# Effect of block copolymers on the interfacial tension between two 'immiscible' homopolymers

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The effect of block copolymers on the interfacial tension $\sigma$ was investigated for poly(ethylene oxide) (PEO)/poly(dimethylsiloxane) (PDMS) and for PDMS/polystyrene (PS). With PEO/PDMS the additives were the triblock copolymers PDMS-block-PEO-block-PDMS [P(DMS-EO-DMS)] and PEO-block-PDMS-block-PEO [P(EO-DMS-EO)]. For the former additive the number of monomeric units of the end blocks varied between 4 and 32 and that of the middle block between 23 and 77; these numbers are 70 and 52, respectively, for the latter. In the case of the system PS/PDMS, the diblock copolymer PS-block-PDMS [P(S-DMS)], consisting of 430 S and 68 DMS units, was studied. The effects turned out to be largest for the system PDMS/PEO/P(DMS-EO-DMS); it was therefore studied in greater detail within the temperature range of 70–150°C. Upon addition of increasing amounts of copolymer, $\sigma$ falls rapidly to $\sim 10\%$ of its initial value and levels off as the critical micelle concentration ($<0.5\,\mathrm{wt}\%$ in the PEO phase at 100°C) is surpassed. Similarly, at a given concentration of the additive, $\sigma$ approaches a limiting value as the number of monomeric units in the PDMS block is increased above 15. In contrast to the value of $\sigma$ of the pure blend, which is practically independent of temperature, that of the ternary system increases markedly with temperature. The results are compared with the predictions of Vilgis and Noolandi.

(Keywords: block copolymers; diblock copolymers; interfacial tension)

## INTRODUCTION

By the blending of chemically different polymers one can sometimes combine their characteristics to obtain new materials[1,2]. However, since most of the polymers are incompatible, the resulting high interfacial tension $\sigma$ and poor adhesion often lead to weak, brittle blends with small degrees of dispersion. Compatibilizers, such as block and graft copolymers, can alleviate these problems. Efforts were therefore made to study the compatibilizing activity of diblock copolymers[3–6]; also investigated were the surface tension of solutions of block copolymers in low molecular weight solvents and of polymer melts[7–11].

Patterson et al. have measured $\sigma$ by the spinning-drop method[12–14]. They added to poly(dimethylsiloxane) (PDMS) and poly(ethylene oxide)-block-poly(propylene oxide) [P(EO-PO)] 2% of various copolymers. The highest $\sigma$ reduction was obtained with a 60/40 PDMS-PEO diblock copolymer (namely from $\sigma = 8.3$ to $2.3\,\mathrm{mN\,m^{-1}}$). After having added 0.17 wt% block copolymer a sharp decrease, down to 55% of the original value, was observed. Riess et al. have studied the quaternary system poly(butadiene) (PB), polystyrene (PS), PS-block-PB [P(S-B)] and styrene[15–18]. The interfacial tension $\sigma$ was measured at 25°C by the spinning-drop method. In each sample 6.4 wt% of the homopolymer

were dissolved in styrene. In the presence of 2.6 wt% P(S-B) in the PB-rich phase, $\sigma$ decreased from $8.8 \times 10^{-2}$ to $2.8 \times 10^{-2}\,\mathrm{mN\,m^{-1}}$; upon the addition of 14.1 wt% P(S-B) it was halved again.

The subsystem PS/PB/P(S-B), in which the monomeric styrene is lacking, was investigated by Anastasiadis et al.[19] by the hanging-drop method at 145°C. The critical micelle concentration ($CMC$) of the block copolymer was found to be at $\sim 1.6\,\mathrm{wt}\%$.

Elemans et al.[20] have studied the following system at 20°C: PS ($M_n = 51.2\,\mathrm{kg\,mol^{-1}}$)/high density polyethylene (PE, $M_n = 30.3\,\mathrm{kg\,mol^{-1}}$)/PS-block-PE ($M_n^{PS} = 8.5$, $M_n^{PE} = 11.5\,\mathrm{kg\,mol^{-1}}$). By using the breaking thread method they obtained a $CMC$ of $\sim 0.75\,\mathrm{wt}\%$ of the block copolymer and a decrease of $\sigma$ from 5 to $1\,\mathrm{mN\,m^{-1}}$. The contact angle method resulted in a similar reduction, but a considerably lower $CMC$ ($\sim 0.2\,\mathrm{wt}\%$).

