Macromol. Symp. **2004**, *214,* 85-96

Structure-Property Relationships in Rubber-Modified Styrenic Polymers

Walter Heckmann, Graham Edmund McKee, Falko Ramsteiner*

BASF Aktiengesellschaft, Polymer Research, D-67056 Ludwigshafen, Germany
E-mail: walter.heckmann@basf-ag.de

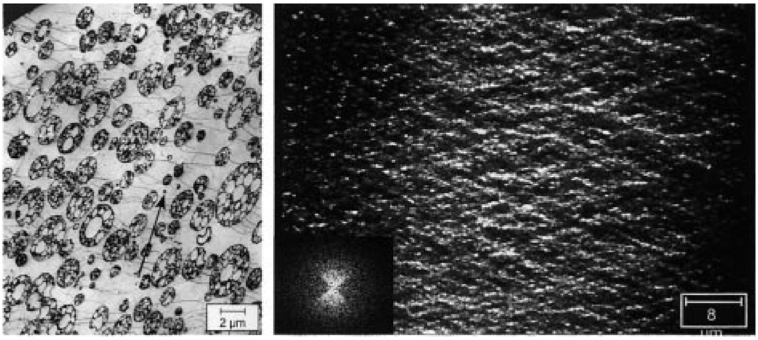
Summary: Styrenic polymers and copolymers are often impact modified with rubber particles. The efficiency of rubber toughening depends mainly on the size of the rubber particles and the degree of cross-linking. The deformation rate, the temperature, the orientation of the polymer molecules and the efficiency of rubber grafting also influence rubber toughening. It is thought that on impact, cavitation inside the rubber particles occurs which reduces the detrimental dilatational stress in the bulk polymer without forming cracks in the brittle matrix or at the rubber-matrix interface. Crazing and shearing are facilitated if the rubber particles can easily cavitate. This can be achieved by either avoiding too much cross-linking or by adding oil (silicone oil in the case of ABS) into the rubber particles, which acts as nuclei for void formation. An electron spectroscopic imaging method is described which allows visualizing the location of the oil. Already after cooling silicone oil modified ABS samples down to liquid nitrogen temperature rubber cavitation is observed. This cavitation is caused by the thermal stress developing due to the differences in thermal expansion coefficient between the rubber phase and the SAN-matrix and is facilitated by silicone oil. Voiding also leads to an increase of light scattering, which can be detected by an optical microscope using dark field illumination.

Keywords: ABS; electron microscopy; electron spectroscopic imaging; gloss; grafting; impact behavior; particle size distribution; rubber cross-linking; silicone oil

Introduction

Polystyrene (PS) and poly(styrene-co-acrylonitrile) (PSAN) are rigid polymers because they do not have a pronounced segmental mobility in the chain backbone below their glass transition temperature. Therefore they are brittle in impact testing. To improve this situation, the materials are often modified with rubber particles, leading to high-impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS) or acrylonitrile-styrene-acrylate (ASA). In these rubber-modified products, impact energy can be dissipated by crazing which is triggered in the stress field near the rubber particles. Crazing is favored by relatively large particles as demonstrated in the case of HIPS were crazes have formed perpendicular to the deformation direction (Figure 1a). In ABS, besides crazing, shear yielding is the predominant deformation mechanism if the rubber particles are small (usually of the order of 300 nm). These small particles favor a local plain stress situation in the region between the particles, with the consequence that a transition from crazing to shear deformation and macro-crazing can occur.

DOI: 10.1002/masy.200451007



a b

Figure 1. Micrographs of a) crazes in HIPS (TEM) b) shear bands in rubber-modified PVC (optical micrograph and Fourier transform image).

In Figure 1b such a shear yielding behavior is shown for a deformed rubber-modified PVC sample. Crazing, macro-crazing and shear yielding are the most important deformation mechanisms for most polymers. Taking a closer look at a deformed HIPS sample shows that besides the crazes, voids are also visible within the rubber phase (Figure 2). The role and importance of void formation within the rubber particles is still not clear but it was recently studied by Bucknall et al. for ABS [1] and for rubber-modified PMMA by Béguelin et al.[2]. In both investigations it was assumed that void formation is an essential prerequisite for crazing.

