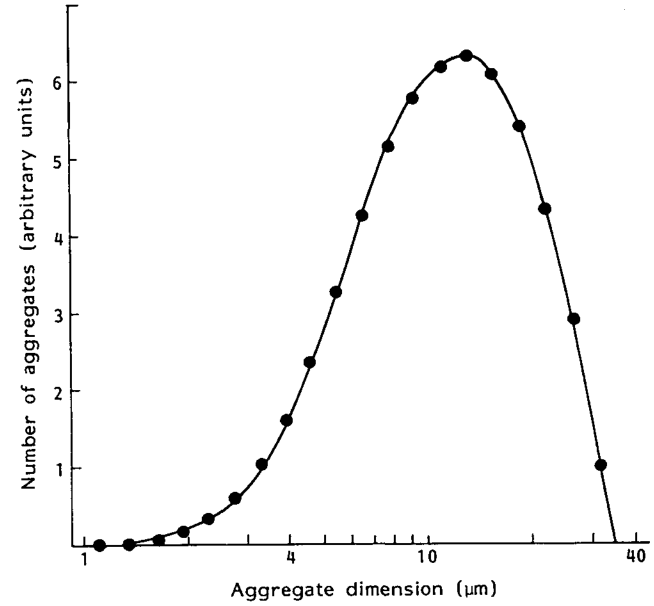

Figure 1 Aggregate size distribution of unmodified silica particles in the water phase. The units for the number of aggregates are arbitrary

---

*To whom correspondence should be addressed

0032-3861/89/020254-05$03.00

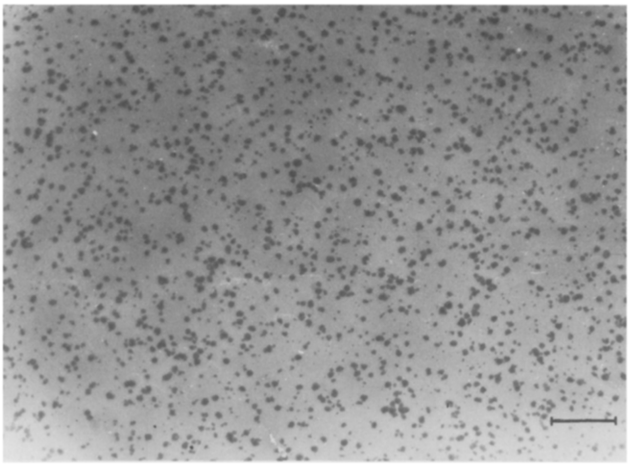

Figure 2 Silica particles extracted during the first period of the emulsion polymerization (0.7% PVAc in the aqueous phase). The scale bar is 250 nm

the reaction mixture and, after 10 minutes, the continuous dosage of the monomer was started under monomer starved conditions.

The monomers applied were technical products. They were used after conventional purification. The quartz powder, Suprasil, (GDR) had an average particle diameter of 26 nm obtained by electron microscopy and a specific surface area of 180 m^2/g obtained by the BET adsorption method. All other chemicals were of analytical grade.

The separation of the dispersed matter from the dispersion medium was carried out by centrifugation. The polymer–filler system was then dried under vacuum for more than one week.

The ultrasonic velocity was determined by measuring the pulse travelling time in the system over a constant distance. The sound frequency was 1 MHz and the pulse frequency 1 kHz. A computer was used to check all the necessary parameters (temperature, time, pulse travelling time) and calculated the sound velocity. The accuracy of the absolute velocity determination was 0.5 m/s. A transmission electron microscope BS 613 (Tesla, USSR) was used to take the micrographs.

Measurements of heat capacity were carried out using a DSC-2C calorimeter (Perkin-Elmer) at scanning rates of 20 K/min. Glass transition temperatures T_g, jumps in the specific heat capacity ΔC_p at the glass transition and the width of the glass transition range ΔT were calculated from second heating runs.

^1H n.m.r. relaxation measurements of transversal magnetization were carried out at a resonance frequency of 88 MHz using a SXP 4-100 spectrometer (Bruker). The samples were annealed under a nitrogen atmosphere for 24 h at 443 K. Then, the samples were charged under a nitrogen atmosphere of about 0.1 Pa into glass ampoules.

