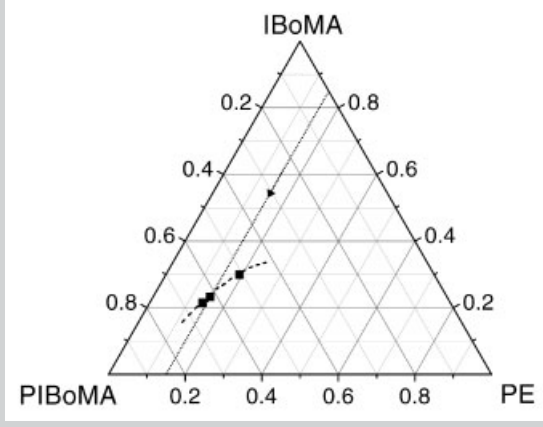
Summary: Solutions containing 15 wt.-% of a low-molar-mass polyethylene (PE) in isobornyl methacrylate (IBoMA), containing 0, 5 or 10 wt.-% of 1,4 butanediol dimethacrylate (BDDMA) as crosslinker, were polymerized using either benzoyl peroxide (BPO), at 80 °C, or dicumyl peroxide (DCPO), with a thermal cycle attaining 150 °C, as initiators. Phase separation of an amorphous PE-rich phase took place when carrying out the reaction at temperatures higher than the PE melting temperature. Partial crystallization of PE was observed when cooling to room temperature. Depending on the initial amount of BDDMA, the fraction of PE that was phase separated varied between 57 and 66% of the initial amount, with crystalline fractions in the range of 15 to 42%. The use of IBoMA as a reactive solvent of PE has two main advantages over other reactive solvents reported in the literature: a) it has a very low vapor pressure, and b) its free-radical polymerization gives a polymer with a relatively high glass transition temperature.



Part of the cloud-point curve for IBoMa, PIBoMA and PE solutions at 80 °C.

Isobornyl Methacrylate as a Reactive Solvent of Polyethylene

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Received: March 8, 2004; Revised: May 14, 2004; Accepted: May 17, 2004; DOI: 10.1002/mame.200400061

Keywords: blends; miscibility; phase separation; polyethylene (PE); reactive processing

Introduction

The polymerization-induced phase separation of solutions of a thermoplastic polymer in thermoset precursors (reactive solvent), may be used to generate a multiphasic material with some improved properties (mechanical, thermal, optical, etc.), with respect to those of the pure components. In particular, these formulations are used to toughen the generated polymer network or to facilitate processing of the thermoplastic polymer.[1,2] Part of the literature in this field may be found under the heading of semi-interpenetrated polymer networks (semi-IPNs or IPN-like materials), although this terminology is misleading because in most of these systems phase separation prevents the interpenetration of both polymers.

Several vinyl monomers (including a divinyl monomer as crosslinker), have been reported as reactive solvents for polyethylene (PE): styrene (S),[3–8] butyl methacrylate (BMA),[3,9,10] solutions of S and BMA,[11,12] dodecyl methacrylate (DMA),[13] solutions of methyl methacrylate (MMA) and DMA (PE is not soluble in pure MMA),[10,13] solutions of MMA and BMA,[10,14,15] solutions of ethyl methacrylate (EMA) and DMA,[10,15] solutions of EMA and BMA,[10,14] and solutions of MMA and 2-ethylhexyl methacrylate (EHMA).[14] In all of these systems PE was dissolved in the reactive solvent at an adequate high temperature (usually above its melting temperature), leading to a homogeneous solution. Adding small amounts of an initiator and a divinyl monomer, and performing the free-radical polymerization, led to multiphasic materials exhibiting PE-rich and thermoset-rich regions.