Current theories treat the effect of block copolymer addition for the following types of systems: Noolandi and Hong[21,22] have dealt with mixtures of homopolymers A and B, plus a block copolymer A-B and a solvent. Vilgis and Noolandi[23] have extended the theory to block copolymers of the type X-Y, i.e. to a situation where the blocks differ from each homopolymer. The theory of Leibler[24] was set up for systems A/B/A-B and A/B/A-B-A....B, i.e. multiblock copolymers made up of A and B.

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**Table 1** Characteristic data of the polymer samples

| | $M_n$ (kg mol$^{-1}$) | $M_w$ | $M_w/M_n$ | $P_n$ | Producer |
|---|---|---|---|---|---|
| **Homopolymers** | | | | | |
| PDMS 100 | 103 | 177 | 1.71 | 1350 | Wacker[a] |
| PEO 35 | 32 | 41 | 1.27 | 727 | Höchst[b] |
| PS 80 | 80 | 85 | 1.06 | 770 | PSS[c] |
| **Block copolymers[d]** | | | | | |
| P(DMS$_4$-EO$_{23}$-DMS$_4$) | P(DMS$_{16}$-EO$_{14}$-DMS$_{16}$) | P(DMS$_{23}$-EO$_{37}$-DMS$_{23}$) | | | |
| P(DMS$_4$-EO$_{37}$-DMS$_4$) | P(DMS$_{16}$-EO$_{37}$-DMS$_{16}$) | P(DMS$_{32}$-EO$_{37}$-DMS$_{32}$) | | | |
| P(DMS$_4$-EO$_{77}$-DMS$_4$) | P(DMS$_{32}$-EO$_{77}$-DMS$_{32}$) | | | | |
| P(EO$_{70}$-DMS$_{52}$-EO$_{70}$) | | | | | |
| P(S$_{430}$-DMS$_{68}$) | | | | | |

[a] Wacker GmbH, D-W 8000 Munich, Germany
[b] Höchst AG, D-W 6230 Frankfurt/Main 80, Germany
[c] PSS, D-W 6500 Mainz, Wöhlerstr. 2-6, Germany
[d] The subscripts indicate the number of monomeric units. All the block copolymers were synthesized in the Max-Planck-Institut für Polymerforschung, Mainz

## EXPERIMENTAL

### Materials

The characteristic data[25-28] of the polymer samples, are given in *Table 1*. The subscripts in the abbreviations for the block copolymers give their degree of polymerization.

The density of PDMS was measured in the temperature range from 70 to 150°C with 10 ml pycnometers and evaluated together with literature data[28,29]. The thermal expansion coefficient of glass was considered[30]. The density $\rho$ of PDMS can be expressed as:

$$\rho_{PDMS} = 997.13 - 0.870\vartheta \qquad (1)$$

if $\rho$ is given in kg m$^{-3}$ and the temperature $\vartheta$ in °C. The density of PEO was measured in the same manner. Because of its high viscosity, it was necessary to add a layer of n-dodecane (taken account of in the evaluation) in order to be able to read the meniscus properly. The data were again evaluated together with published values[29-31]. The density of PEO can be expressed as:

$$\rho_{PEO} = 1139.62 - 0.788\vartheta \qquad (2)$$

For PS the following equation[32] was used:

$$\rho_{PS} = 1086.5 - 0.619\vartheta + 1.36 \times 10^{-4}\vartheta^2 \qquad (3)$$

In all cases it was assumed that the addition of a small amount of copolymer to the homopolymer does not change its density, particularly since the copolymers contain the same blocks as the homopolymers.

### Interfacial tension measurements

The interfacial tensions were measured by means of a sessile drop apparatus which had been recently constructed. With this device, pictures of the drops are recorded using a CCD video camera. The dimensions of this phase are evaluated on a computer which also registers the actual temperature.

From the shape of the drop, the $\sigma$ between the two phases under observation is obtained according to the equation of Porter[33-35], which is applicable as long as $h/r < 0.5$:

$$\sigma = \Delta\rho g h^2 (0.5000 - 0.3047 h/r + 1.219 h^3/r^3) \qquad (4)$$

where $\Delta\rho$ is the density difference between the two coexisting phases, $r$ is half the maximum diameter of the drop, $h$ its height and $g$ the gravitational constant.

