

# Block-graft copolymers on the basis of a styrene–butadiene diblock copolymer

M. Fischer\* and G. P. Hellmann†

Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, D-64289 Darmstadt, Germany

(Received 3 November 1995; revised 23 January 1996)

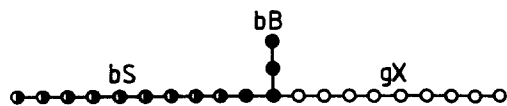
Grafting from the diblock copolymers  $\alpha b\beta$  leads to block-graft copolymers of the form  $\alpha b\beta g\gamma$ , the chemistry and architecture of which can be varied over wide limits. A family of compatibilizers for polymer blends can be prepared from one anionically produced and thus expensive copolymer, by a radically initiated grafting process, which is a comparatively cheap method. When  $\alpha b\beta$  is asymmetric, with the block  $b\beta$  carrying the graft  $g\gamma$  being short, the resulting copolymer  $\alpha b\beta g\gamma$  is essentially a diblock copolymer  $\alpha b\gamma$ . The preparation of the block-graft copolymers  $SbBgX$ , where X is methyl methacrylate (MMA) or cyclohexyl methacrylate (CHMA) is discussed. These are based on a diblock copolymer  $SbB$  of styrene and butadiene and are grafted with MMA or CMMA. These copolymers compatibilize blends of polystyrene (PS) (or poly(phenylene ether) and poly(vinyl chloride) (PVC) (or styrene–acrylonitrile (SAN) copolymer). Attention is focused on the reaction kinetics as monitored by conventional methods and by transmission electron microscopy. The microscopic analysis shows the ongoing progress of the grafting reaction as well as the mutual miscibility of all polymers in the system. Copyright © 1996 Elsevier Science Ltd.

(Keywords: block-graft copolymer; SB copolymer; compatibilizer)

## INTRODUCTION

Appropriately designed block copolymers<sup>1</sup> are efficient compatibilizers for polymer blends<sup>2,3</sup>. However, the copolymer chains must be adjusted carefully for each new blend, and this causes synthetic problems. The block copolymers that come to mind first are made by anionic copolymerization, with this technique yielding the best defined products. In particular, terblock copolymers have proven to be efficient as compatibilizers<sup>4,5</sup>. However, anionic copolymerization will probably not be a route to compatibilizers of general applicability, since the technique is expensive and confined to only a few monomers.

An alternative method is grafting from block copolymers<sup>6</sup>. Of particular interest are the diblock copolymers  $SbB$  of styrene and butadiene, grafted radically with vinyl monomer branches X:



Many different *block-graft* copolymers  $SbBgX$  can be made from one  $SbB$  that is anionically produced and commercially available. The grafts X are attached to the butadiene block  $bB$ . If this block is short and the graft long, the block-graft copolymer  $SbBgX$  is basically a diblock copolymer of the form  $SbX$ <sup>7,8</sup>.

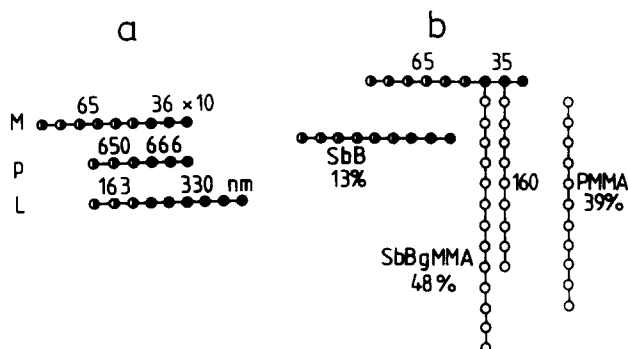
In this present report, the synthesis, the morphology and the behaviour in blends of  $SbBgX$  block-graft copolymers with methacrylate grafts, i.e. X is methyl methacrylate (MMA) or cyclohexyl methacrylate (CHMA) are discussed. Attention is focused on  $SbBgMMA$ , the synthesis of which was monitored with transmission electron microscopy (TEM). This copolymer is particularly interesting because the three blocks, i.e.  $bS$ ,  $bB$  and  $gMMA$ , are mutually incompatible. Since three polymers co-exist during the grafting process, i.e.  $SbB$ , the homopolymer PMMA and the block-graft copolymer  $SbBgMMA$ , the system is morphologically very complex.