RESULTS AND DISCUSSION

Qualitative results

Unmodified silica particles exhibit a very strong tendency to form large aggregates in aqueous media. The aggregate size distribution is shown in *Figure 1*. The aggregate diameter ranges from about 1 μm to about 35 μm, as can be seen from this figure, whereas the single particle diameter obtained by electron microscopy is 26 nm with a very narrow size distribution. Obviously, the aggregates contain more than a thousand silica particles. These aggregates of silica particles will be dispersed in an ideal manner if emulsion polymerization is carried out in their presence. Then the particles appear as single particles and only a very small number of small sized aggregates can be observed, as is seen in *Figure 2*. In general, the same behaviour was observed when methyl methacrylate, vinyl acetate or styrene were used as monomers. The loss of aggregative behaviour of the silica particles due to the polymerization indicates the existence of a modified layer around these particles. As a result of this process, the final latex particles contain the finely dispersed silica particles[2].

During the emulsion polymerization process, ultrasonic velocity measurements were taken in order to monitor the monomer to polymer conversion[1]. The change in ultrasonic velocity arising from the addition of quartz powder to water is in the range $|\Delta V| < 1.0$ m/s (i.e. $|\Delta V/V| = 7 \times 10^{-4}$) up to quartz fractions of about 8 % v/v. Therefore, the ultrasonic velocities of reaction mixtures which contain various amounts of filler particles (from 0 to about 8 % v/v) and which were polymerized to the same conversion (i.e. the same monomer and polymer volume fraction) should be equal. However, there are differences in the ultrasonic velocities of these mixtures after the start of the reaction (*Table 1*), although the concentrations of initiator and polymer are identical. The pure silica–water mixture shows a slight decrease in ultrasonic velocity with an increasing silica content according to the model of ultrasound propagation in disperse systems developed by Hashin[3], whereas the reaction mixtures show a distinct increase in the ultrasonic velocity with an increasing silica content. This behaviour indicates the existence of a polymer layer around those particles with different elastic properties than the bulk polymer. The volume fraction of this layer cannot be calculated from these data because the elastic constants of this surface coated material are not known and because the small velocity differences are of the same order of magnitude as the accuracy of measurement.

Quantitative results

D.s.c. results

In general, the width of the glass transition region of the polymer in polymer–silica systems determined by d.s.c. measurements is not influenced by the amount of filler[5]. The influence of filler concentration on the glass transition temperature and on the jumps in specific heat

Table 1 Ultrasound velocities

$\varphi(SiO_2)^a$	ΔV (mixture)^b	ΔV (reaction)^c	Absolute ΔV^d
0	0	0	0
0.002	−0.1 m/s	+0.8 m/s	+0.9 m/s
0.009	−0.4 m/s	+1.2 m/s	+1.6 m/s
0.016	−0.7 m/s	+1.8 m/s	+2.5 m/s

[a] $\varphi(SiO_2)$: silica volume fraction
[b] ΔV (mixture): ultrasound velocity difference between the mixture containing Suprasil and the pure water
[c] ΔV (reaction): ultrasound velocity difference between reaction mixtures with and without Suprasil at 30% monomer conversion
[d] Absolute ΔV: total ultrasound velocity difference (ΔV (reaction) $-$ ΔV (mixture))