The block copolymers were exclusively added to the

denser component forming the drop, since they are only sparingly soluble in the matrix phase. Solutions of the additives were prepared by preblending the powders, or — like Gaines and Bender[9] — by freeze-drying the components from a common solution (here from benzene). The copolymer concentrations are given in terms of weight per cents of the copolymer blended into the drop. This procedure is analogous to that of Koberstein[14] and Elemans *et al.*[20] who have also added the copolymer to the drop or to the thread, respectively. Patterson *et al.*[12] proceeded somewhat differently, mixing the three components several days by rolling. The system was then allowed to stand until phase separation took place and the top and bottom clear phases were used for the measurements. However, this method cannot be applied with the present systems because of the high viscosity of the components.

Drops of appropriate size were obtained by melting weighed amounts of the material in aluminium foil under vacuum. Mixtures of PEO, PDMS and the block copolymers were investigated in the temperature range of 70–150°C in the presence of air. Measurements with the system PS/PDMS/P(S-DMS) were performed under nitrogen atmosphere from 150 to 220°C. The statement of Bajaj *et al.*[36] that PS and PDMS do not decompose under these conditions could be verified.

## RESULTS AND DISCUSSION

### PEO/PDMS

The interfacial tension $\sigma$ measured for this blend at 100°C is 10.6 mN m$^{-1}$; this value agrees well with that (10.2 mN m$^{-1}$) reported by Roe[29] for the same temperature, but somewhat different chain lengths of the components: PEO ($M = 6$ kg mol$^{-1}$) and PDMS (viscosity = 60 000 cSt). In spite of these differences the results should be comparable, since the molecular weight dependence of $\sigma$ frequently follows the empirical $M_n^{-2/3}$ law, like the surface tension[14,37] and often reaches its limiting values already for molecular weights on the order of 10 kg mol$^{-1}$. As shown in *Figure 1*, $\sigma$ turns out to be practically independent of temperature.

How $\sigma$ changes upon the addition of different amounts of block copolymers to the PEO phase of the blend is demonstrated in *Figure 2* at 100°C for the triblock copolymer P(DMS$_{32}$-EO$_{37}$-DMS$_{32}$). The data points
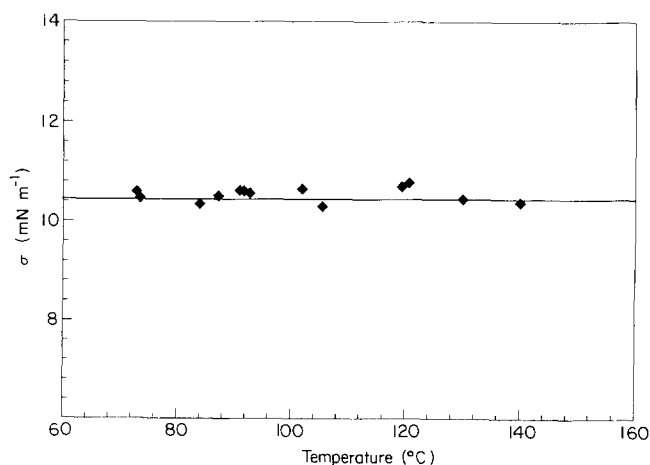


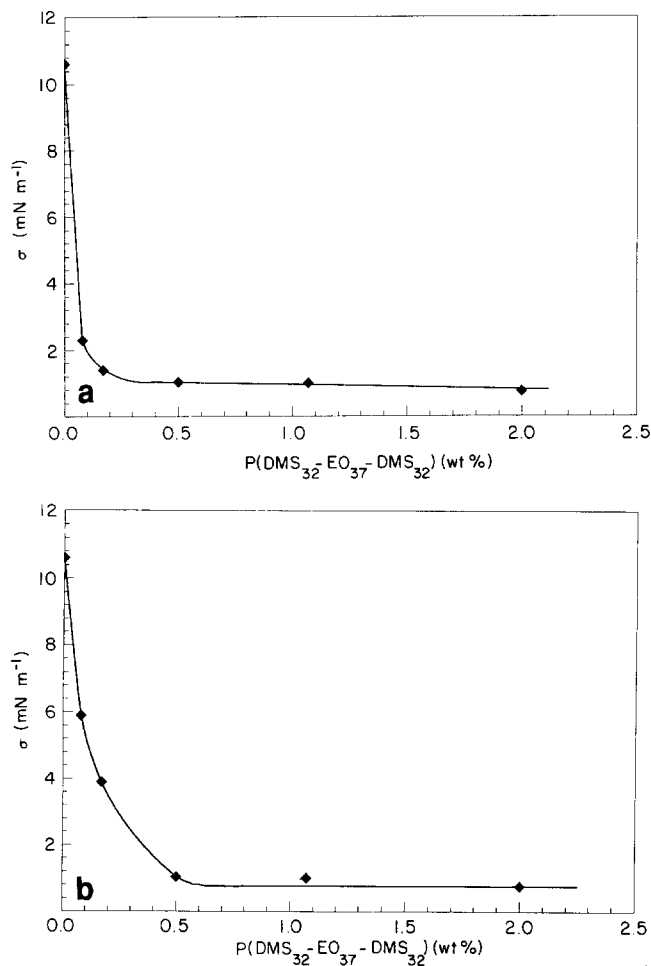**Figure 1** Temperature dependence of the interfacial tension $\sigma$ for the polymer blend PEO 35/PDMS 100 (in kg mol$^{-1}$)

**Figure 2** Interfacial tension $\sigma$ of the system PEO 35/PDMS 100/ P(DMS$_{32}$-EO$_{37}$-DMS$_{32}$) (in kg mol$^{-1}$) at 100°C, as a function of the concentration of the triblock copolymer P(DMS$_{32}$-EO$_{37}$-DMS$_{32}$) in the PEO-rich phase. (a) Values read for 100°C from the first series of measurements performed to determine $\sigma(T)$ for different constant starting concentrations of the additive in the PEO phase; (b) as in (a), but values taken from the third series of measurements with the same samples

were obtained in the following manner: for each composition of the PEO drop, $\sigma(T)$ was determined at intervals of $\sim 5$–10 K. After reaching temperature constancy (typically 1 h was required) at least 10 measurements (normally requiring $\sim 15$ min in total) were made for each temperature; since $\sigma$ does not vary systematically with time even below the *CMC*, the average values were plotted as a function of temperature, $\sigma$ read for 100°C and shown in *Figure 2* as a function of the concentration of the additive. *Figure 2a* gives the results for the first temperature sweep performed with a given droplet and *Figure 2b* for the third one.

The most obvious result of these measurements is the fact that $\sigma$ can only be reproduced in repetitive measurements (i.e. in different temperature sweeps) as long as the concentration of the additive in the droplet is $>0.5$ wt%; below that value $\sigma$ increases with each measuring series. This observation can be rationalized in the following way: in the course of these measurements the interface is depleted of the block copolymer due to its migration into the PDMS phase which initially does not contain this component; for low concentrations of the additive there exists no reservoir within the PEO phase to compensate for this loss. Only if the concentration of P(DMS$_{32}$-EO$_{37}$-DMS$_{32}$) in PEO

exceeds the *CMC* such a substitution of the lost material is possible and $\sigma$ becomes independent of time. According to the present data, the *CMC* should be $<0.5$ wt% at 100°C. In view of the situation described above, all data reported in the following for the different additives refer exclusively to concentrations well above the corresponding *CMC* in the phase that contains the copolymer. The $\sigma$ values, measured with 2 wt% of the different additives, are given in *Table 2*.

One interesting question concerning the interfacial activity of different block copolymers refers to the optimum number of monomeric units. For this reason it was investigated to what extent $\sigma$ is reduced at a given constant additive concentration in the PEO phase for different *m* values in the block copolymer P(DMS$_m$-EO$_n$-DMS$_m$) where *n* was chosen to be 37. The results for 2 wt% and 100°C are shown in *Figure 3*.

From *Figure 3* it can be concluded that the ability of the additive to reduce $\sigma$ only increases in the range of low *m* values, whereas it levels off as soon as *m* exceeds a certain critical number, which is $\sim 15$ in the present case. According to this result it is useless — in accordance with a corresponding statement in the literature[38] — to raise the number of monomeric units in the DMS end blocks beyond that value, at least for $n = 37$. It is also interesting to note that the dependence of $\sigma(m)$ can smoothly be extrapolated to the $\sigma$ of the binary system, if this value is taken for $m = 0$.