These reactive solvents exhibit some disadvantages for their practical use: a) high vapor pressures implying the need to process the solution at high total pressures, and b) relatively low glass transition temperature (T_g) of the resulting polymer network. A particular reactive solvent that can

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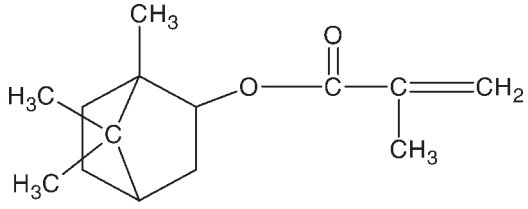

Figure 1. Chemical structure of isobornyl methacrylate (IBoMA).

be used to avoid these drawbacks is isobornyl methacrylate (IBoMA) (Figure 1). This monomer has a very low vapor pressure (3 Torr at 80 °C),[16] and leads to a linear polymer with a glass transition temperature close to 125 °C (onset value measured by DSC).[17,18] The kinetics of its free-radical polymerization has been recently investigated.[18,19]

The aim of this paper is to show the feasibility of using IBoMA as a reactive solvent of PE. In order to obtain homogeneous solutions at the lowest possible temperature, thus minimizing monomer losses due to evaporation, a low-molar-mass PE (PE wax) was selected for this study. A similar approach was recently employed to study the phase separation phenomena during the polymerization of styrene in the presence of PE.[8]

The polymerization-induced phase separation was performed isothermally at 80 °C. To estimate the fraction and crystallinity of phase-separated PE, plaques of final materials were also obtained with a thermal cycle attaining a maximum value of 150 °C.

Experimental Part

Materials

Isobornyl methacrylate (IBoMA, Aldrich) was used as received. It contained 150 ppm of *p*-methoxyphenol (MEHQ, methyl ether hydroquinone) as inhibitor. The selected cross-linker was 1,4-butanediol dimethacrylate (BDDMA, Aldrich), also used as received. Formulations containing 0, 5 and 10 wt.-% BDDMA dissolved in IBoMA, were used. Benzoyl peroxide (BPO, Akzo-Nobel), in an amount of 2 wt.-% in the solution of acrylic monomers, was used as initiator of the polymerization at 80 °C. Dicumyl peroxide (DCPO, Merck-Schuchardt), also in an amount of 2 wt.-%, was used to initiate the polymerization of plaques.

The polyethylene wax (PE, Petrolite), had a number-average molar mass, $\overline{M}_n = 484$ g/mol, and a mass-average molar mass, $\overline{M}_w = 548$ g/mol. Its melting temperature was 77 °C (determined at the maximum of the endothermic peak by DSC), with a heat of fusion equal to 236 J/g. Using 293 J/g as the heat of fusion of a PE crystal,[20] leads to a crystallinity of 81%. To analyze the phase separation process at 80 °C and to characterize phase-separated materials, initial solutions containing 15 wt.-% PE (expressed as a fraction of total mass) were used. A series of materials containing 5 wt.-% PE was also prepared to estimate the plasticizing effect of the PE dissolved in the acrylic polymer.

Thermal Cycles Used for the Polymerization

Formulations including BPO as initiator were polymerized isothermally at 80 °C. DCPO was used to obtain plaques using a mold consisting of two glass plates coated with a silicone release-wax, spaced by a 2 mm diameter rubber cord, and held together with clamps. The molds were placed in an oven at 130 °C during 2 h, then the temperature was increased to 150 °C at 2 °C/min, and the samples were kept during another 2 h at this temperature. After cooling down overnight from oven temperature to room temperature, the samples were demolded.

Techniques

Cloud-point temperatures were determined using a light-transmission device described in the literature.[21] The cloud-point was determined at the onset of the decrease of the intensity of transmitted light when decreasing the temperature at a rate of 0.1 °C/min.

Transmission optical microscopy (TOM) was employed to determine the cloud-point time in the course of the polymerization performed at 80 °C, and to obtain micrographs of the resulting morphologies both at 80 °C and at room temperature (with or without crossed polarizers). An Olympus BX 50 microscope provided with a CCD-camera Jai M10 and a hot stage (Linkam CSS 450) was used for these purposes.

Different techniques were used to characterize the final materials obtained as plaques. Fracture surfaces obtained at room temperature were observed by scanning electron microscopy (SEM, LEO Gemini 1530), without employing etching or staining techniques. DSC (Pyris 1, Perkin-Elmer) was employed to determine the heat of fusion of phase-separated PE, as obtained after cooling the plaques in the oven and after annealing the material in the DSC at 70 °C during 3 h. Heating scans were carried out at 10 °C/min under nitrogen. Dynamic mechanical analysis (DMA) was used to determine the glass transition temperature (T_g) of the acrylic polymer, defined as the onset temperature of the sharp decrease of the logarithm of the storage modulus. DSC could not be used to determine the whole set of T_g values due to the partial superposition of the glass transition temperature with the PE melting peak for some of the formulations. A Perkin-Elmer DMA-7 operating at 1 Hz in the three-point bending mode was used. The heating rate was 10 °C/min and dimensions of the specimens were: length = 20 mm (span = 15 mm), width = 3 mm, and thickness = 2 mm. Three samples of every formulation were analyzed.