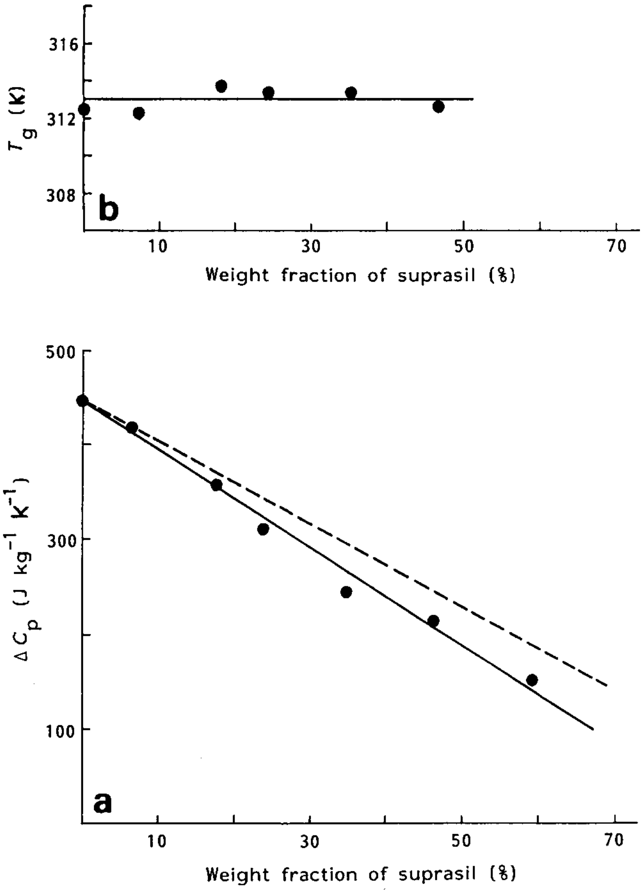

Figure 3 (a) Variation of the glass transition temperature T_g and (b) the jump in specific heat capacity ΔC_p of PVAc with the Suprasil weight fraction (----, calculated from chemical composition; ●, experimental)

capacity is shown in *Figures 3* and *4* for PVAc and PMMA, respectively.

The jump in specific heat capacity, ΔC_p, at the glass transition temperature shows a characteristic behaviour. The ΔC_p-concentration dependences of both polymer–filler systems deviate considerably from values calculated from the chemical composition. This result can be explained by assuming an interfacial layer of thickness, d. The portion of the polymer chains bound at the immobile particle surface cannot contribute to the glass transition because its molecular mobility is hindered. This portion lowers the jump in C_p. This decrease is proportional to the filler volume fraction. Using the known filler particle diameter and the $\Delta C_p(0)$ value of the pure polymeric component, the interfacial layer thickness, d, can be calculated from the d.s.c. data:

$$\frac{d}{r}=\left[\left(1-\frac{\Delta C_p}{\Delta C_p(0)(1-C_f)}\right)\left(\frac{1-C_f}{C_f}\right)\frac{\rho_f}{\rho_p}+1\right]^{1/3}+1$$

where C_f is the weight fraction of filler, and ρ_f and ρ_p are the densities of filler particle and polymer, respectively. The resulting interfacial layer thicknesses are 1.4 ± 0.9 nm in the PVAc–filler system and 2.2 ± 0.9 nm in the PMMA–filler system. The values are averages calculated from data up to a filler concentration of 80 % w/w.

Hence, the glass transitions measured are relaxation processes of the unbounded matrix polymer in terms of this model. In the literature[6–9], changes in the glass transition temperature as a function of filler content have been discussed as filler effects in the same way. However, our results show that the silica powder does not influence the glass transition temperature of PVAc (*Figure 4*), whereas there is a considerable increase in the glass transition temperature of PMMA, from 0 to 20 % w/w silica. The different concentration dependences of T_g are in contrast to the corresponding concentration dependences of the ΔC_p of both samples.

It is interesting to note that the variation of the T_g of the PMMA is within the usual region of the glass transitions of PMMA polymers with different tacticities[4]. A modification of the tacticity of PMMA may be caused by polymerization within the boundary layer at the particle surfaces, or a different adsorption of chains having different tacticities.

A ^{1}H-h-n.m.r. investigation of matrix-PMMA polymerized with and without silica does not show any differences in the tacticity of these samples. The tacticity of the PMMA attached at the particle surfaces could not be detected during this investigation because of its close binding to the particles and because of the resulting broad signal. Therefore, no unambiguous explanation of this tacticity effect could be offered until now.