Another important aspect of the efficiency of additives consisting of block copolymers concerns possible

**Table 2** Interfacial tension $\sigma$ between PEO and PDMS at 100°C without and with addition of 2 wt% of different block copolymers to the former polymer

| Copolymer | $\sigma$ (mN m$^{-1}$) |
|---|---|
| None | 10.60 |
| P(DMS$_4$-EO$_{23}$-DMS$_4$) | 7.25 |
| P(DMS$_4$-EO$_{37}$-DMS$_4$) | 7.25 |
| P(DMS$_4$-EO$_{77}$-DMS$_4$) | 8.60 |
| P(DMS$_{16}$-EO$_{14}$-DMS$_{16}$) | 0.76 |
| P(DMS$_{16}$-EO$_{37}$-DMS$_{16}$) | 1.16 |
| P(DMS$_{23}$-EO$_{37}$-DMS$_{23}$) | 0.80 |
| P(DMS$_{32}$-EO$_{37}$-DMS$_{32}$) | 0.70 |
| P(DMS$_{32}$-EO$_{77}$-DMS$_{32}$) | 0.70 |
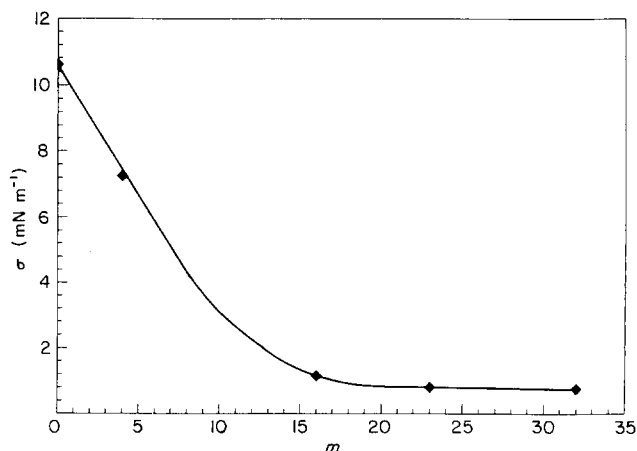


**Figure 3** Interfacial tension $\sigma$ of a phase separated mixture of PEO 35 containing 2 wt% P(DMS$_m$-EO$_n$-DMS$_m$) and PDMS 100 as a function of *m* for $n = 37$ at 100°C; *n* and *m* are the numbers of monomeric units contained in the blocks of the copolymer. The value for the polymer blend in the absence of additives is also given at $m = 0$
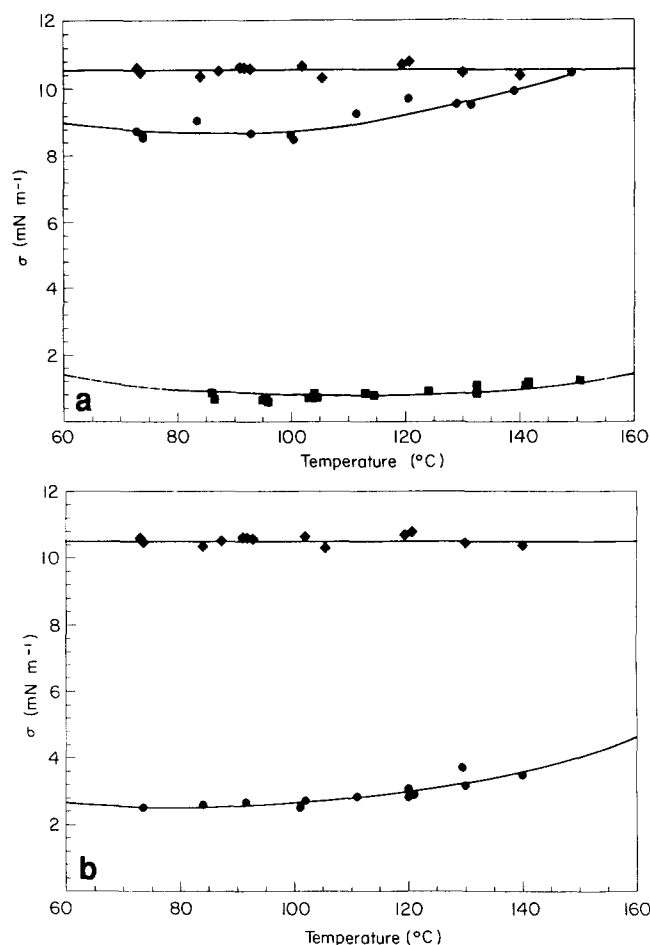
**Figure 4** Interfacial tension $\sigma$ between phase separated mixtures of PEO 35 containing 2 wt% of different block copolymers and PDMS 100 as a function of temperature. For the sake of comparison, the data for the binary system are also given. The subscripts in the abbreviations used for the additives signify the number of monomeric units in the blocks. (a) PEO 35/PDMS 100 ($\blacklozenge$); 2 wt% P(DMS$_4$-EO$_{77}$-DMS$_4$) ($\bullet$); 2 wt% P(DMS$_{32}$-EO$_{77}$-DMS$_{32}$) ($\blacksquare$). (b) PEO 35/PDMS 100 ($\blacklozenge$); 2 wt% P(EO$_{52}$-DMS$_{70}$-EO$_{52}$) ($\bullet$)

differences between samples of the ABA and BAB type. This question is dealt with in *Figure 4* which gives $\sigma(T)$ for different additives present at a concentration of 2 wt% in the PEO phase (i.e. well in excess of the corresponding *CMC* values).

First of all it can be seen from these plots that the efficiencies of P(DMS$_{32}$-EO$_{77}$-DMS$_{32}$) and of a sample with the inverse block architecture, namely P(EO$_{52}$-DMS$_{70}$-EO$_{52}$), are similar, the former being somewhat more active than the latter at all temperatures. As already shown in *Figure 3*, the chain length of the end blocks of P(DMS$_4$-EO$_{77}$-DMS$_4$) is obviously too low to yield effects that are comparable with that of the above two products. In contrast to the binary system, $\sigma$ is no longer independent of temperature for ternary systems. In all cases the $\sigma$ values increase with temperature and it appears that they would pass a minimum on the low temperature side of the measuring interval.

Since $d\sigma/dT$ is related to the entropy differences between the bulk phases and the interfacial layer, the above dissimilarities in the behaviour of binary and ternary systems imply temperature induced changes in the configurations of the additives in the different phases and in their partition coefficients; in other words, they can be rationalized in terms of temperature-dependent *CMC*s.

## PS/PDMS

As compared with the blend studied so far, the PEO component was exchanged with PS. Measurements were performed with the additive P(S$_{430}$-DMS$_{68}$), consisting of 430 S and 68 DMS units, to obtain information concerning the effects that result with diblock copolymers. The data for additive concentrations in the denser phase (PS) of 2 and 4 wt%, respectively, are shown in *Figure 5*.

For this binary system, $\sigma$ turns out to decrease as the temperature is raised. The diblock copolymer is obviously considerably less efficient than the triblock copolymers studied above; in addition to the differences in the number of blocks the additives contain, the high molar mass of P(S-DMS) and the dissimilar degrees of polymerization of its two parts could explain the lower efficiency. The fact that the $\sigma$ values still differ markedly for 2 and 4 wt% of the additive in the PS phase can be taken as an indication that the *CMC* is in the present case probably higher by a factor of five to ten than with the system of the last section. In contrast to the situation with the system in the absence of additives, $\sigma$ increases slightly with temperature in their presence.

### Theoretical aspects

Various attempts have been made to calculate the $\sigma$ for phase separated mixtures of homopolymers in the presence of copolymers. None of them, however, can in its rigorous form be directly applied to the present situation. Either some basic assumptions are not fulfilled by the actual systems or some unrealistic simplifications had to be made in the calculations.

The only approach[24] that allows for multiblock copolymers starts from the assumption that the polymer pairs are nearly compatible; its conclusions — for instance that multiblock copolymers should be less efficient as compared with the corresponding diblock additives — need therefore not be valid for the present systems. Other theories[21-23] treat quaternary mixtures, consisting of the homopolymers A and B plus a copolymer of the AB or XY type and a low molecular weight solvent. Since these calculations yield expressions for $\Delta\sigma$, the reduction of $\sigma$ resulting from the addition of block copolymers, as a function of molecular and
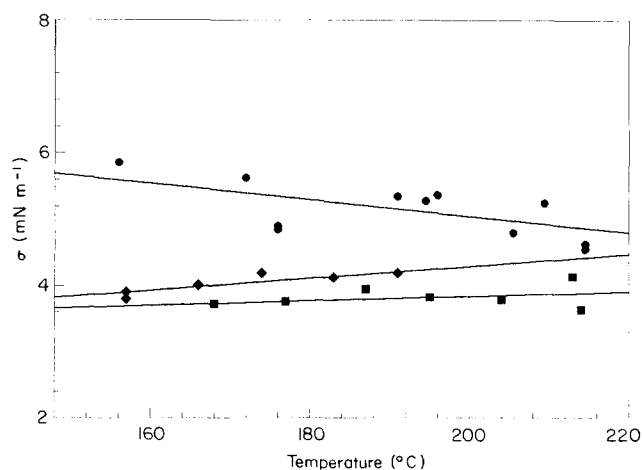


**Figure 5** Interfacial tension $\sigma$ between phase separated mixtures of PS 80 and PDMS 100 as a function of temperature and the same dependence in the presence of 2 and 4 wt% of the diblock copolymer P(S$_{430}$-DMS$_{68}$) in the PS phase. The subscripts in the abbreviation used for the additive signify the number of monomeric units in the blocks: PS 80/PDMS 100 ($\bullet$); 2 wt% P(S$_{430}$-DMS$_{68}$) ($\blacklozenge$); 4 wt% P(S$_{430}$-DMS$_{68}$) ($\blacksquare$)

thermodynamic parameters, one pertinent result is briefly recalled and compared with the present experimental findings.

By means of a simplified analytical calculation Vilgis and Noolandi[23] have obtained the following relation for $\Delta\sigma$ in the case of totally symmetric A/B/A-B systems:

$$\Delta\sigma \simeq -\frac{1}{Z_C}\exp[(1/2)Z_C\chi_{AB}\varphi_P] \qquad (5)$$

where $Z_C$ is the degree of polymerization of the symmetric block copolymer, $\chi_{AB}$ is the interaction parameter between the two types of monomeric units and $\varphi_P$ is the volume fraction of the dominant homopolymer in the respective bulk phase $[\varphi_A(-\infty)=\varphi_B(+\infty)=\varphi_P]$.

The above equation — according to which $\sigma$ should depend exponentially on the copolymer molecular weight, as well as on the interaction parameter and the homopolymer volume fraction — does not account for the formation of micelles and for the fact that $\sigma$ approaches a limiting value as soon as the additive concentration exceeds the *CMC*; it also does not predict the saturation effect observed upon an augmentation of $Z_C$ (cf. *Figure 3*); at present it is unclear whether this levelling off in the efficiency of the additives with increasing chain length can also be observed at concentrations below the *CMC*. The larger reduction of $\sigma$ in the case of PEO/PDMS as compared with PS/PDMS, on the other hand, can be well rationalized in terms of equation (5) by the larger $\chi_{AB}$ values for the former blend.

## CONCLUSIONS

A study has been performed on the effect of the addition of block copolymers on the $\sigma$ between two incompletely miscible homopolymers. P(DMS-EO-DMS) added to the homopolymers PEO and PDMS turned out not only to be the most effective among the present systems, but also when compared with literature data. The explanations for this observation are the high incompatibility of the homopolymers, the favourable molecular weight of the additive and, very likely, the fact that the additive is a triblock and not a diblock copolymer. The reasoning concerning the higher efficiency of tri- as compared with diblock copolymers is at variance with most theoretical predictions, but in agreement with the results of a recent computer simulation[39] according to which two 'stickers' should be more efficient than one. The variation of the molar mass of the blocks has demonstrated that a degree of polymerization of 10–15 for the end blocks suffices to produce a sharp reduction in $\sigma$. The *CMC* of P(DMS-EO-DMS) in PEO is much less than that of the other additives in the corresponding homopolymer.

The reported experimental results are in qualitative agreement with the predictions of Vilgis and Noolandi[23] according to which $\sigma$ should decrease exponentially with the degree of polymerization of the additive and the incompatibility of the two homopolymers, as measured by the interaction parameter $\chi_{AB}$.

## ACKNOWLEDGEMENTS

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