## EXPERIMENTAL

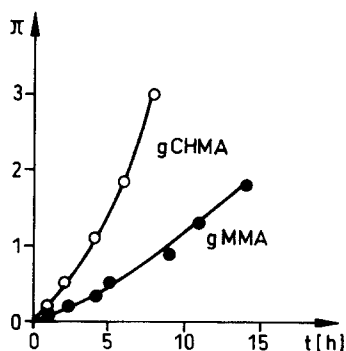
The poly(styrene-*b*-butadiene)  $SbB$  was prepared anionically for this project by BASF AG. It is monodisperse with an overall molecular weight of  $M_w = 101 \times 10^3$  ( $M_w/M_n = 1.08$ ) and a molecular weight for the styrene block of  $M_w = 65 \times 10^3$  ( $M_w/M_n = 1.04$ ). The transition between the blocks  $bS$  and  $bB$  is tapered.  $SbB$  is shown in Figure 1a, in order to point out an ambiguity of representation: the block  $bS$  is twice as long as the block  $bB$ , when based on the molecular weight. However, blocks are equal, when based on the degree of polymerization, while the block  $bB$  is found to be twice as long as the block  $bS$  when based on the number of carbon atoms in the polymer backbone. The schematic formulae used in this paper are based on the molecular weight. Details of the grafting reactions are described in the next section. The conversion of the monomers MMA and CHMA was measured gravimetrically and by Fourier transform infrared (FTi.r.) spectroscopy. Samples were taken from the

\* Present address: BASF AG, D-67056 Ludwigshafen, Germany

† To whom correspondence should be addressed



**Figure 1** Schematic formulae: (a) the diblock copolymer *SbbB* (half circles for *bS*, full circles for *bB*), based on the molecular weight (*M*), the degree of polymerization (*p*) and the contour length (*L*); (b) the *SbbB*/PMMA/*SbbgMMA* blend produced by grafting from *SbbB*, based on wt% of the components and, for the block-graft copolymer *SbbgMMA* (open circles for *gMMA* and *PMMA*), the average molecular weights ( $\times 10^{-3}$ )



**Figure 2** Monomer conversion  $\pi$  (equation (1)) of the MMA and CHMA grafting as a function of time

polymerization system and then dried, at gradually increasing temperatures. The homopolymers, poly(methyl methacrylate) (PMMA) and poly(cyclohexyl methacrylate) (PCHMA), were extracted with acetone. Gel permeation chromatography (g.p.c.) was performed by using a PMMA calibration. For the transmission electron

microscopy (TEM) analysis, films (0.1  $\mu\text{m}$  thick) were cast from toluene, which is a non-selective solvent for this polymer system. Ultrathin sections were cut at room temperature, sometimes after fixation of the morphology at high temperatures (but not above the glass transition). The butadiene phases were stained with  $\text{OsO}_4$ . Mechanical relaxation spectroscopy was performed with a torsion pendulum, at 10 Hz.

**RESULTS AND DISCUSSION**

*Grafting with methyl methacrylate*

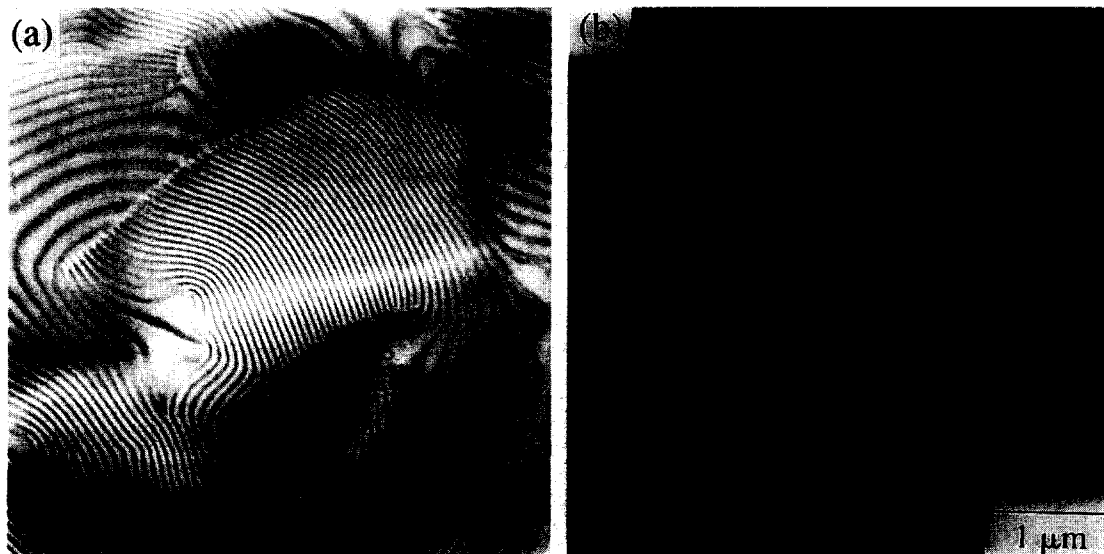
Grafting of *SbbB* with MMA, which leads to the block-graft copolymer poly(styrene-*b*-(butadiene-*g*-methyl methacrylate)), *SbbgMMA*, was investigated kinetically, first with conventional methods, i.e. gravimetry, FTi.r. spectroscopy, g.p.c. and extraction, and then with TEM.

The system *SbbB*/MMA was polymerized isothermally at 80°C in rapidly stirred toluene, at a concentration of 25% (wt/vol) (*SbbB* + MMA), which was a compromise: the reaction was quite fast, due to the low solvent content, but the system did not vitrify at high conversions, as it would have done in the bulk, without toluene. The concentrated solution demixed into two phases, at high MMA conversion<sup>5</sup>, and then the reaction continued heterogeneously. The MMA conversion shown in *Figure 2* is defined by the weight ratio, as follows:

$$\pi(t) = R - m_{\text{MMA}}(t)/m_{\text{SbbB}}(t = 0)$$

$$R = (m_{\text{MMA}}/m_{\text{SbbB}})(t = 0)$$

The initial ratio (*R*) of MMA to *SbbB* was 3, which seems unusually low. However, this amounts to the fairly common weight ratio of MMA to *bB* of 9, and only the butadiene block *bB* counts for the grafting. The curve in *Figure 2* is curved upwards, probably due to the increasing viscosity in the system (the kinetics of grafting in demixed systems of this type are discussed in detail in ref. 8). The reaction was stopped at  $\pi = 1.8$ , where more than half of the MMA was polymerized (total conversion corresponding to  $\pi_{\infty} = 3$ ).



**Figure 3** Electron micrographs of (a) the *SbbB* diblock copolymer and (b) the *in situ SbbB*/PMMA/*SbbgMMA* blend at a very low conversion ( $\pi = 0.2$ ): black, *bB*; grey, *bS*; white, *gMMA* and PMMA

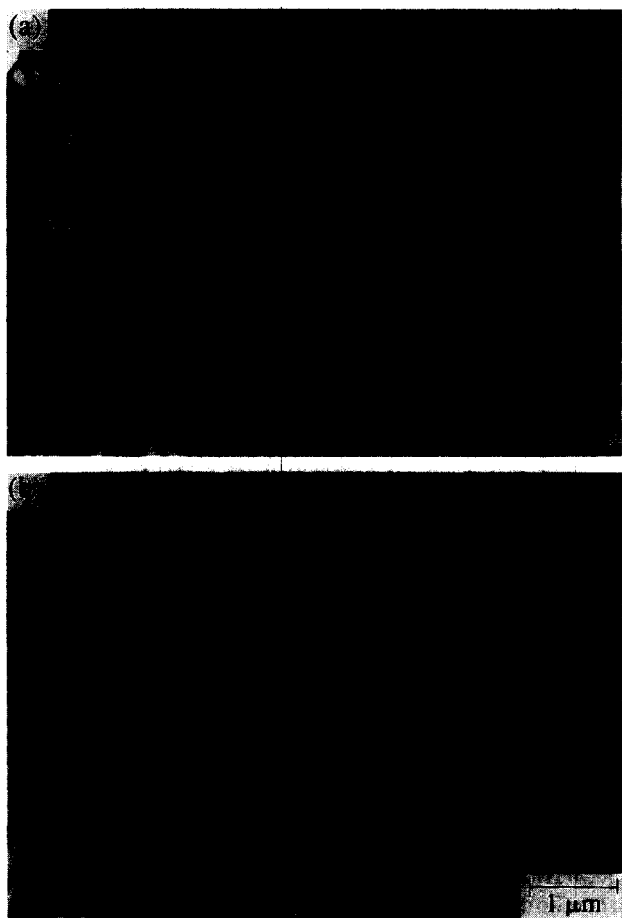


Figure 4 *In situ* blend morphologies at low conversions: (a)  $\pi = 0.3$ ; (b)  $\pi = 0.5$

Dibenzoylperoxide was used as an initiator, at the low concentration of  $1 \text{ mmol mol}^{-1}$  (MMA) which yielded long homopolymer chains of PMMA and gMMA grafts with a molecular weight  $M_w = 160 \times 10^3$  ( $M_w/M_n = 2.1$ ), as measured by g.p.c. after extraction of the PMMA with acetone.

Radical grafting always leads to complex *in situ* blends that consist, besides the graft copolymer, of the yet ungrafted backbone polymer and the homopolymer corresponding to the grafts, in this case S**b**B and PMMA. The homopolymer is an undesired by-product. However, methacrylates graft readily. The fraction  $f_{\text{PMMA}}$  of the homopolymer PMMA was, constantly at all values of  $\pi$ , accordingly found to be fairly low:

$$f_{\text{PMMA}} = m_{\text{PMMA}}(\pi) / (m_{\text{MMA}}(\pi = 0) - m_{\text{MMA}}(\pi)) \cong 0.6 \quad (2)$$

The ungrafted S**b**B could not be extracted, so that the 'pure' block-graft copolymers obtained after removing the PMMA were, in fact, S**b**B/S**b**BgMMA blends.

The fraction of the ungrafted S**b**B could therefore not be determined, but it can, however, be calculated. It is given by the following expression:

$$f_{\text{SbB}} = m_{\text{SbB}}(\pi) / m_{\text{SbB}}(\pi = 0) = (1 - g/p)^p \quad (3)$$

where  $g$  is the number of grafts per S**b**B chain:

$$g = (1 - f_{\text{PMMA}})\pi(M_{\text{SbB}}/M_{\text{PMMA}}) \quad (4)$$

and  $p = 666$ , the degree of polymerization of the *b*B block. The probability of one butadiene unit being grafted is  $g/p$ . With increasing  $\pi$ ,  $g$  grew linearly (equation (4)), and the final values at  $\pi = 1.8$  were  $g = 1.0$  and  $f_{\text{SbB}} = 0.37$ .