Plaques obtained from formulations containing 15 wt.-% PE were successively extracted with methanol, 2-butanone and *o*-xylene in a Soxhlet device, to assess the possible presence of a gel fraction in the system devoid of BDDMA, or the presence of PE grafted to the polymer network in formulations with BDDMA. The gel fraction was dried under vacuum at 65 °C, ground, mixed with spectroscopic-grade KBr and analyzed by Fourier-transformed infrared spectroscopy (FTIR Nexus, Thermo Nicolet GmbH).

Results and Discussion

Phase Separation During the Isothermal Polymerization at 80 °C

The cloud-point temperature of solutions with 15 wt.-% PE in IBoMA, was 74.5 °C, meaning that at the selected polymerization temperature (80 °C), the initial solutions were homogeneous. The cloud-point time in the course of reaction at 80 °C was close to 12 min. At this time a liquid-liquid phase separation process occurred, leading to a dispersion of amorphous PE-rich droplets in the acrylic matrix.

Figure 2a shows a micrograph of this dispersion taken 2 min after the cloud-point. Figure 2b–d are micrographs taken between crossed polarizers at room temperature, after complete reaction at 80 °C, showing a fine dispersion of PE crystals in the acrylic matrix synthesized with 0, 5 and 10 wt.-% BDDMA, respectively. In every case, PE-rich domains were segregated at 80 °C during the polymerization reaction.

The cloud-point conversion for formulations devoid of BDDMA was estimated by making solutions of PE, IBoMA and PIBoMA (the linear polymer was obtained from the plaques obtained by polymerization of unmodified IBoMA), and determining cloud-point compositions at 80 °C. A similar approach was recently used to determine cloud-point conversions in PE/styrene solutions.[8] Conversions determined in this way were the same as those determined in situ in the course of polymerization.[8]

Figure 3 shows a portion of the cloud-point curve in the desired composition range. The dotted line represents the evolution of a sample containing 15 wt.-% PE. Phase separation begins at a conversion of about 0.77 (due to the fact that the molar mass distribution of PIBoMA obtained at 80 °C might be different than the one obtained using the thermal cycle employed for the plaques, the cloud-point curve should be regarded as an estimation of the true one). The cloud-point conversion should be lower when adding BDDMA to the initial formulation, reflecting the lower solubility of PE in a crosslinked network.

Characterization of the Plaques

Both SEM and DSC were employed to assess the presence of a dispersion of PE crystals in the acrylic matrix. Formulations containing 15 wt.-% PE and different amounts of BDDMA (0, 5 and 10 wt.-%), showed the presence of a fine dispersion of PE crystals in the acrylic matrix. However, formulations prepared with 5 wt.-% PE did not show any sign of phase separation, meaning that PE remained as a solution in the acrylic polymer.

Samples obtained from the plaques prepared with formulations containing 15 wt.-% PE, were successively extracted with methanol, 2-butanone and *o*-xylene. The formulation devoid of BDDMA was completely solubilized. The gel fraction remaining after the extraction

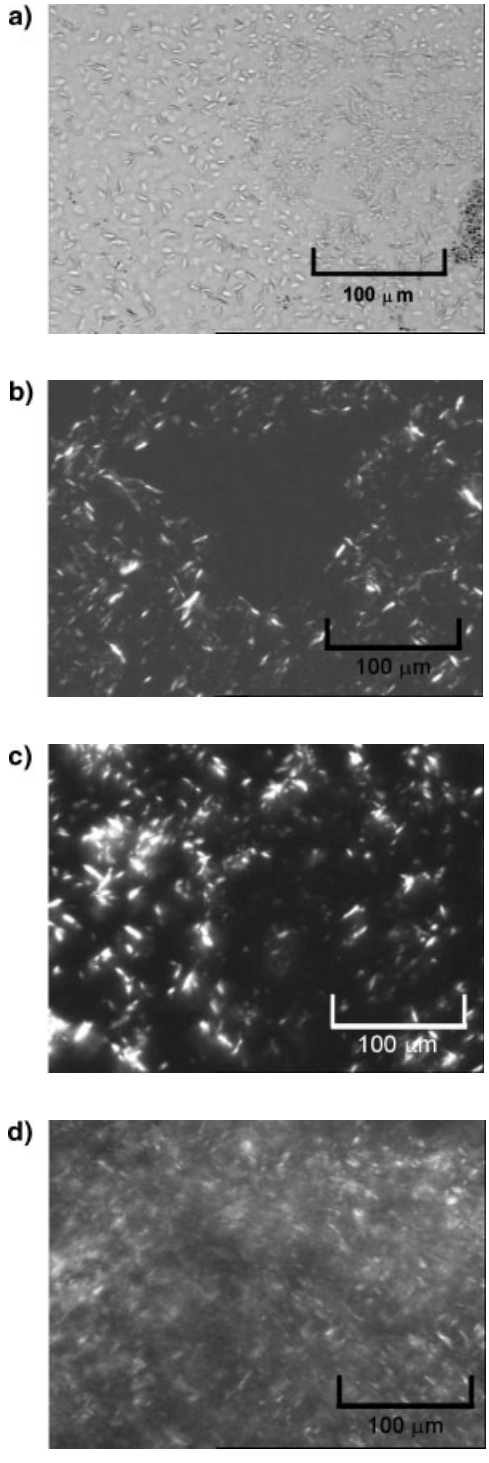

Figure 2. TOM micrographs showing a dispersion of PE domains in the acrylic matrix for formulations containing 15 wt.-% PE; (a): micrograph obtained at 80 °C without crossed polarizers, for a sample devoid of BDDMA, 2 min after the cloud point, (b) to (d): micrographs obtained at room temperature with crossed polarizers, after 30 min reaction at 80 °C and a cooling rate of 1 °C/min, for formulations containing 0, 5 and 10 wt.-% BDDMA, respectively. The bar indicates 100 μm.

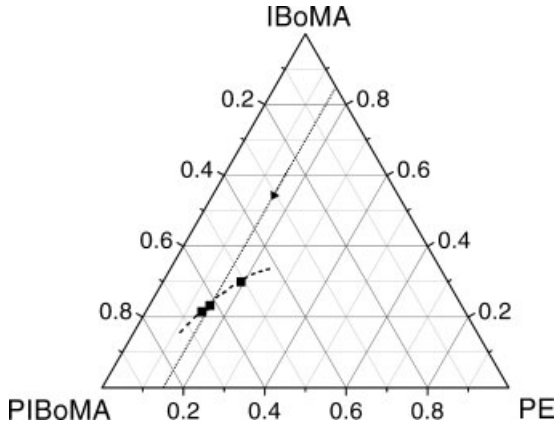

Figure 3. Part of the cloud-point curve in the region of interest, for IBoMa, PIBoMA and PE solutions at 80 °C.

process, in formulations containing 5 and 10 wt.-% BDDMA, was analyzed by FTIR. Characteristic PE-bands at 719 cm^{-1} and 729 cm^{-1},[22] were absent meaning that PE was not grafted to the polymer network, at least in a significant amount to be detectable by FTIR (chain transfer reactions could have been responsible for such a grafting). Therefore, the PE fraction remaining dissolved in the acrylic polymer after phase separation could be extracted with appropriate solvents.

As an example, Figure 4 illustrates the fine dispersion of PE crystals observed in a SEM micrograph for a formulation containing 15 wt.-% PE and 10 wt.-% BDDMA.

Table 1 shows the glass transition temperatures of the acrylic polymer in the final blend, as determined by DMA. For those formulations where T_g values could also be determined by DSC, it was verified that values reported in Table 1 were very close to the onset values measured by DSC.