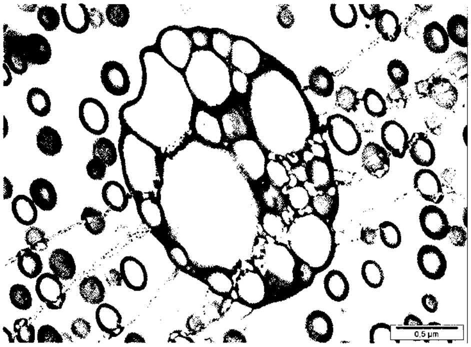


Figure 2. TEM micrograph of a deformed HIPS sample.

The present paper will illustrate the importance of rubber particle size distribution, degree of rubber cross-linking, efficiency of rubber grafting and deformation temperature on the impact behavior of ABS. The importance of void formation and the influence of the addition of silicone oil on rubber cavitation will also be discussed.

The Efficiency of Rubber Toughening

A. Rubber particle size and deformation temperature

In Figure 3 TEM micrographs of two solution-polymerized ABS (LABS) samples with different particle size distributions are shown. LABS 321 has a 12% rubber content in the form of salami-like particles with a diameter up to 3 µm, whereas LABS 312 has a rubber content of 15% and a bimodal particle size distribution with smaller particles [3]. The effectivity of rubber modification on impact energy is demonstrated in the impact strength, versus temperature curve (Figure 3). Obviously the sample with larger particles shows a higher impact strength which we think is due to a more effective craze-formation compared to the smaller particles. The smaller particles are too small to induce effective crazing and too large to induce shear yielding. What is also to be seen is that an increase in impact toughness is only observed when the deformation temperature is higher than the glass transition temperature of the rubbery phase which is between -70 and -90°C in the examples (mechanical damping below -60°C, ISO DIN 6721/3).

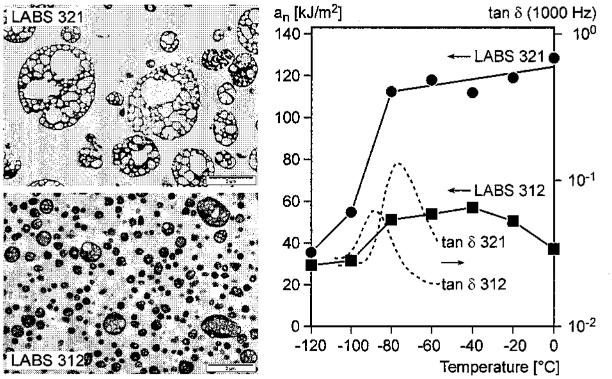


Figure 3. TEM micrographs of LABS samples with different particle size distributions and corresponding impact strength a_n and damping (tan δ).

B. Rubber grafting

An important presupposition for good impact behavior is the necessity of sufficient rubber grafting. Normally the rubber particles must be surrounded by a closed grafted shell. In Figure 4a such a grafted shell is shown for HIPS where the grafted PS-shell around the rubber particles was made visible by dissolving the matrix polystyrene and the included PS with

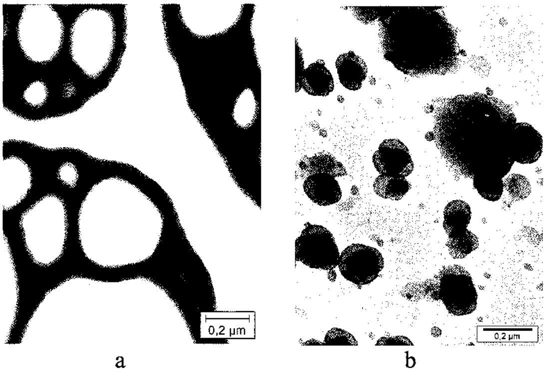


Figure 4. TEM micrographs of grafted shells around rubber particles in a) HIPS and b) ABS.