Recent investigations have shown that the glass transition temperature of polystyrene is also not influenced by the amount of filler[5]. Hence, the influence of filler

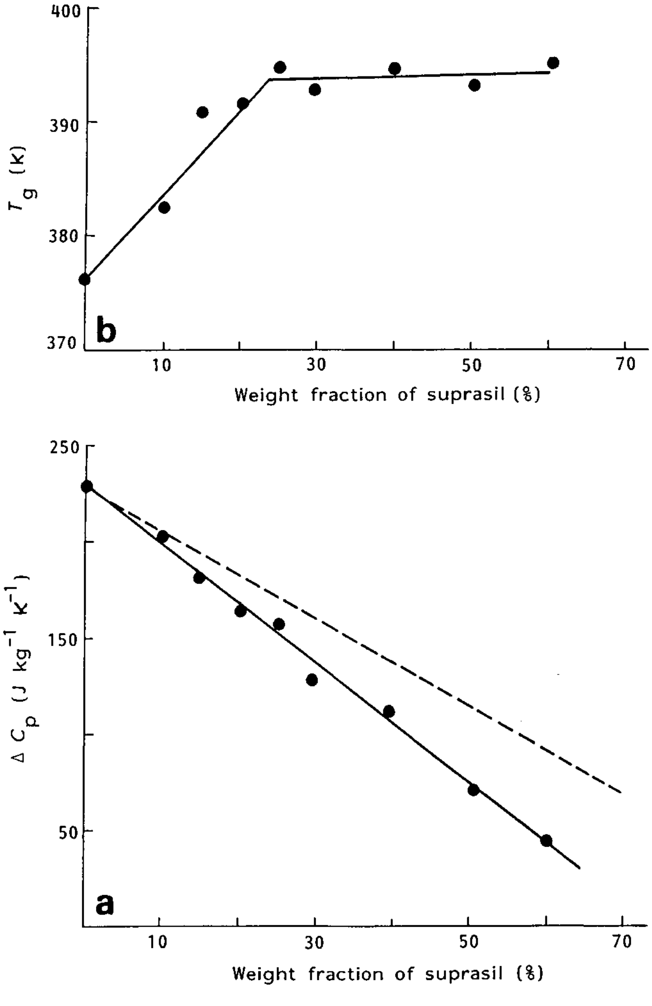

Figure 4 (a) Variation of the glass transition temperature T_g and (b) the jump in specific heat capacity ΔC_p of PMMA with the Suprasil weight fraction

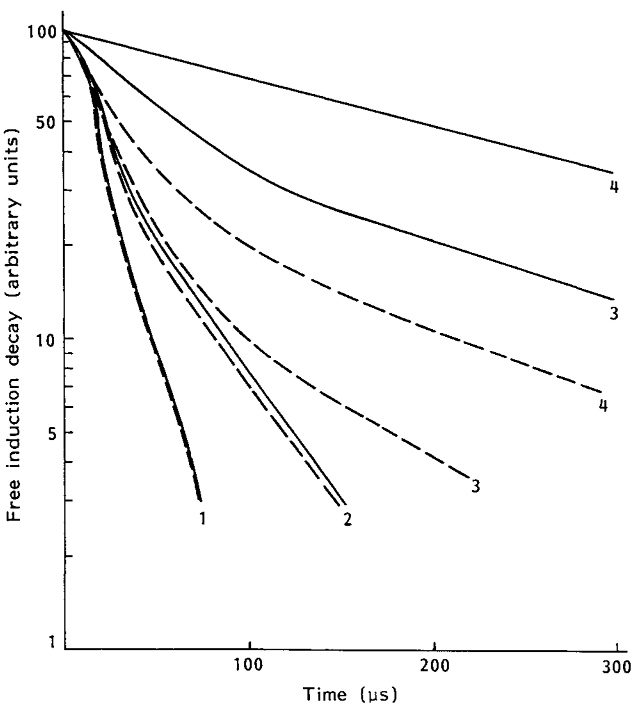

Figure 5 Free induction decay (arbitrary units) as a function of temperature. ———, pure PMMA; ----, PMMA–Suprasil system containing 66 wt% Suprasil. Curve 1: $T \leqslant 300$ K; curve 2: $T = T_g$; curves labelled 3: $T = 440$ K; curves labelled 4: $T = 450$ K

volume fractions on glass transition temperatures has not yet been understood in detail.