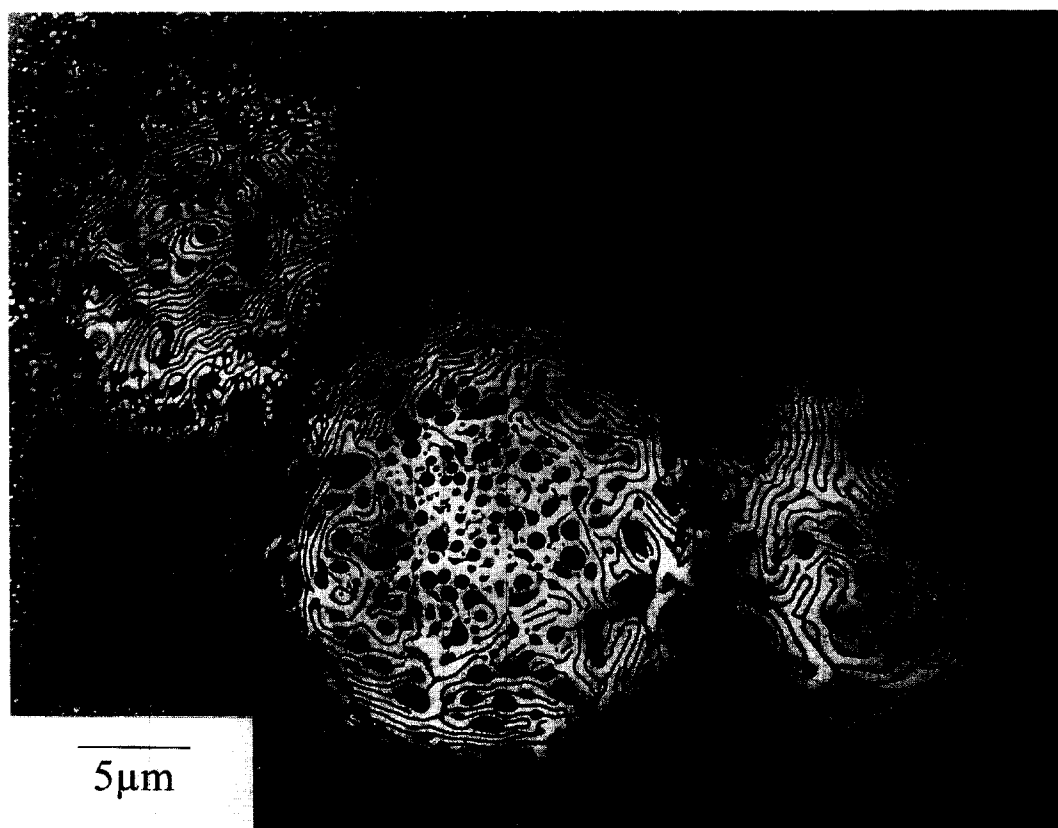


Figure 5 The blend of Figure 4b, shown at a lower magnification

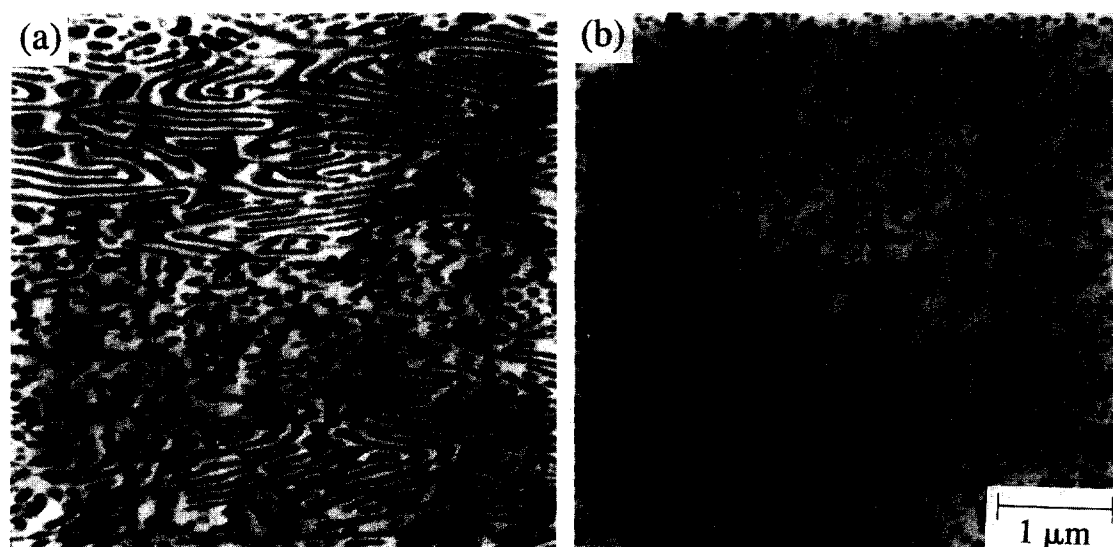


Figure 6 *In situ* blend of morphologies at high conversions: (a)  $\pi = 1.3$ ; (b)  $\pi = 1.8$

The number of grafts  $g$  is averaged over the  $SbB/SbBgMMA$  blend. If the ungrafted  $SbB$  is excluded, the number of grafts on the pure block-graft copolymer  $SbBgMMA$  is, at  $\pi = 1.8$  given by the following:

$$G = g/(1 - f_{SbB}) = 1.6 \quad (5)$$

(Note that  $g$ ,  $p$  and the molecular weights  $M_{SbB}$ ,  $M_{PMMA}$  are number average values.)

In conclusion, the block-graft copolymer  $SbBgMMA$  consists of a styrene block ( $M_n = 63 \times 10^3$ ), a butadiene block ( $M_n = 34 \times 10^3$ ) and one or two methyl methacrylate grafts ( $M_n = 76 \times 10^3$ ).

In summary, the final raw product of the grafting process, at  $\pi = 1.8$ , should have the composition shown in Figure 1b. About one half of the copolymer  $SbBgMMA$  contains  $gbB$  and  $gMMA$  in similar fractions. There is again an ambiguity here, because the  $gMMA$  grafts and the  $PMMA$  homopolymer are polydisperse. The  $gMMA$  graft appears very long because the figure is based on  $M_w$ , while equations (3) and (5) are based on  $M_n$ .

The kinetics of the grafting reaction were monitored by TEM. Samples were taken during the polymerization, at the MMA conversions  $\pi$  in Figure 2, and converted into cast films. Since toluene is a non-selective solvent, Figures 3–9 can be assumed to show thermodynamically favoured morphologies.

The block copolymer  $SbB$  has a lamellar microstructure (Figure 3a), in which macrodomains of the  $PMMA$  homopolymer appear, at low  $\pi$  values (Figure 3b). At slightly higher  $\pi$  values, the domains develop a complex internal structure (Figure 4). The magnification is the same in all of the pictures shown in Figures 3 and 4. The intermediate stage at  $\pi = 0.5$  is not well represented by Figure 4b. The structure shown is part of a large macrophase that is seen completely in Figure 5, together with neighbouring domains, at a lower magnification. This domain structure gives way, at high  $\pi$  values, to a lamellar and finally micellar microstructure (Figure 6) in a matrix of  $PMMA$ .

It is easy to interpret Figures 3–5. Obviously, the black-and-white pattern of the stripes indicates the  $SbB$  phase and the featureless white domains indicate the

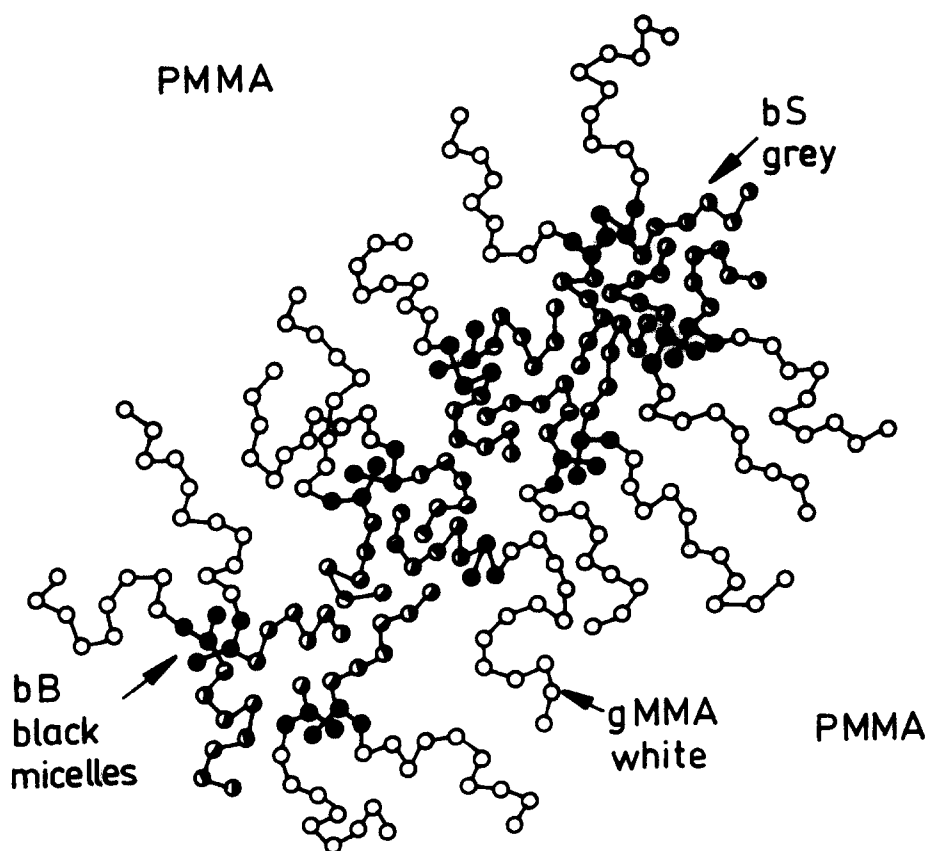
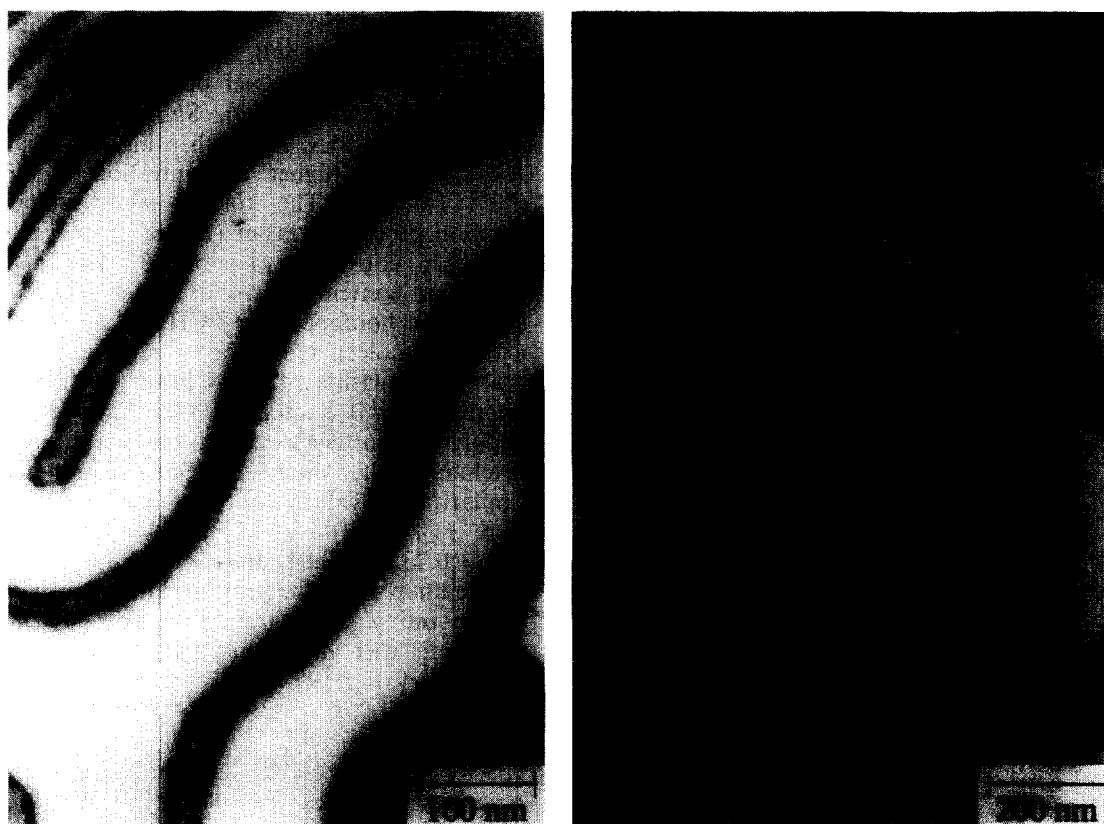
$PMMA$  phase. Less obvious is that the lamellae ‘floating’ inside the  $PMMA$  domains are made of the block-graft copolymer  $SbBgMMA$ . This is revealed by the magnifications shown in Figure 7. The lamellae within the  $PMMA$  domains have dotted surfaces, with the black dots being the  $OsO_4$  stained  $bB$  blocks of the  $SbBgMMA$  chains. The reason for the dots is indicated in the schematic picture: the long  $bS$  blocks form the (grey) continuous monolayer on the inside of the lamellae while the  $gMMA$  grafts (also long) merge, invisibly, on the surface with the (white)  $PMMA$  phase. Between the two monolayers, the  $bB$  blocks should form an intermediate (black) layer. However, the  $bB$  blocks are simply too short to fill a coherent layer, and are forced to form an arrangement of micelles, i.e. of black dots.

No dotted lamellae are found inside the  $SbB$  phase. The  $SbBgMMA$  copolymer prefers evidently the  $PMMA$  phase. However, it is also a compatibilizer for the system  $SbB/PMMA$ : wherever the  $SbB$  and  $PMMA$  phases touch, the interface is covered by a dotted lamella of the block-graft copolymer, as is also shown in Figure 7.

The lamellae and micelles in Figure 6, at high  $\pi$  values, are composed predominantly of  $SbBgMMA$ . Inclusions of ungrafted  $SbB$  that are still frequent at intermediate  $\pi$  values (Figure 8) are easy to spot. The micellar structure of the final product at  $\pi = 1.8$  (Figure 6b) does not now seem to contain  $SbB$ . However, TEM is not quantitative. The small share of 13 wt% of ungrafted  $SbB$  indicated in Figure 1b may well be hidden in some of the micelles in Figure 6b.

In any case, the final product can, after extraction of the  $PMMA$ , be considered an almost pure  $SbBgMMA$  block-graft copolymer with one or two grafts per chain. It features the co-continuous microstructure shown in Figure 9a. The white lamellae are the  $gMMA$  grafts, while the small white domains are unextracted  $PMMA$ . The backbones  $SbB$  of the copolymer appear black-grey, but are not well separated.