MEK/acetone directly on a TEM grid. The covalently bonded grafted PS molecules however cannot be extracted and so the grafted shell becomes visible. The grafted molecules give rise to a good adhesion between the PBu rubber particles and the PS matrix, and this is very important. The same is true for rubber particles in ABS prepared in emulsion, as shown in Figure 4b, where the rubber particles are grafted with SAN. In the literature it is discussed that a low degree of grafting and also a degree of grafting causes agglomeration of rubber particles during processing. This is undesired; it causes especially gloss and sometimes also mechanical problems [4]. Aoki [5] has discussed this problem by means of thermodynamic arguments. Due to insufficient grafting the incompatibility between PBu and PSAN leads to an increasing tendency to agglomerate. According to the model of Aoki too high a degree of grafting, where the grafted molecules are in a more extended chain conformation, will also cause agglomeration, because matrix chains are expelled from the grafted chains due to excluded volume effects. These two situations really cause agglomeration as was shown by experiment. Aoki found an optimal grafting level, which was specified at about 0.4 [5], where the grafting degree is defined as the ratio of the weight of the grafted SAN copolymer to that of the rubber particles. Entropic repulsion is assumed which suppresses rubber agglomeration. Hasegawa and coworkers [6] have pointed out that the graft density (number of grafted molecules per unit surface area of the particle) is the important parameter which influences rubber agglomeration. The optimum graft density was found to be about 0.08 nm^{-2} independent of particle content and particle size. This suggests that the optimum grafting density is determined essentially by the surface force between the particles. More recently Ahn and coworkers [7] found the optimum graft ratio at 0.6 where a good dispersion of the rubber particles was observed. When the ratio was 0.68 the particles tended to agglomerate but less severe compared to a lower graft ratio of e.g. 0.35.

C. Rubber cross-linking

In addition to the particle size and the degree of grafting the degree of cross-linking is also an important parameter, which influences toughness. In Figure 5 the torsion modulus of an emulsion ABS before and after annealing at 280 °C for 30 minutes is shown. Due to the annealing the glass transition temperature of the rubber phase has shifted by about 10 °C to higher values[8] and that means, that the degree of cross-linking is significantly higher in the annealed sample compared to the original sample. This additional cross-linking has a strong influence

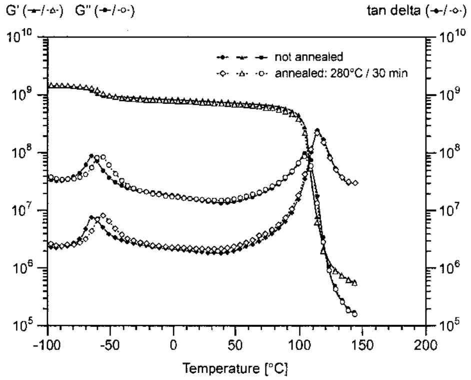


Figure 5. Complex torsion modulus of ABS before and after annealing at 280°C for 30 min.

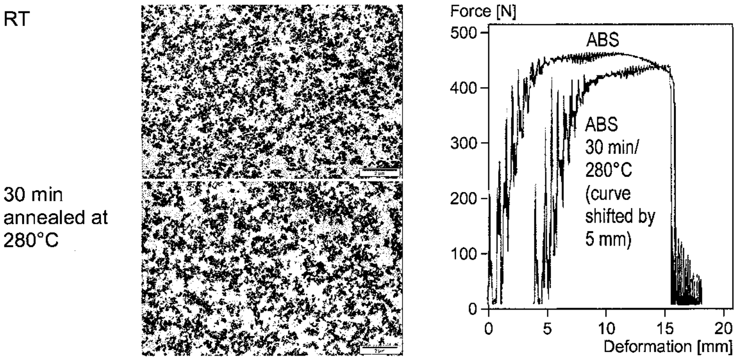
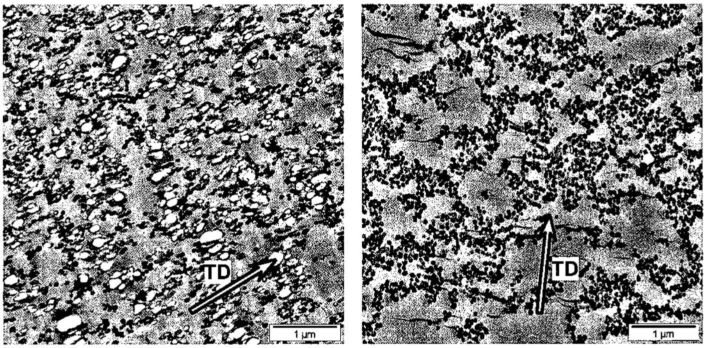


Figure 6. TEM micrographs of undeformed ABS samples before and after annealing and corresponding force-deflection diagrams in impact strength test.

on the impact behavior, as can be seen from the force deflection diagram recorded during an impact test (Figure 6). To make it more clear the deformation curve of the annealed specimen was shifted along the deformation axis compared to the original sample by 5 mm. Thus the deformation at fracture is reduced by annealing or cross-linking from 15 to 10 mm. The loss



a b

Figure 7. TEM micrographs of deformed a) unannealed and b) annealed compression moulded ABS samples.