The T_g values of the acrylic polymer increased with the amount of BDDMA as expected, and decreased with the addition of PE due to its incomplete segregation from the matrix. The decrease of T_g produced by the dissolved PE in samples containing 5 wt.-% PE, may be compared with the

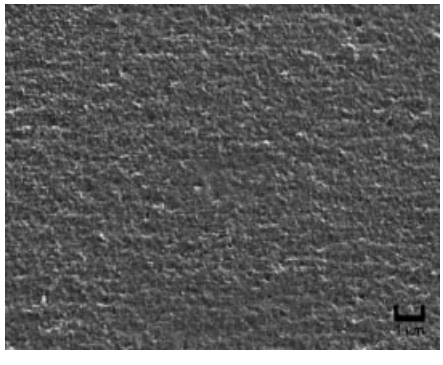

Figure 4. SEM micrograph of a sample containing 15 wt.-% PE and 10 wt.-% BDDMA. The bar indicates 1 μm.

Table 1. Glass transition temperatures (T_g) of the acrylic polymer in the final blend and estimations of the fraction of phase separated PE (f) and its crystallinity (C).

PE	BDDMA	T_g	f	C
wt.-%	wt.-%	K	%	%
0	0	394	–	–
5	0	368	–	–
15	0	352	57	42
0	5	405	–	–
5	5	373	–	–
15	5	362	59	15
0	10	413	–	–
5	10	388	–	–
15	10	375	66	38

values predicted with the Fox equation:[23]

$$1/T_g = w_{PE}/T_{g,PE} + (1 - w_{PE})/T_{g,A} \quad (1)$$

where $w_{PE} = 0.05$ is the mass fraction of PE dissolved in the acrylic matrix, and $T_{g,PE}$ and $T_{g,A}$ are the glass transition temperatures of pure PE (taken equal to 153 K),[24–27] and of the acrylic polymer (taken from Table 1 at the particular BDDMA content), respectively.

Predicted values of T_g are: 365, 374 and 381 K (for BDDMA = 0, 5 and 10 wt.-%), compared with experimental values of 368, 373 and 388 K, reported in Table 1. The Fox equation provides a reasonable estimation of the plasticizing effect of PE, except for the more crosslinked acrylic network where deviations are significant.

Formulations containing 15 wt.-% PE exhibited lower glass transition temperatures than samples obtained with 5 wt.-% PE (Table 1). This means that the mass fraction of PE dissolved in the acrylic polymer was higher than 5 wt.-%, a fact that provides an indirect proof of the absence of phase separation in samples containing 5 wt.-% PE. Using the experimental T_g values for samples containing 15 wt.-% PE, the Fox equation may be used to determine the residual mass fraction of PE dissolved in the acrylic polymer, w_{PE}. The fraction of phase-separated PE is then given by:

$$f(\%) = 100 \cdot (1 - w_{PE}\ 85/15) \quad (2)$$

These fractions are indicated in Table 1 for the different formulations containing 15 wt.-% PE. A slight increase from $f = 57\%$ to $f = 66\%$ results by increasing the crosslinker content from 0 to 10 wt.-%. This slight increase may simply reflect the lack of accuracy of the Fox equation to describe the more crosslinked acrylic network. In any case, the increase in crosslinking density does not seem to be a significant driving force for the segregation of PE from the acrylic matrix.

The crystallinity of the phase-separated PE fraction was determined by DSC. Figure 5 shows DSC thermograms for

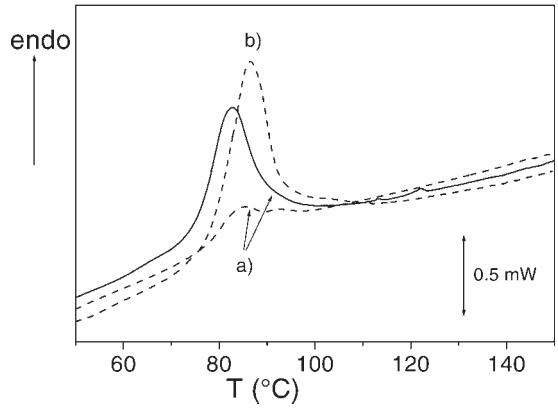

Figure 5. DSC thermograms for a formulation containing 15 wt.-% PE and no BDDMA. Curve a) (full line) corresponds to the 1st run performed for the material obtained directly from the plaque; curve a) (dashed line) represents the 2nd run carried out after cooling from 180 °C to 40 °C, at 15 °C/min; curve b) corresponds to a 2nd run performed after cooling from 180 °C to 70 °C, at 15 °C/min, annealing at 70 °C during 3 h, cooling and rescanning.

a formulation containing 15 wt.-% PE and no BDDMA. The 1st run corresponds to the material obtained directly from the plaque after the slow overnight cooling in the oven. Using the experimental value of the heat of fusion, the value reported for a PE crystal (293 J/g),[20] and the estimated fraction of phase-separated PE (*f*), leads to a 42% crystallinity, as reported in Table 1. The amount of crystalline PE decreased significantly after a fast cooling from 180 °C. However, annealing the material during 3 h at 70 °C enabled to recuperate the initial crystallinity. A small shift of the melting peak to higher temperatures was also observed.

Figure 6 and 7 show DSC thermograms for materials obtained with 5 and 10 wt.-% BDDMA, respectively. In spite of the fast cooling rate, the crystallinity of the sample was the same in both runs, within experimental error. An-

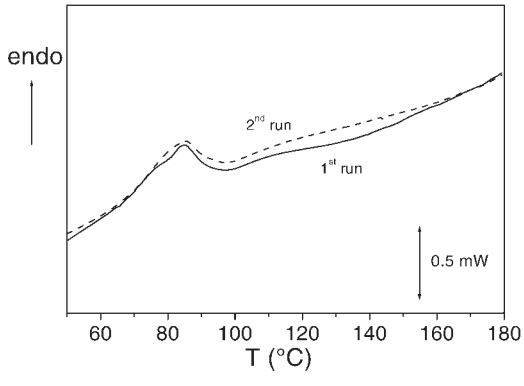

Figure 6. DSC thermograms for a formulation containing 15 wt.-% PE and 5 wt.-% BDDMA. 1st run: material obtained directly from the plaque; the 2nd run was performed after cooling from 180 °C to 40 °C, at 15 °C/min.

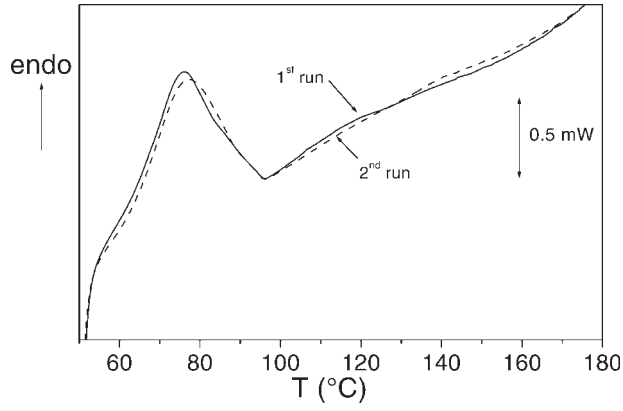

Figure 7. DSC thermograms for a formulation containing 15 wt.-% PE and 15 wt.-% BDDMA. 1st run: material obtained directly from the plaque; the 2nd run was performed after cooling from 180 °C to 40 °C, at 15 °C/min.

nealing at 70 °C did not produce any change in the crystallinity values of the original samples, reported in Table 1. Therefore, crosslinking the acrylic matrix enabled to keep the crystallinity of PE domains independently of the cooling rate.

The low crystalline fraction obtained for blends with 5 wt.-% BDDMA, as compared with formulations devoid of BDDMA or containing 10 wt.-% BDDMA, is an unexpected finding. A better characterization of morphologies would be necessary to try to explain this experimental observation.

Conclusions

IBoMA was used as a convenient reactive solvent of PE due to its low vapor pressure and the high glass transition temperature of the acrylic networks derived from it. Phase separation took place in the course of polymerization generating a dispersion of PE domains in the acrylic matrix. The crystallinity of these domains at room temperature varied with the amount of crosslinker used in the initial formulation. The use of a crosslinker enabled to keep a constant crystallinity value, independent of the cooling rate.

Although morphologies generated in this study consisted of a dispersion of PE-rich domains in an acrylic matrix, an increase in either the PE molar mass or its amount in the initial formulation would lead to phase-inverted morphologies. In this case, the aim of dissolving the PE in acrylic monomers is to facilitate its processing.

Acknowledgement: The financial support of the *University of Mar del Plata, CONICET* and *ANPCyT* (Argentina), is gratefully acknowledged. *M. Schnell* acknowledges the financial aid of *DAAD* (Germany) for his stages in *INTEMA*. The *Max-Planck-Institut für Polymerforschung*, Mainz (Germany), is gratefully acknowledged for performing SEM measurements.

[1] J. P. Pascault, R. J. J. Williams, in: "*Polymer Blends Vol. 1: Formulation*", D. R. Paul, C. B. Bucknall, Eds., Wiley, New York 2000, pp. 379–415.
[2] R. W. Venderbosch, H. E. H. Meijer, P. J. Lemstra, *Makromol. Chem., Makromol. Symp.* **1993**, *75*, 73.
[3] E. Borsig, J. Hrouz, A. Fiedlerovà, M. Ilavský, *J. Macromol. Sci., Chem.* **1990**, *A27*, 1613.
[4] E. Borsig, A. Fiedlerovà, K. G. Haüsler, R. M. Sambatra, G. H. Michler, *Polymer* **1993**, *34*, 4787.
[5] R. Greco, M. F. Astarita, A. Fiedlerovà, E. Borsig, *Adv. Polym. Technol.* **1994**, *13*, 65.
[6] E. Borsig, A. Fiedlerovà, K. G. Hausler, G. H. Michler, R. Greco, *Macromol. Symp.* **1994**, *83*, 147.
[7] J. G. P. Goosens, S. Rastogi, H. E. H. Meijer, P. J. Lemstra, *Polymer* **1998**, *39*, 6577.
[8] A. Liskova, H. Berghmans, *J. Appl. Polym. Sci.* **2004**, *91*, 2234.
[9] M. Lazár, L. Hrcková, U. Schulze, J. Pionteck, E. Borsig, *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 261.
[10] J. Hu, U. Schulze, J. Pionteck, E. Borsig, *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 1285.
[11] R. Greco, A. Fiedlerovà, U. Schulze, E. Borsig, *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32*, 1957.
[12] E. Borsig, R. Thomann, A. Fiedlerovà, R. Mülhaupt, *J. Appl. Polym. Sci.* **2001**, *81*, 2615.
[13] U. Schulze, G. Pompe, W. Meyer, A. Janke, J. Pionteck, A. Fiedlerovà, E. Borsig, *Polymer* **1995**, *36*, 3393.
[14] U. Schulze, A. Fiedlerovà, G. Pompe, E. Meyer, A. Janke, J. Pionteck, E. Borsig, *Polymer* **1998**, *39*, 1289.
[15] J. Hu, U. Schulze, J. Pionteck, *Polymer* **1999**, *40*, 5279.
[16] A. Matsumoto, K. Mizuta, T. Otsu, *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2531.
[17] M. Schnell, Ph.D. thesis, Johannes Gutenberg-Universität, Mainz, Germany, 2003.
[18] E. R. Soulé, J. Borrajo, R. J. J. Williams, *Macromolecules* **2004**, *37*, 1551.
[19] R. A. Hutchinson, S. Beuermann, D. A. Paquet, Jr., J. H. Mc Minn, C. Jackson, *Macromolecules* **1998**, *31*, 1542.
[20] B. Wunderlich, C. M. Cormier, *J. Polym. Sci., Part B: Polym. Phys.* **1967**, *5*, 987.
[21] C. Krause, Ph.D. thesis, Johannes Gutenberg-Universität, Mainz, Germany, 1996.
[22] K. Tashiro, R. S. Stein, S. L. Hsu, *Macromolecules* **1992**, *25*, 1801.
[23] T. G. Fox, *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
[24] D. E. Kline, J. A. Sauer, A. E. Woodward, *J. Polym. Sci.* **1956**, *22*, 455.
[25] F. P. Reding, J. A. Faucher, R. D. Whitman, *J. Polym. Sci.* **1962**, *57*, 483.
[26] F. C. Stehling, L. Mandelkern, *Macromolecules* **1970**, *3*, 242.
[27] Y. T. Shieh, C. M. Liu, *J. Appl. Polym. Sci.* **2001**, *82*, 3591.

