Macromol. Symp. 2009, 283–284, 223–229 DOI: 10.1002/masy.200950929

# Tensile Properties of Self-Crosslinkable Poly(n-butyl methacrylate-*co*-*N*-methylolacrylamide) Films Prepared by Emulsion and Microemulsion Latexes

*Jacobo Aguilar,[1] Martín Rabelero,[1] Eduardo Mendizábal,[2] Sergio M. Nuño-Donlucas,[1] Martín Arellano,*[1] Jorge E. Puig[1]*

**Summary:** The gel content, swelling degree and mechanical properties of self-crosslinkable poly(n-butyl methacrylate-co-N-methylolacrylamide) films made by two-stage emulsion (using sodium dodecyl sulfate as surfactant) or microemulsion (using cetyltrimethylammonium bromide as surfactant) polymerization processes in the presence of variable amounts of the chain transfer agent, n-butyl mercaptan, are reported here. Latexes made by microemulsion polymerization contain much smaller nanoparticles with lower amount of gel than those obtained by the emulsion process. Stress-strain tests in uncured and cured films indicate that microemulsion-made films are tougher and exhibit smaller deformations at break.

**Keywords:** mechanical properties; microemulsion polymerization; poly(butyl methacrylate-co-N-methylolacrylamide); self-crosslinkable film

## Introduction

One of the major applications of acrylic and vinyl polymers made by emulsion polymerization is for various water-borne coatings and films.[1–3] In these types of applications, the colloidal dispersion of polymer particles in water (latex) is transformed into a void-free and mechanically coherent polymer film.[4] To improve their mechanical properties and to increase their adhesion to substrates, vinyl and acrylic polymer films are usually modified with small amounts of a functional monomer such as N-methylolacrylamide (NMA), acrylic acid or methacrylic acid.[5–13] When NMA is used as the functional monomer, self-crosslinkable latexes are obtained that form films with increased tensile strength, toughness, impact, abrasion and solvent resistance.[14,15] In order to produce coherent, mechanically strong polymer films, it is necessary to reduce the microgel content (i.e., the amount of crosslinked polymer chains) in the parent latex particles, which should contain linear chains that can diffuse across particle-particle interfaces during film formation to give good interparticle adhesion.[4] The occurrence of crosslinking after film formation guarantees mechanically strong films.

Similarly to its emulsion counterpart, microemulsion polymerization allows the synthesis of colloidal dispersions of high-molar mass polymer particles with fast reaction rates, but in the nanosize range.[16,17] However, the mechanism of polymerization is different for the two processes and often, polymers with different characteristics or morphology from the ones produced by emulsion polymerization

---

[1] Departamentos de Ingeniería Química, Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Blvd. Marcelino García Barragán # 1451, S.R., C.P. 44430, Guadalajara Jalisco, México
Fax: (33) 36197316;
E-mail: marellan@cencar.udg.mx

[2] Departamento de Química, Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Blvd. Marcelino García Barragán # 1451, S.R., C.P. 44430, Guadalajara Jalisco, México

Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY InterScience®

are obtained by microemulsion polymerization.[18–24]

Recently, Krishnan et al. reported the synthesis of copolymers of n-butyl methacrylate (BMA) and NMA in the presence of varying amounts of $CBr_4$ by a two-stage emulsion polymerization process, which had negligible crosslinking before curing and produced high gel content on thermal curing.[25] They examined the characteristics of the films but no mechanical properties were reported.

In this work we report the synthesis of similar BMA and NMA copolymers made by two-stage emulsion or microemulsion polymerization processes using a different chain transfer agent, n-butyl mercaptan (n-BM), with the goal to produce self-crosslinkable films with improved mechanical properties. The aim was to determine the effect of the different methods of preparation (i.e., latex particles of different sizes and molar masses) in the characteristics (gel content and swelling index) and the mechanical properties of uncured and cured films made by casting.

## Experimental Part

n-Butyl methacrylate (BMA), 99% pure from Aldrich, was passed through a DHR-4 column (Scientific Polymer Products) to remove the inhibitor. N-methylolacrylamide (NMA), from TCI America, was used as received. n-Butyl mercaptan, 99% pure from Aldrich, was used as chain transfer agent. Sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were both 99% pure from Aldrich. Potassium persulfate, 99% pure from Aldrich, and 2,2-azobis(2-methylpropionamidine) dihydrochloride (V-50), 99% pure from Wako Chemicals, were used as initiators. Deionized and bi-distilled water was used. $NaHCO_3$ (95% purity from Fermont) was used as a buffer to maintain the pH constant.