of toughness due to annealing appears to be caused by a transition in the deformation mechanism. Therefore the deformation process was studied by means of TEM on deformed samples. In Figure 7 a TEM micrograph of the original unanneald but deformed sample is compared to the corresponding annealed sample (Figure 7 b). In the non-annealed sample much void formation has occurred and so called macro-crazes have formed perpendicular to the tensile direction. These macro-crazes consist of voids and stretched fibrillar-like material between the voided particles oriented parallel to the tensile direction. We believe that void formation facilitates the shearing process between the cavitated particles in ABS. In the annealed case, however, cavitation is drastically reduced and only some conventional crazes have developed which bridge the particle free regions. Obviously due to cross-linking, the resistance to void formation has been increased and this must be the reason for the reduction in impact resistance to failure. This also demonstrates, that void formation in combination with shearing and stretching is an important event during the deformation process in ABS and crazing and shearing are facilitated by cavitation within the rubber particles.

D. Influence of silicone-oil on the impact behavior

Already in 1982 Morbitzer and coworkers[9] and recently also Bucknall[1] have shown that the addition of small amounts of silicone-oil can influence the mechanical properties of ABS. In Figure 8 the influence of a very small amount of silicone-oil on the impact resistance of ABS-samples is shown. Obviously with only 0.025% of silicone-oil a significant increase of the impact resistance can be observed. For a better understanding of this effect we tried to find out where the silicon oil is located. The oil could be located in the matrix phase (either segregated or dissolved on a molecular basis), in the rubber phase, again dissolved or as a separate phase or in the interface between the rubbery particles and the matrix. Dynamic mechanical measurements (Figure 9) reveal no influence of the silicone oil on the glass

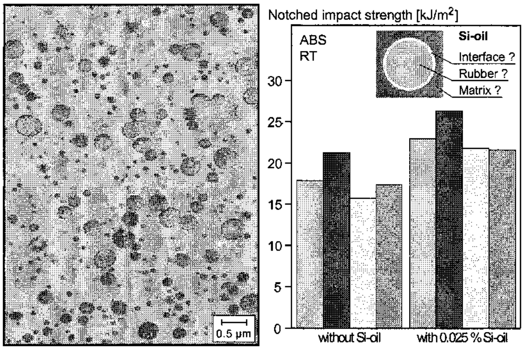


Figure 8. TEM micrograph of an unmodified emulsion ABS sample and notched impact strength of normal ABS and ABS modified with silicone-oil.

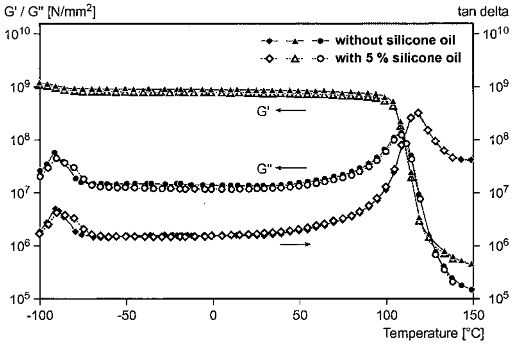


Figure 9. Dynamic mechanical properties of ABS without and with 5% silicone oil.

transition temperature of the SAN matrix, here shown for a high silicone oil content of 5%. The glass transition temperature of the rubber phase, however, is broadened by the addition of oil to higher temperatures

To decide where the silicone oil is located we recorded a silicone elemental distribution map by means of electron spectroscopic imaging (ESI). This can be done by an analytical electron microscope where an energy filter is integrated in the column as realized in the LEO 912 Omega (Figure 10). The energy filter consists of magnetic prisms, which deflect electrons of

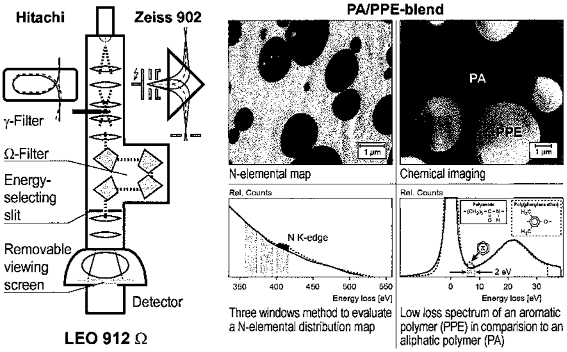


Figure 10. Detecting a nitrogen elemental distribution map by ESI.

different energy loss to different extents. In the back focal plane of the filter the electron energy loss spectrum is produced. With an energy selecting slit electrons of a special energy loss can be selected and used for imaging. Normally a total of three images with a 5 to 10 eV energy window are recorded. Two images in front of the edge are used to calculate the background, which is subtracted from the image under the edge resulting in the elemental distribution map. In Figure 10 this is shown for a N-distribution in a polyamide/ poly(phenylene ether) blend (PA/PPE)[10]. In the case of the ABS-samples we used the Si L2,3-edge for imaging because under the K-edge the signal was too weak. In Figure 11 the Si elemental distribution map of such a silicon oil-modified ABS sample is shown. For intensity reasons the silicon oil concentration was 0.43%. As it is clearly seen, the silicon oil has quantitatively concentrated inside the rubber particles and not in the interface or in the matrix. This is also clear by comparing the electron energy loss spectra on a rubber particle and in the PSAN matrix (Figure 11). Thus it is to be expected that any improvement of toughness by small amounts of silicone-oil is mainly caused by a promotion of deformation processes at the rubber particles. Bucknall[1] has shown that if an ABS sample is cooled down to liquid nitrogen temperatures and then warmed up to RT again, several voids inside the rubber particles of the ABS modified with silicone oil can be observed, whereas the rubber particles in an unmodified product are mainly unchanged. We did the same experiments and came to similar results (Figure 12). We find voids within the rubber particles of silicon oil modified

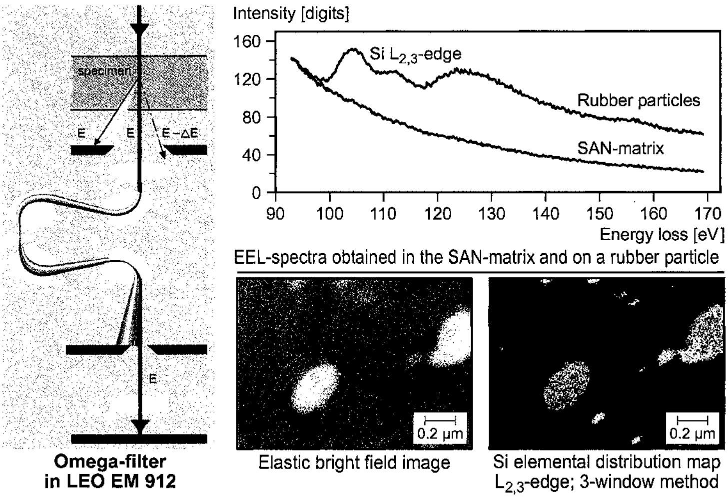


Figure 11. Silicone elemental distribution map of ABS modified with silicone oil obtained by ESI.

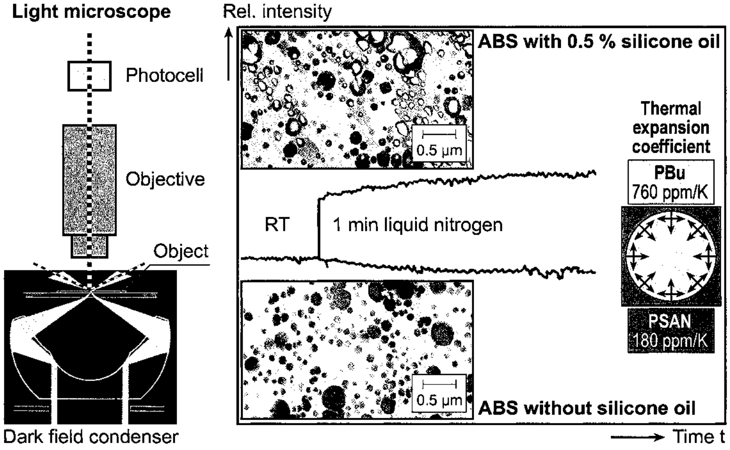


Figure 12. Intensity of light scattering before and after cooling silicone oil modified and unmodified ABS samples to liquid nitrogene temperature.

ABS after cooling down the sample to liquid nitrogen temperature followed by warming up to room temperature. There was no void formation in an unmodified sample. The voiding effect can also be followed by measuring the scattered light under a dark field condenser in an optical microscope [11, 12]. The scattered light intensity significantly increases in the silicone oil-modified sample and is nearly unchanged in the unmodified sample. Bucknall has shown, that due to the different thermal expansion coefficients between the rubber phase and the PSAN a strong stress is built up inside the particles and this stress can relax by voiding. This occurs more easily in the particles modified with silicone oil. This relaxation of the rubber particles by voiding is the reason why we observe a broadening of the glass transition temperature of the rubber phase to higher temperatures. Those relaxed rubber particles show a higher glass transition temperature compared to the particles still under stress (higher free volume)[1,9]. By cooling down to different temperatures and subsequently measuring the light scattering after warming to room temperature we have found, that void formation begins between -80 and -90°C, this is close to the glass transition temperature of the rubber phase (Figure 13).

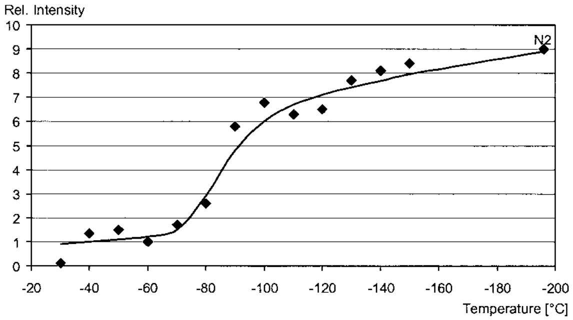


Figure 13. Relative intensity of scattered light of thin ABS films modified with silicone oil and cooled to different temperatures.

Void formation within the rubber particles will also happen during an impact test. Due to the silicone oil, cavitation within the rubber particles obviously will occur more easily compared to the unmodified ABS and so crazing and shearing are facilitated and a higher impact resistance is observed. In contrast to this, on thermal cross-linking the rubber particles become more resistant to cavitation, resulting in embrittlement.

Conclusion

It was shown, that the efficiency of rubber toughening in ABS depends on several parameters. Beside of the deformation rate, which was not discussed, the most important parameters are

- the particle size distribution
- rubber grafting
- degree of cross-linking
- deformation temperature
- ease of void formation

Especially void formation in rubber particles has a more important influence on the impact strength than was supposed in the past. However, it is still open to question, which of the following three mechanisms prevails, namely

- whether crazes are initiated after void formation
- whether the precursor of a craze in the matrix can only easily form a real craze, if the adjacent rubber particle cavitates to compensate the local volume strain or
- both deformation structures occur simultaneously

Void formation can be facilitated by adding an appropriate silicone oil whereby the silicone-oil is concentrated in the rubber particles as shown by ESI. Even small amounts lead to an improvement in toughness. Further important parameters are adequately grafted rubber particles of the correct particle size, which can internally cavitate but are strong enough to bridge deformation zones like crazes.

[1] C. B. Bucknall, D. S. Ayre, D. J. Dijkstra, *Polymer* **2000**, *41*, 5937.
[2] Ph. Béguelin, Ch. J. G. Plummer, H. H. Kausch, "*Polymer Blends and Alloys*", G. O. Shonaike, G. P. Simon, Eds., Marcel Dekker, New York 1999, p. 549.
[3] F. Ramsteiner, G. E. McKee, W. Heckmann, W. Fischer, M. Fischer, *Acta Polym.* **1997**, *48*, 553.
[4] M. C. O. Chang, R. L. Nemeth, *J. Appl. Polym. Sci.* **1996**, *61*, 1003.
[5] Y. Aoki, *Macromolecules* **1987**, *20*, 2208.
[6] R. Hasegawa, Y. Aoki, M. Doi, *Macromolecules* **1996**, *29*, 6656.
[7] K. H. Ahn, D. H. Ha, B. D. Lee, J. G. Doh, J. H. Choi, *Polym. Eng. Sci.* **2002**, *42*, 605.
[8] L. E. Nielson, *J. Macromol. Sci. Rev.* **1969**, *69*, 77.
[9] L. Morbitzer, G. Humme, K. H. Ott, K. Zabrocki, *Angew. Makromol. Chem.* **1982**, *108*, 123.
[10] W. Heckmann, W. Probst, F. Hofer, W. Grogger, *14th International Congress on Electron Microscopy,* Cancun 1998, Proceedings Vol. II, p. 867.
[11] W. Heckmann, *15th International Congress on Electron Microscopy,* Durban 2002, Proceedings Vol. I, p. 587.
[12] F. Ramsteiner, W. Heckmann, G. E. McKee, M. Breulmann, *Polymer* **2002**, *43*, 5995.