N.m.r. results

Measurements of the free induction decay (f.i.d.) give an insight into the structural heterogeneities of the submolecular (few nm) region. The magnetic dipole–dipole interaction determines the time and the shape of the f.i.d. below the glass transition temperature of polymers as in a rigid lattice. The decay time is within the range of 15 μs, and the curve of f.i.d. has a gaussian shape. Above the T_g, the dipole–dipole interaction is averaged in a characteristic manner and structural differences can be observed. The f.i.d. of PMMA and the PMMA–Suprasil system are plotted as a function of temperature in *Figure 5*. As can be seen from this figure, the f.i.d. shows a distinct bicomponental decay, apart from the f.i.d. of pure PMMA at $T \gg T_g$. This bicomponental decay is known from literature[10] in the case of pure PMMA. The two components of the f.i.d. signal are characterized by two different decay times, a short ($T_{2,s}$) and a long ($T_{2,l}$) one. At very high temperatures only the 'long component' could be observed, as indicated by the simple exponential decay of the signal of PMMA at 450 K. The f.i.d. signals of the PMMA–Suprasil system are shifted in the temperature scale to higher temperatures as compared with the temperature dependence of the f.i.d. of the pure PMMA. Whereas the pure PMMA shows a simple exponential decay at temperatures $T(0;1) \geqslant 450$ K, this temperature is shifted to $T(0;2) \geqslant 468$ K, $T(0;3) \geqslant 483$ K, and to $T(0;4) \geqslant 508$ K in systems containing 15, 33 and 66 % w/w Suprasil, respectively.

In the literature, PMMA is commonly assumed to be an amorphous polymer. However, from the n.m.r. point of view the existence of two components of the f.i.d. from 150 K (rigid lattice) up to about 450 K is an indication of heterogeneity. Furthermore, in refs. 11–13, it is shown that solid iso- and syndiotactic PMMA prepared from a solution contain aggregates, i.e. stereocomplexes. These aggregates can be destroyed at a temperature of about 473 K (ref. 14). Therefore, we assume that similarly ordered structures are present in the PMMA investigated here, and that these structures are thermo-reversible, as indicated by the thermo-reversibility of the T_2 curves. Consequently, the short decay time of the f.i.d. is caused by these ordered structures.

If the temperature is increased, the ordered PMMA regions dissolve and at very high temperatures the f.i.d. is only determined by the long time component of the 'ideal' amorphous PMMA. Obviously, the presence of immobile filler particles and the grafting and/or adsorption of PMMA chains at the particle surfaces retard the destruction of these ordered regions. This retardation results from the hindrance of the molecular mobility of PMMA chains attached to the filler particle surfaces as discussed previously. The effects of variations of the molecular weight distribution of the PMMA caused by polymerization in the presence of fillers are negligible in the systems investigated.

Therefore, it is possible to identify mass fractions of mobility hindered and unhindered polymer chains using the proton fractions of the short time (P_s) and the long time component (P_l) of the f.i.d. at $T(0;1)$ as a function of filler concentration in order to calculate the additional part of hindered chains due to the particle surfaces (*Figure 6*). Obviously, the hindrance of molecular motion is a function of distance from the filler particle surface. Nevertheless, we introduce an effective distance, d', which characterizes the separation of hindered and unhindered polymer regions. Assuming the same density of the PMMA in both regions one can calculate this effective thickness, d', of the hindered part (volume fraction φ_h) around the particles at a volume fraction Φ_p of the PMMA in the system from:

$$\frac{d'}{r} = \left[\frac{1 - \Phi_p(1 - \varphi_h)}{1 - \Phi_p}\right]^{1/3} - 1$$