Surprisingly, the small butadiene block  $bB$  shows up clearly in the mechanical relaxation spectrum of  $SbBgMMA$ . There are two maxima (Figure 10), with the upper, at  $110^\circ\text{C}$ , for the  $bS$  blocks and  $gMMA$  grafts, and the lower, at  $-80^\circ\text{C}$  for the  $bB$  blocks.



**Figure 7** High magnifications of the blend of *Figure 4a*, showing lamellae of the *SbBgMMA* block-graft copolymer, internally grey (*bS* blocks) with black dots on the surface (*bB* blocks, see schematic picture). On the right, two domains of *SbB* are seen which are also covered by a surface lamella of *SbBgMMA*

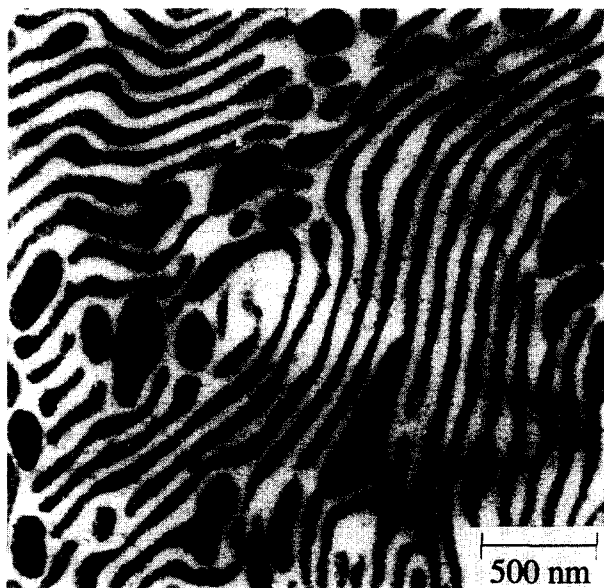


Figure 8 *In situ* blend morphology at an intermediate conversion ( $\pi = 0.9$ ), showing residual minidomains of *SbB* in a lamellar structure of *SbBgMMA*

Grafting with cyclohexyl methacrylate

The grafting of *SbB* with CHMA, which leads to the block-graft copolymer poly(styrene-*b*-(butadiene-*g*-cyclohexyl methacrylate)), *SbBgCHMA*, was carried out as with MMA, but with a higher initial ratio, i.e.  $R = 5$ , and a higher concentration of *SbB*/CHMA (30% (wt/vol)). The kinetics were similar, but the reaction proceeded faster (Figure 2). It was stopped at a higher conversion i.e.  $\pi = 3$ . The higher initial monomer content led to a higher  $f_{PCHMA}$  (equation (2)) of the homopolymer PCHMA, but the grafts had a similar molecular weight value  $M_w$ . The number of grafts  $g$  (equation (4)) was lower and the fraction of ungrafted *SbB* (equation (3)) higher than in the copolymer *SbBgMMA*, but the number of grafts  $G$  (excluding the ungrafted *SbB*, equation (5)) was similar. The values for the final product at  $\pi = 3$  were  $f_{PCHMA} = 0.72$ ,  $M_w = 210 \times 10^3$  ( $M_w/M_n = 2.1$ ),  $f_{SbB} = 0.43$ ,  $g = 0.84$ , and  $G = 1.5$ .

The analysis of the grafting kinetics using TEM was disappointing. Since the *bS* blocks and the *gCHMA* grafts mix with each other and with the homopolymer



Figure 9 Extracted block-graft copolymers: (a) *SbBgMMA*; (b) *SbBgCHMA*

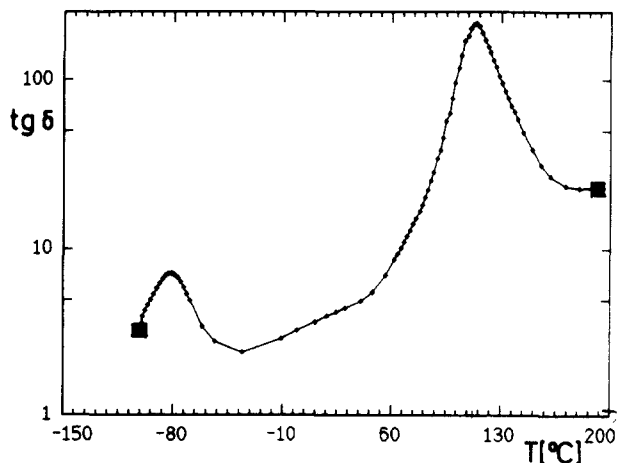


Figure 10 Mechanical relaxation spectrum of the extracted *SbBgMMA* copolymer, showing the glass transition of the *bB* blocks at low temperature and that of the *bS* blocks and the *gMMA* grafts at high temperature

PCHMA, there is no separation into three phases. The simple microstructure of the extracted final block-graft copolymer *SbBgCHMA* is shown in Figure 9b.

Blends

The block-graft copolymers *SbBgMMA* and *SbBgCHMA* proved to be excellent compatibilizers for blends, as discussed in ref. 7 for blends PVC/PS.

Relevant to the compatibilizer effect of these copolymers is Figure 11, which shows blend structure after annealing and, therefore, coarser than it was immediately after melt mixing. As expected from a good compatibilizer, the copolymer chains fill the interfaces in monolayers that are indicated by black dots. It is remarkable that Figure 11 shows the blend with *SbBgCHMA*. This copolymer as such did not yield interesting morphologies, because *bS* and *gCHMA* are miscible. However, in the interfaces of the PVC/PS blend, *bS* and *gCHMA* are separated, with the *bS* blocks



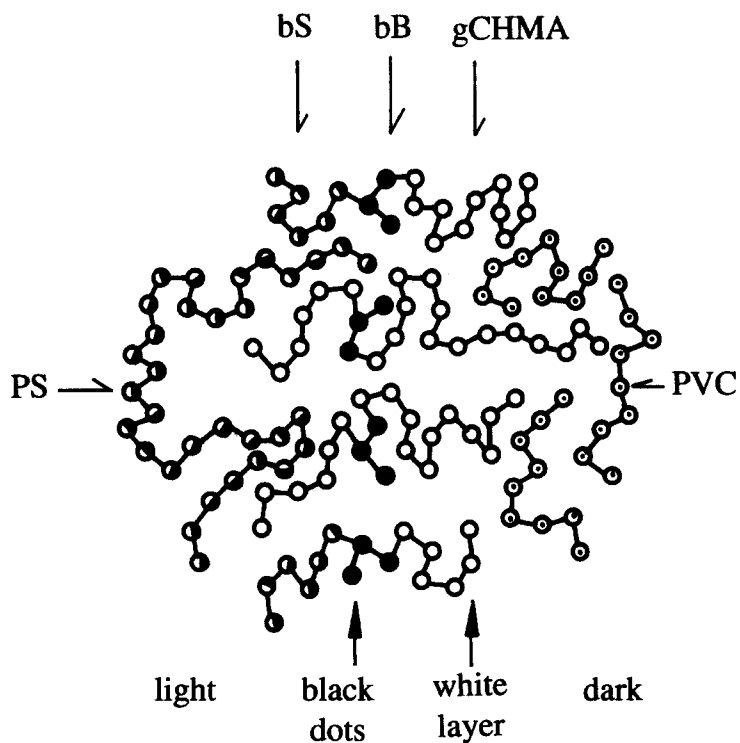
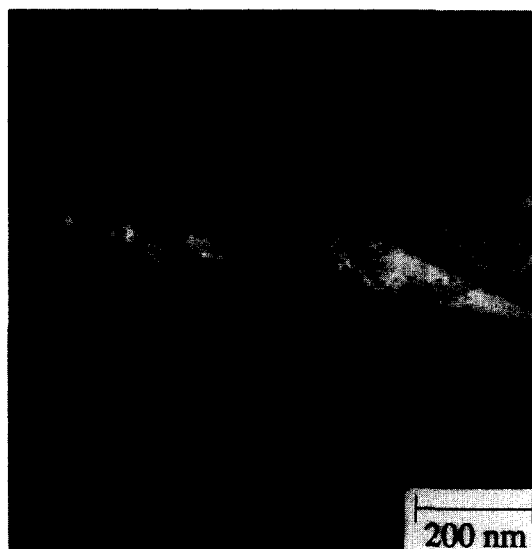
**Figure 11** Blend of PVC/PS(1:1), containing 20 wt% of the block-graft copolymer *SbBgCHMA*, after melt mixing followed by annealing at 190°C for 1 h: white, PVC; grey, PS; black dots (in the interfaces), copolymer

pointing into the PS and the gCHMA-grafts pointing into the PVC phase. The entire block-graft chains are not actually seen in *Figure 11*, but only the stained *bB* blocks, as in *Figure 7*. This is indicated schematically in *Figure 12*.

The electron micrograph shown in *Figure 12* reveals an interesting detail that was not easy to produce. In most pictures of the compatibilized blends, the block-graft copolymer chains could be identified in the blends only because the *bB* blocks were black. However, the gCHMA grafts would be visible as well, being chemically different from the PVC phase which they penetrate. Usually, however, the methacrylates and PVC were degraded so heavily by the electron beam that both appeared white. However, very short electron irradiation left the PVC phase fairly dark. This made the gMMA grafts visible in *Figure 12*, appearing as a white layer in the interfaces between the black dots of the *bB* blocks and the grey phases of PVC.

#### ACKNOWLEDGEMENTS

Financial support from the Bundesminister für Wirtschaft through the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AiF, Project No. 9511) is gratefully acknowledged. We thank Dr F. Gruber from BASF AG for the preparation of the *SbB* diblock copolymer.



**Figure 12** The blend of PVC/PS/*SbBgCHMA* of *Figure 11*, but after a very short electron beam irradiation time: dark, PVC; light, PS. The *SbBgCHMA* copolymer shows its *bB* blocks (black dots, as in *Figure 11*) and its gCHMA grafts as a monolayer between the dots and the dark PVC phase (see schematic picture)

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