The emulsion and microemulsion latexes were prepared in two stages in a 250 mL glass reactor. The first stage consisted in the batch polymerization of BMA (seed stage) whereas the second one was semi-continuous carried on under monomer starving conditions of BMA and NMA to produce a copolymer shell. The compositions of the initial emulsion and microemulsion are indicated in Table 1. In the first stage, the batch polymerization of BMA was carried out for both processes for 45 min at 70 °C under $N_2$-atmosphere. In the second stage, the mixture indicated in Table 1 for emulsion and microemulsion processes and n-BM (in variable concentration) were fed at a rate of 0.7 $cm^3$/min. To determine conversion by gravimetry at the end of the first and second stages, the polymer was precipitated from the latexes by adding excess methanol (reagent grade from Bassel), recovered by filtration and dried in an oven to constant weight. Final latexes at the end of both stages were also collected for particle size and molar mass determinations.

Particle size was measured at 90°-angle and 25 °C in a Malvern 4700 quasielastic light scattering (QLS) apparatus equipped with a He-Ne laser ($\lambda = 664$ nm). To minimize particle-particle interactions and reduce multiple light scattering, latexes were diluted with water up to 100 times. Besides, the particle size and size distribution were determined in a JEOL CX 100 transmission electron microscope (TEM).

**Table 1.**
Recipes for latex preparation.

| Emulsion polymerization | | Microemulsion polymerization | |
|---|---|---|---|
| Component | Amount (g) | Component | Amount (g) |
| First stage | | | |
| Water | 88.5 | Water | 88.5 |
| BMA | 10.5 | BMA | 10.5 |
| SDS | 0.1278 | CTAB | 1.92 |
| KPS | 0.0735 | V-50 | 0.105 |
| $NaHCO_3$ | 0.0725 | $NaHCO_3$ | 0.072 |
| Second stage | | | |
| Water | 19.3 | Water | 38.75 |
| BMA | 79.8 | BMA | 27.5 |
| NMA | 2.4 | NMA | 0.82 |
| SDS | 0.66 | CTAB | 1.5 |
| n-BM[a] | 0.001–0.003 | n-BM[a] | 0.001–0.003 |

[a] $m_{n\text{-}BM}/m_{BMA}$.

Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

One drop of latex diluted up to 100 times was deposited on a grid; then two drops of a 2 wt % phosphotungstic acid aqueous solution was added, and the grid dried overnight. The particle diameters were measured directly from each micrograph (a minimum of 300 particles was measured for each latex).

For measuring molar mass distribution and average molar masses of the soluble fraction, the copolymer was precipitated by adding excess methanol. Surfactant was eliminated from the copolymer by water washing, and then the copolymer was dried in an oven, and redispersed in water to eliminate the residual surfactant by dialysis. The surfactant-free copolymer was recovered by filtration, washed with deionized water and dried. To remove the gel fraction, samples were placed in a vial with HPLC-grade tetrahydrofurane (Aldrich) for one week, filtered, and the solvent from the filtrate was evaporated to obtain the sol fraction. Then the sol fraction was dissolved in HPLC-grade THF (3 mg/cm$^3$) and injected into a Perkin Elmer LC-30 gel permeation chromatograph (GPC) equipped with a refractive index and a multi-angle light scattering detectors to determine molar mass distributions.

The gel fraction and the swelling index of the uncured and cured films were determined by gravimetry. Water from the latex samples was evaporated at 40 °C (atmospheric pressure = 640 mm Hg) for 48 h in a forced-convection oven to produce the uncured films (1.2-1.4 mm in thickness). For the curing process, a sample of each film was heated at 150 °C during 30 min. The films were placed in a vial with toluene (99% pure from Aldrich) for one week (a polymer-to-solvent weight ratio of 1/100 was used). The suspensions were filtered with a 2-μm pore size filter to obtain the gel, which was dried in a forced-convention oven to constant weight. The gel fraction was calculated as the mass of the dried gel weight divided by the original mass of the polymer sample. The swelling index (SI) was calculated as the ratio of the mass of the swollen gel to that of the dried gel.