where φ_h was calculated by the proton fractions

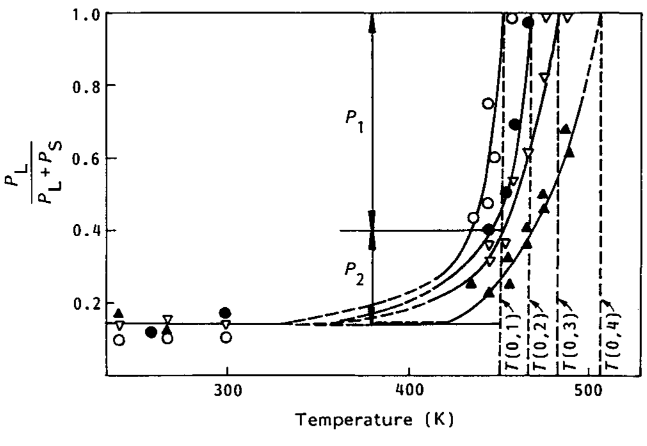

Figure 6 Proton fractions (P) of the two components of the f.i.d. of PMMA as a function of temperature. P_l and P_s are the proton fractions of the long and short time components of the f.i.d. respectively. The symbols on the curves indicate the weight percent of Suprasil: ○, 0%; ●, 15%, ▽, 33%; ▲, 66%

$$\varphi_h = \frac{P_1}{P_1 + P_2}$$

Depending on the polymer volume fraction Φ_p, the effective thickness d' levels exponentially to a limit $d'(0) = 14.4$ nm. The characteristic length of this exponential dependence (i.e. the characteristic dimension of the modified polymer surface layer) is about 9 nm. This value is in the same order of magnitude as the value derived from d.s.c. data. The values are only rough estimates because of the rigorous assumptions in the interpretations of the experimental results and in the corresponding calculations. The differences may arise from the different frequency scales of the experiments and the corresponding length scales observed by the methods.

Because of this short range interaction of filler particles inside an amorphous polymer matrix it is necessary to apply very small sized filler particles in order to alter the bulk properties of the polymer. Most of the technical filler systems, e.g. chalk or titanium dioxide, are too large to modify the polymer at moderate concentrations of the filler.

CONCLUSIONS

Emulsion polymerization in the presence of quartz powder filler particles is a useful procedure for producing polymer composites. Electron micrographs of these products show an ideal distribution of the inorganic material within both the dispersion medium and the polymeric matrix. The properties of the polymer, which is bound to the filler particle surface, differ from those of the amorphous bulk polymer. Ultrasonic velocity measurements, d.s.c. and n.m.r. experiments were carried out in order to determine the thickness of this modified polymer shell. A shell thickness in the range of 2 nm was found using d.s.c. A shell thickness of up to 9 nm was obtained by using n.m.r.

ACKNOWLEDGEMENTS

The authors wish to thank their colleagues for helpful discussions. The financial support of the Kombinat VEB Chemische Werke Buna is gratefully acknowledged.

REFERENCES

1 Hergeth, W.-D., Peller, M. and Hauptmann, P. *Acta Polym.* 1986, **37**, 468

2 Hergeth, W.-D., Starre, P., Schmutzler, K. and Wartewig, S. *Polymer* 1988, **29**, 1323

3 Hashin, Z. *J. Appl. Mech.* 1962, **29**, 143

4 Biros, J., Larina, T., Trekoval, J. and Pouchly, J. *Colloid Polym. Sci.* 1982, **260**, 27

5 Steinau, U.-J., Bittrich, H.-J. and Hergeth, W.-D. to be published

6 Lipatov, Yu. S. 'Physical Chemistry of Filled Polymers', Izd. Khimija, Moscow, 1977 (in Russian)

7 Howard, G. J. and Shanks, R. A. *J. Macromol. Sci.-Phys.* 1981, **B9**, 67

8 Howard, G. J. and Shanks, R. A. *J. Appl. Polym. Sci.* 1981, **26**, 399

9 Alfthan, E., De Ruvo, A., and Rigdal, M. *Intern. J. Polym. Mat.* 1979, **7**, 163

10 Wobst, M. *Thesis*, Technical University Leuna–Merseburg, Merseburg, GDR, 1985

11 Belnikevich, N. G., Mrkvickova, L. and Quadrat, O. *Polymer* 1983, **24**, 713

12 Schomaker, E., Vorenkamp, E. J. and Challa, G. *Polymer* 1986, **27**, 256

13 Dybal, J., Spevacek, J. and Schneider, B. *J. Polym. Sci. B, Polym. Phys.* 1986, **24**, 657

14 Spevacek, J., Schneider, B., Dybal, J., Stork, J., Baldrian, J. and Pelzbauer, Z. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 617