Copolymer films were prepared by casting the latexes at 40 °C for 48 h. For mechanical tests, some films were cured at 150 °C for 30 min. Stress-strain tests were carried out at $15 \pm 1$ °C and a displacement rate of 5mm/min in an SFM-10 United universal testing machine according to the ASTM D-882 standard.

## Results and Discussion

In both emulsion and microemulsion polymerization processes, conversions were high ($\geq 90\%$) at the end of the seed (first) and feed (second) stages. Particle size at the end of the seed stage was ca. 42 (± 3) nm for the microemulsion process and ca. 103 (± 3) nm for the emulsion process; during the feed stage, particles grow to about 63 (± 2) nm and 235 (± 15) nm for the microemulsion and emulsion processes, respectively, and remain within that size range independently of the amount of n-BM (the difference between the average particle sizes determined by QLS and TEM fall within the experimental error). In all cases, the particle size distribution was narrow with polydispersity below 1.15. The much larger relative particle growth observed in emulsion polymerization is due to the higher final solid content achieved in this process (45%) compared to that (25%) obtained in microemulsion polymerization. The particle growth in both the emulsion and microemulsion polymerizations indicates that both monomers (BMA and NMA) added during the second stage polymerized over the seed particles.

Number-average ($M_n$) and weight-average ($M_w$) molar masses of the sol fraction (soluble polymer) obtained at the end of the second stage for both processes are reported in Table 2. The addition of n-BM diminishes the molar mass of the sol fraction and this effect is stronger in the emulsion-made copolymers than in the microemulsion-made ones. This could be the result of the much larger microemulsion particle number density compared to that in the emulsion polymerization process, which

Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

**Table 2.**
Effect of the concentration of n-BM on average molecular masses ($M_w$ and $M_n$).

| $m_{n\text{-}BM}/m_{BMA}$ (g/g) | $M_w \times 10^{-3}$ (Dalton) | $M_n \times 10^{-3}$ (Dalton) | $M_w/M_n$ |
|---|---|---|---|
| | Emulsion | | |
| 0 | 3000 | 2700 | 1.1 |
| 0.001 | 170 | 146 | 1.2 |
| 0.003 | 83 | 33 | 2.5 |
| | Microemulsion | | |
| 0 | 946 | 643 | 1.5 |
| 0.001 | 470 | 128 | 3.7 |
| 0.003 | 421 | 70 | 6.1 |

leads to a much lower local concentration ratio of chain transfer agent-to-monomer in the former. However, this issue has not been addressed in the literature, as far as we know. Experiments are underway to corroborate this hypothesis.

Table 3 reports the gel fraction and the swelling indexes for both uncured and cured films. As expected from the results of Krishnan et al.,[25] both the uncured and cured casted films made by emulsion polymerization in the absence of chain transfer agent contain large gel fraction, 0.85 and 0.86, respectively, indicating that most of the polymer produced in the feed stage was crosslinked even before the polymer was thermally cured at elevated temperature. The presence of n-BM reduces drastically the gel content of the uncured emulsion based films, but also causes that the gel content practically does not increase after curing. Moreover, the low swelling index of the emulsion-made films (Table 3) indicates that the gel fraction has a high crosslinking density. This can be explained by the lower average molar mass of the soluble fraction (Table 3), which causes that upon curing at high temperature, the formation of a network with small molecular mass between crosslinking points. By contrast, the gel fraction of the uncured film made by microemulsion polymerization in the absence of n-BM is much lower (0.21) but the gel fraction in the cured film increased substantially up to 0.78 (Table 3). This demonstrates the advantage of microemulsion polymerization over emulsion polymerization since it produce films that have lower premature crosslinking fraction. The presence of n-BM also decreases the gel fraction of the microemulsion-made uncured films which are lower than those of the emulsion-made polymers. The curing of the films increased the gel fraction to values higher than those of the emulsion-made films. The higher swelling index of the films prepared with microemulsion copolymer suggests net-

**Table 3.**
Effect of n-BM concentration on gel fraction and swelling index.

| $m_{n\text{-}BM}/m_{BMA}$ (g/g) | Uncured films | | Films cured at 150 °C for 30 min | |
|---|---|---|---|---|
| | gel fraction | swelling index | gel fraction | swelling index |
| | Emulsion | | | |
| 0 | $0.85 \pm 0.01$ | $5.2 \pm 0.25$ | $0.86 \pm 0.01$ | $5.3 \pm 0.26$ |
| 0.001 | $0.18 \pm 0.01$ | $2.3 \pm 0.03$ | $0.21 \pm 0.02$ | $3.6 \pm 0.03$ |
| 0.003 | $0.12 \pm 0.01$ | $1.5 \pm 0.02$ | $0.12 \pm 0.01$ | $3.0 \pm 0.14$ |
| | Microemulsion | | | |
| 0 | $0.21 \pm 0.02$ | $2.1 \pm 0.20$ | $0.78 \pm 0.02$ | $35.2 \pm 0.60$ |
| 0.001 | $0.15 \pm 0.03$ | $1.4 \pm 0.15$ | $0.60 \pm 0.01$ | $28.6 \pm 1.05$ |
| 0.003 | $0.10 \pm 0.03$ | $1.2 \pm 0.15$ | $0.50 \pm 0.03$ | $27.7 \pm 1.62$ |

Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

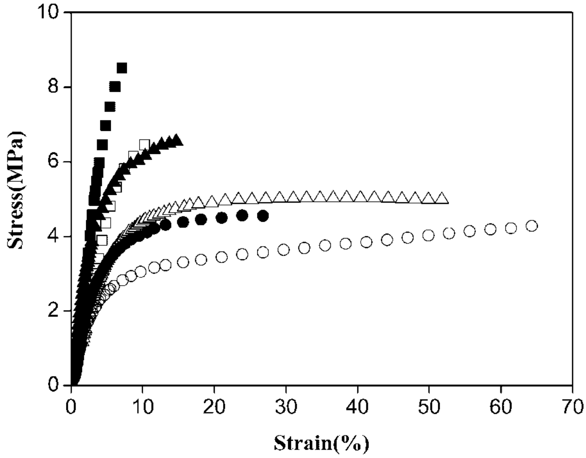

***Figure 1.***
Stress-strain curves for specimens made from emulsion latex as a function of n-BM concentration ($m_{n\text{-}BM}/m_{BMA}$): uncured (□) 0, (△) 0.001, (○) 0.003; cured (■) 0, (▲) 0.001, (●) 0.003.

work with lower crosslinking density (larger molecular mass between crosslinking points) compared to the films prepared with emulsion copolymers.

Figure 1 depicts stress-strain tests performed in uncured (i.e., without thermal treatment) and cured casting films prepared from emulsion latexes at various n-BM concentrations. The shape of the stress-strain curves of samples reveals a uniform extension behavior for the uncured films obtained from latexes made without n-BM; this curve is typical of a hard and brittle polymer.[26,27] An apparent yield point is observed for samples in which n-BM was used in the polymerization, and the stress at this point decreases as the n-BM concentration increases and the curves are typical of hard and ductile polymers.[26,27]

The stress-strain curves of the films prepared from microemulsion latexes are shown in Figure 2. The stress-strain curves

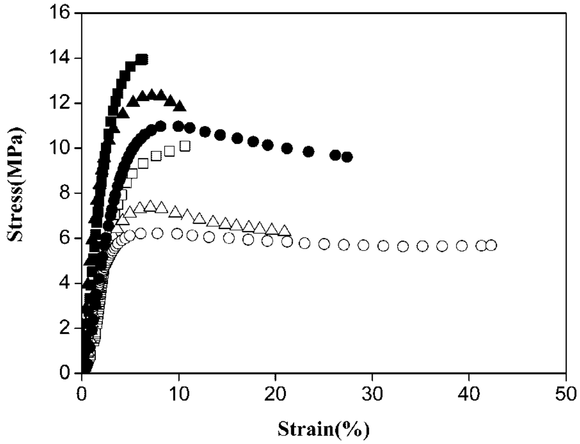

***Figure 2.***
Stress-strain curves for specimens made from microemulsion latex as a function of n-BM concentration ($m_{n\text{-}BM}/m_{BMA}$): uncured (□) 0, (△) 0.001, (○) 0.003; cured (■) 0, (▲) 0.001, (●) 0.003.

Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

*Table 4.*
Summary of tensile properties (Young modulus (E), tensile strength ($\sigma_p$), elongation at break ($\varepsilon_b$), and toughness) of films prepared using emulsion and microemulsion latex.

| $m_{n\text{-}BM}/m_{BMA}$ (g/g) | Uncured | | | | Cured | | | |
|---|---|---|---|---|---|---|---|---|
| | E (MPa) | $\sigma_p$ (MPa) | $\varepsilon_b$ (%) | Toughness $\times 10^{-6}$ (J/m$^3$) | E (MPa) | $\sigma_p$ (MPa) | $\varepsilon_b$ (%) | Toughness $\times 10^{-6}$ (J/m$^3$) |
| | Emulsion | | | | | | | |
| 0 | $176 \pm 8$ | $6.9 \pm 0.9$ | $12.8 \pm 2$ | $0.6 \pm 0.2$ | $225 \pm 4$ | $9.2 \pm 0.7$ | $8.7 \pm 2$ | $0.3 \pm 0.1$ |
| 0.001 | $125 \pm 6$ | $3.9 \pm 0.6$ | $61.0 \pm 8$ | $1.9 \pm 0.3$ | $196 \pm 7$ | $6.8 \pm 0.9$ | $18.0 \pm 5$ | $0.9 \pm 0.2$ |
| 0.003 | $79 \pm 5$ | $3.3 \pm 0.5$ | $72.0 \pm 7$ | $2.0 \pm 0.4$ | $181 \pm 7$ | $3.8 \pm 0.4$ | $27.0 \pm 4$ | $0.9 \pm 0.2$ |
| | Microemulsion | | | | | | | |
| 0 | $244 \pm 18$ | $10.6 \pm 0.8$ | $11.3 \pm 1$ | $0.8 \pm 0.1$ | $315 \pm 5$ | $16.1 \pm 0.7$ | $11.4 \pm 3$ | $1.0 \pm 0.4$ |
| 0.001 | $237 \pm 12$ | $8.2 \pm 0.7$ | $17.5 \pm 5$ | $1.3 \pm 0.4$ | $295 \pm 9$ | $12.2 \pm 0.5$ | $11.8 \pm 1$ | $1.0 \pm 0.4$ |
| 0.003 | $204 \pm 9$ | $7.1 \pm 0.8$ | $40.1 \pm 7$ | $2.4 \pm 0.2$ | $272 \pm 7$ | $10.8 \pm 0.6$ | $28.7 \pm 5$ | $2.6 \pm 0.6$ |

in general depict a yield point, after which cold-drawing with necking develop in such a way that the stress decreases as the strain increases up to the break point (hard and ductile polymer behavior). Only the sample without n-BM shows a different mechanical response because the breaking point is very close to the yield point.

The increase in ultimate strain and the decrease in ultimate strength and yield stress of the uncured films as the content of n-BM increases, observed in both emulsion- and microemulsion-made films (Table 4), is a consequence of the lower molar masses (Table 3) and the lower crosslinking of chains during polymerization induced for the augment of n-BM in the initial composition. The increase in toughness (for both uncured and cure films) as the content of n-BM increases (Table 4) is also a consequence of the lower crosslinking formation during polymerization, which results in a higher degree of polymer diffusion across the particle interfaces during the film formation process. In summary, the difference of the mechanical properties can be explained considering the different factors which have a crucial role in film formation process: (i) particle size, (ii) the minimum film-formation temperature (MFT) that is usually close to the glass transition temperature ($T_g$), (iii) the gel fraction of the parent polymer particles, and (iv) the molar mass of the soluble and dangling chains. In both cases, the MFT is near to the $T_g$'s of the emulsion-made film (33 °C) and the microemulsion-made film (35 °C) In this sense, the larger particles of the latex prepared by emulsion have a negative influence to the polymer interdiffusion that takes place in the last step of polymer film formation when the fusion occurs among adjacent particles. By contrast, the latex particle obtained by microemulsion polymerization are much smaller, in consequence a better interdiffusion process can occur and due to the larger superficial area and the larger molecular mass of the soluble and dangling chains, a larger formation of entanglements may occur and more coherent film is obtained.

## Conclusions

Here it was shown that a larger reduction in the amount of gel of uncured films made by microemulsion polymerization latexes is obtained compared to the films made by emulsion polymerization ones.

When n-BM is used the gel content in uncured films is decreased when using latex prepared by both emulsion and microemulsion polymerization. However only the films prepared with latex made by microemulsion polymerization increased greatly the crosslinking formation upon curing. The mechanical tests indicate substantial differences in the mechanical response of the emulsion- versus microemulsion-made

Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

films before and after curing. These differences are explained in terms of differences in molar masses of the soluble fraction, gel fraction before film formation and after curing, and particle size.

[1] G. P. A. Turner, "*Introduction to Paint Chemistry and Principles of Paint Technology*", 2nd ed., Chapman and Hall, London **1980**.

[2] R. Satguru, J. Mcmahon, J. C. Padget, R. G. Coogan, *J. Coat. Tech.* **1994**, *66*, 47.

[3] P. A. Steward, J. Hearn, M. C. Wilkinson, *Adv. Coll. Poym. Sci.* **2000**, *86*, 195.

[4] M. A. Winnik, in, "*Emulsion Polymerization and Emulsion Polymers*", P. A. Lovell, M. S. El-Aasser, Eds., Wiley, New York **1997**, p. 467.

[5] R. H. Yocum, E. B. Nyqusit, "*Functional Monomers: Their Preparation, Polymerization, and Application*", Marcel and Dekker, New York **1973**.

[6] E. N. Rostovskii, L. M. Novichkove, *Acad Sci USSR Zh Prikl.* **1966**, *41*, 1.

[7] J. B. Frías, J. E. Puig, E. Mendizábal, *Soc Plast Eng Tech Papers* **1993**, *XXXIX*, 3460.

[8] S. Kamogawa, *Kogyo Kagaku Zasshi.* **1958**, *61*, 1024.

[9] S. Kamogawa, *Kogyo Kagaku Zasshi.* **1959**, *62*, 117.

[10] M. Hidalgo, J. Guillot, J. Y. Cavaille, *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1991**, *49*, 103.

[11] H. K. Kagawushi, Y. Sugi, Y. Ohisuka, *J. Appl. Polym. Sci.* **1981**, *26*, 1649.

[12] J. B. Frías, J. F. López, N. Alonso, E. Mendizábal, J. E. Puig, *Polym. Bull.* **1993**, *31*, 285.

[13] J. E. Puig, S. Corona-Galván, A. Maldonado, P. C. Schulz, B. E. Rodríguez, E. W. Kaler, *J. Colloid. Interf. Sci.* **1990**, *137*, 308.

[14] G. B. Bufkin, J. R. Grawe, *J. Coat. Tech.* **1978**, *50*, 41.

[15] P. Volfova, L. Chrastova, L. Cernakova, J. Mrenica, J. Kozankova, *Macromol. Symp.* **2001**, *170*, 283.

[16] J. E. Puig, in: "*The Polymeric Materials Encyclopedia*", vol. *6* J. C. Salamone, Ed., CRC Press, Boca Ratón **1996**, p. 4333.

[17] C. C. Co, R. de Vries, E. W. Kaler, in: "*Reactions and Shyntesis in Surfactant Systems*", Surf. Sci. Series, vol. *100*. J. Texter, Ed., Marcel Dekker, New York 2001, p. 455.

[18] A. P. Full, J. E. Puig, L. U. Gron, E. W. Kaler, J. R. Minter, T. H. Mourey, J. Texter, *Macromolecules* **1992**, *25*, 5157.

[19] R. Y. Qian, L. H. Wu, D. H. Shen, D. H. Napper, R. A. Mann, D. F. Sangster, *Macromolecules* **1993**, *26*, 2950.

[20] C. Wu, K. K. Chan, K. F. Woo, R. Y. Quian, X. H. Li, L. S. Chen, D. H. Napper, G. L. Tan, A. J. Hill, *Macromolecules* **1995**, *28*, 1592.

[21] S. Roy, S. Devi, *J. Appl. Polym. Sci.* **1996**, *62*, 1509.

[22] S. C. Pilcher, W. T. Ford, *Macromolecules* **1998**, *31*, 3454.

[23] N. Sosa, R. D. Peralta, R. G. López, L. F. Ramos, I. Katime, C. Cesteros, E. Mendizábal, J. E. Puig, *Polymer* **2001**, *42*, 6923.

[24] W. Jiang, W. Yang, X. Zeng, S. Fu, *J. Polym. Sci. Part A Polym. Chem.* **2004**, *42*, 733.

[25] S. Krishnan, A. Klein, M. S. El-Aasser, E. D. Sudol, *Macromolecules* **2003**, *36*, 3152.

[26] L. E. Nielsen, R. F. Landel, "*Mechanical Properties of Polymers and Composites*", 2nd ed., Marcel Dekker, New York **1994**.

[27] I. M. Ward, "*Mechanical Properties of Solid Polymers*", 2nd ed., Wiley, New York **1985**.

Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim