The influence of multiblock copolymers containing polysulfone and poly(tetramethylene oxide) segments on the phase behavior in polymer blends

L. Häußler[*], D. Pospiech, K. Eckstein, D. Jehnichen

Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

Abstract

The phase structure of polysulfone/poly(tetramethylene oxide) multiblock copolymers (PSU/PTMO BCP) strongly depends on the molecular weight of the coupled blocks. Non-phase separated structures are obtained using low molecular PTMO blocks. These block copolymers show a single T_g that follows the miscibility rule by Fox. Block copolymers with longer PTMO blocks have a phase separated morphology that is characterized by the coexistence of an amorphous PSU phase, an amorphous PTMO phase as well as crystallized PTMO domains.

The influence of the block copolymer composition in blends with high molecular PSU was investigated. Blends of PSU and PSU/PTMO block copolymers are miscible if the molecular weight of the PSU segment exceeds the entanglement molecular weight twice. Otherwise, partial phase separation into a PSU-rich and BCP-rich phase is observed in the blend. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Blending of polymers is one of the most important tools to develop new materials with special properties [1]. However, most polymers are thermodynamically immiscible [2] which leads to weak interfacial adhesion, and interfacial strength and unstable morphologies, finally resulting in reduced mechanical properties [3]. Therefore, compatibilization of polymer blends has been investigated intensively. One possible method is to add block copolymers (BCP) consisting of segments of the blend partners to the

mixture [1,4]. In the past, the main part was focused on diblock copolymers. On the other hand, Noolandi [5] demonstrated theoretically that multiblock copolymers with the chemical structure $(A–B)_n$ should also contribute to enhance the miscibility between the components. Noolandi assumes a certain critical length of the multiblock copolymer segments in order to form loops that are large enough to penetrate into the homopolymer phases.

In a previous work, we investigated the influence of polysulfone/liquid crystalline polyester multiblock copolymers in immiscible blends of the corresponding polymers [6]. Systematic examination of solution-casted binary (LCP/PSU; BCP/PSU; BCP/LCP) and ternary (PSU/LCP/BCP) blends showed that a partial

[*]Corresponding author. Fax: +49-351-4658-284
E-mail address: lili@ipfdd.de (L. Häußler)

miscibility between PSU matrix and PSU phase of the block copolymer is achieved if the molecular weight of the PSU segments in the BCP exceeds the entanglement molecular weight M_e more than twice. M_e values for PSU were reported by Fetters et al. [7] (1900 g/mol), by Friedrich [8] (2000 g/mol) and by Schönherr et al. [9] (2500 g/mol).

The results based on thermal investigation by DSC were supported by TEM, SEM and determination of interfacial width by neutron reflectivity [10]. The partial miscibility finally resulted in improved mechanical properties of LCP/PSU blends [6,11].

The aim of the work presented here was to expand the investigations by changing the chemical structure of one of the BCP segments. Thus, the LCP segments were replaced by flexible poly(tetramethylene oxide) (PTMO) segments. Their chemical structure is shown in formula (1).
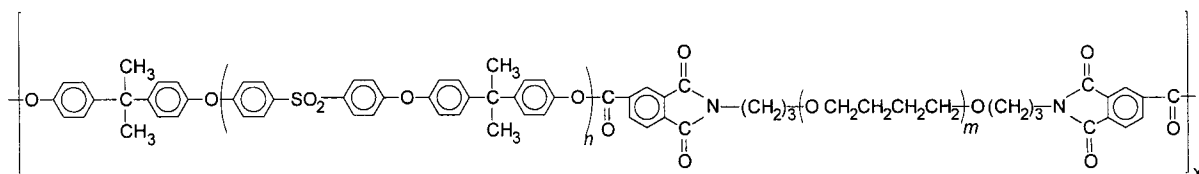
The influence of segment molecular weights on the phase structure of these BCP was discussed recently [12].

2. Experimental

2.1. Synthesis and blend preparation

The synthesis of the PSU/PTMO multiblock copolymers was carried out by a melt transesterification procedure as reported earlier [12]. Blends of BCP and high molecular weight PSU (Polyscience, 30 000 g/mol) were prepared by dissolving both components in chloroform and precipitation of the solution into ethanol. The blend was filtered off and dried in vacuo at 30°C for 4 h.

2.2. DSC measurements

The thermal behavior was investigated using a DSC 7 (Perkin–Elmer Corp.) with Pyris 3.51 software.

Samples of about 8 ± 2 mg were measured in the temperature range of $-60°C$ to $250°C$ at a heating rate of 20 K/min. The T_g values were determined using the Δc_p half step method from the second heating run after cooling at a rate of 80 K/min. The calibration of the device was done at 10 K/min with In and Pb. The thermal lag of the DSC used was 0.2 K per 10 K/min change in heating rate.

Since all samples were measured under the same conditions the correction concerning the heating rate was not realized.

3. Results and discussion

Recently, we published our results on segmented BCP consisting of PTMO and PSU segments [12] that were used for this blend study. The influence of the segment molecular weights was investigated in two BCP series having PTMO segments of either 1150 or 2560 g/mol with PSU segments varied in their molecular weight. The BCP with PTMO blocks of 1150 g/mol showed a non-phase separated structure indicated by a single T_g that followed the known miscibility rule by Fox. This was somewhat unexpected with respect to the interaction parameter that can be calculated from the solubility parameters of the segments [13]. BCP with PTMO blocks of 2560 g/mol are characterized by a phase separated structure. The existence of an amorphous PTMO phase, an amorphous PSU phase as well as crystallized PTMO domains (in case of coupling with short PSU segments) was detected. The crystallinity of these BCP as well as the amorphous state of the BCP with short PTMO segments was confirmed by WAXS investigations.

The completely amorphous state of the BCP with PTMO 1150 g/mol rose our interest in blending these materials with high molecular weight PSU. The non-phase separated structure of these BCP does, in fact, more represent the case of blends of homopolymers

Table 1
T_g values of the blends and of the corresponding blend partners

Blend (PSU/BCP)	Segment molecular weight of PSU in the BCP (g/mol)	Composition (PSU/BCP) (C_A/C_B) (wt%)	T_g[a] blend partner (°C)	$T_{g,meas.}$ BCP-rich phase (2) (°C)	$T_{g,meas.}$ PSU-rich phase (1) (°C)	$T_{g,calc.}$ using Fox (°C)
BCP 1	287		−10			
PSU/BCP 1		25/75		23	169	22
		50/50		25[b]	156[b]	62
BCP 2	1140		15			
PSU/BCP 2		25/75		37	147[b]	45
		50/50		31	156	82
BCP 3	2560		71			
PSU/BCP 3		25/75		90	135[b]	94
		50/50		86	141	121
BCP 4	3560		90			
PSU/BCP 4		25/75			119	114
		50/50			145	136
BCP 5	5210		104			
PSU/BCP 5		50/50			153	141
BCP 6	9040		144			
PSU/BCP 6		50/50			170	166
PSU			190			

[a] Values ref. in our previous work [12].

[b] In general, the T_g values determined deviate from average ±2 K, only the marked [b]values in phase separated blends showed higher deviations. That might be caused on the one hand by the lower PSU content in blends PSU/BCP = 25/75 w/w, and on the other hand by possible differences in composition of blends PSU/BCP 50/50 w/w in case of BCP 1 having short 4,4′-dioxy(diphenylene sulfone) connecting units.

with "random copolymers" as discussed by Dai et al. [14] than blending with block copolymers. The T_g values of the BCP and the high molecular weight PSU used for blending are summarized in Table 1. The T_g values of the BCP were already published in our previous work [12]. They were reproduced by further measurements within the framework of the blend experiments within ±2 K.

The T_g values of the blend components differ significantly enough to allow an estimation about the state of miscibility in their blends.

The DSC data in Table 1 show that the thermal behavior of PSU/BCP blends depends on the PSU segment length in the BCP. The blends with BCP having short PSU segments ≤2560 g/mol show two T_g's referring to phase separation in the blend. However, the two glass transitions approach each other indicating partial miscibility. Fig. 1 shows the DSC curves of blends of BCP 2 (PTMO 1150/PSU 1140) with PSU in comparison to those of the pure blend partners.

In contrast, blends with BCP having PSU segment molecular weights ≥3560 g/mol show only a single T_g

indicating miscibility of the components, as demonstrated in Fig. 2 for blends with BCP 4.

The glass transition behavior of blends with BCP of different segment molecular weights for blend com-
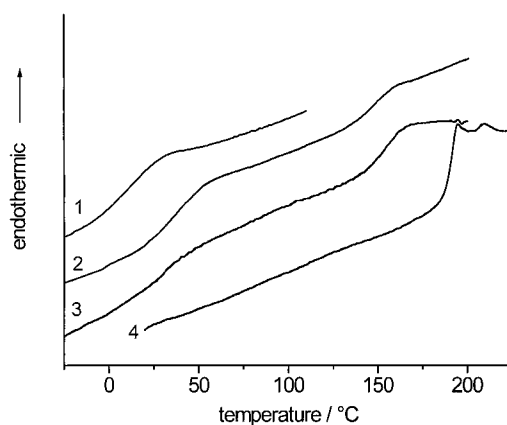

Fig. 1. DSC curves of the second heating run of phase separated blends in comparison to the blend components: (1) BCP 2 (PTMO 1150/PSU 1140); (2) blend PSU/BCP 2 = 25/75 w/w; (3) blend PSU/BCP 2 = 50/50 w/w; (4) PSU (30 000 g/mol).
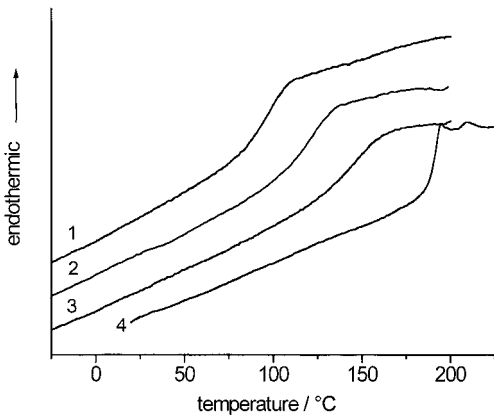
Fig. 2. DSC curves of the second heating run of non-phase separated blends in comparison to the blend components: (1) BCP 4 (PTMO 1150/PSU 3560); (2) blend PSU/BCP 4 = 25/75 w/w; (3) blend PSU/BCP 4 = 50/50 w/w; (4) PSU (30 000 g/mol).
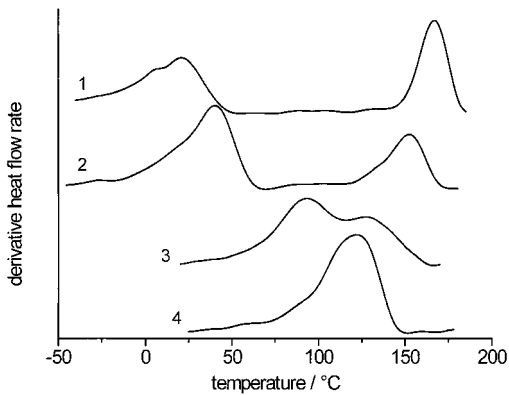

Fig. 3. Derivative heat flow rate of the second heating run in blends of PSU/BCP = 25/75 w/w in dependence on segment molecular weight of PSU in the BCP: (1) blend with BCP 1; (2) blend with BCP 2; (3) blend with BCP 3; (4) blend with BCP 4.

positions of PSU/BCP = 25/75 w/w is illustrated in Fig. 3 by the derivative heat flow curves which are more sensitive for weak, superimposed glass transitions. The development of the phase structure towards miscibility is quite obvious.

Fig. 4 shows the glass transition behavior in dependence on the blend composition. For comparison, the dotted line corresponds to the values calculated by the Fox miscibility rule. The figure shows again the influence of the PSU segment molecular weight on the development of miscibility. Even in the case of the
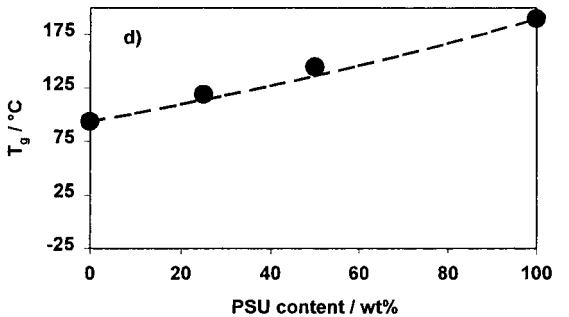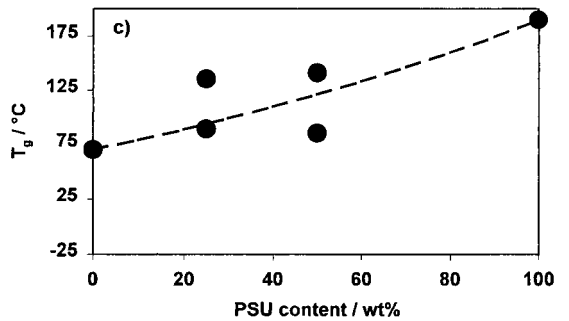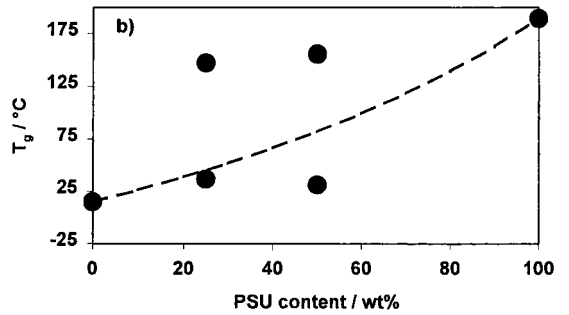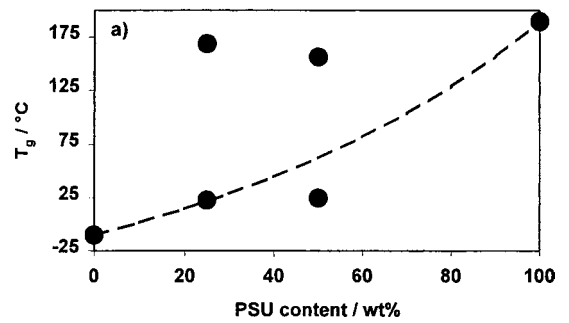

Fig. 4. Influence of the segment molecular weight of PSU in the BCP on the glass transition behavior (T_g) in the blends in dependence on composition: (a) blends with BCP 1; (b) blends with BCP 2; (c) blends with BCP 3; (d) blends with BCP 4.
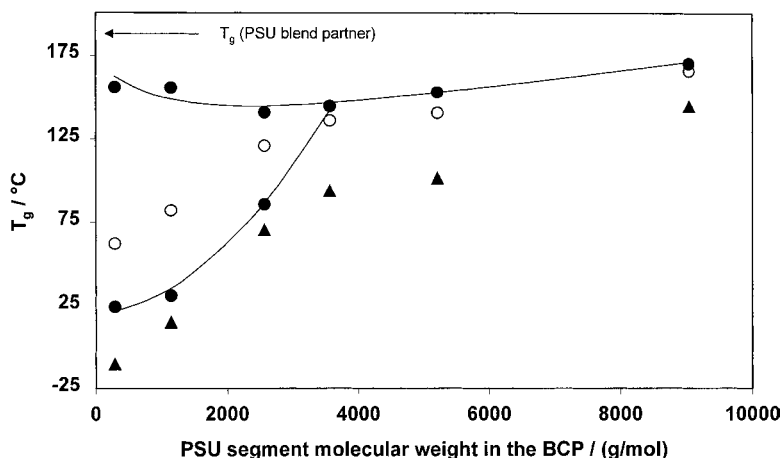
Fig. 5. T_g in the blends in dependence on segment molecular weight of the PSU in the BCP compared to those of the blend partners and the calculated values: ($\rightarrow$) PSU blend partner; ($\blacktriangle$) corresponding BCP; ($\bullet$) experimental values; ($\circ$) calculated values using Fox.

blend of PSU with BCP 1 (which represents a PTMO linked with short 4,4′-dioxy(diphenylene sulfone) units), a partial miscibility is found. The critical molecular weight of PSU segments in the BCP is about 3560 g/mol in the blend compositions examined. The values for the single glass transitions obtained in this case are in good agreement to the values calculated by the Fox equation within the limits of experimental accuracy (Table 1). The experimental T_g's for blends containing 50 wt% PSU and 50 wt% BCP with the values of the blend partners as well as the values calculated by the Fox equation [15] are compared in Fig. 5.

It is obvious from Fig. 5 that the T_g values of both phases come closer to each other as the molecular weight of the PSU segments of the BCP increases. However, the contribution of each blend partner appears to be different. Therefore, an estimation of the contents of PSU as well as BCP in both, PSU-rich (1) and BCP-rich phase (2) in the blends PSU/BCP 1, PSU/BCP 2 and PSU/BCP 3 were done as follows:

Both, the T_g of the PSU-rich and the T_g of the BCP-rich phase were considered as T_g of a miscible blend. The weight fractions of PSU (w_A) and BCP ($w_B = 1 - w_A$) were calculated for each phase by transformation of the Fox Eq. (1) into Eq. (2):

$$\frac{1}{T_g} = \frac{w_A}{T_{g,A}} - \frac{(1 - w_A)}{T_{g,B}}, \tag{1}$$

$$w_A = \frac{1/T_g - 1/T_{g,B}}{1/T_{g,A} - 1/T_{g,B}}. \tag{2}$$

The ratio Φ of the weight fractions determined using (2) corresponds to the ratio of the mass content in the PSU-rich phase 1 with

$$\phi_1 = \frac{w_{1,A}}{w_{1,B}} = \frac{m_{1,A}}{m_{1,B}}, \tag{3}$$

and in the BCP-rich phase 2 with

$$\phi_2 = \frac{w_{2,A}}{w_{2,B}} = \frac{m_{2,A}}{m_{2,B}}. \tag{4}$$

The total content of PSU and BCP in the blend is given by

$$c_A = m_{1,A} + m_{2,A}, \tag{5}$$

$$c_B = m_{1,B} + m_{2,B}. \tag{6}$$

With Eqs. (3) and (5) we obtained

$$\phi_1 \cdot m_{1,B} = c_A - m_{2,A}, \tag{7}$$

and using Eq. (6) for $m_{1,B}$ and Eq. (4) for $m_{2,A}$ yielded Eq. (8):

$$\phi_1 (c_B - m_{2,B}) = c_A - (\phi_2 \cdot m_{2,B}), \tag{8}$$

which gives the mass content $m_{2,B}$ of the BCP in the BCP-rich phase

$$m_{2,B} = \frac{c_A - \phi_1 \cdot c_B}{\phi_2 - \phi_1}. \tag{9}$$

Table 2
Calculation of the composition of the PSU-rich and BCP-rich phase in the blends

Blend (PSU/BCP)	Composition of (PSU/BCP) (C_A/C_B) (wt%)	PSU in the PSU-rich phase $m_{1,A}$ (wt%)	PSU in the BCP-rich phase $m_{1,B}$ (wt%)	BCP in the BCP-rich phase $m_{2,B}$ (wt%)	BCP in the PSU-rich phase $m_{2,A}$ (wt%)
PSU/BCP 1	25/75	16	9	75	0
PSU/BCP 2	25/75	12	13	72	3
PSU/BCP 3	25/75	7	18	70	5
PSU/BCP 1	50/50	33	17	46	4
PSU/BCP 2	50/50	43	7	44	6
PSU/BCP 3	50/50	44	6	28	22

Table 2 shows the results of the distribution of PSU and BCP in both, the PSU-rich and the BCP-rich phase. In blends of PSU/BCP (25/75 w/w) the BCP forms the matrix and the PSU the disperse phase. In this case, more PSU is dissolved in the BCP-rich phase than BCP in the PSU-rich phase. The dissolved content of PSU in the BCP-rich phase increases with increasing segment molecular weight of PSU in the BCP.

In blends of PSU/BCP (50/50 w/w) some differences were observed which might be caused by a phase inversion.

4. Conclusions

Segmented BCP having short PTMO blocks with a molecular weight of 1150 g/mol form a non-phase separated structure showing one single glass transition.

The phase behavior of blends of these BCP with high molecular weight PSU can be controlled by the molecular weights of the BCP segments. Both, phase separated and non-phase separated blends can be obtained. Phase separation was observed in case of using PSU segments with molecular weights ≤2560 g/mol. The analysis of the glass transition behavior indicated a partial miscibility. In contrast, BCP with PSU segments ≥3560 g/mol result in non-phase separated blends.

The results obtained for the blend system PSU with BCP (PTMO/PSU) showed that the formation of a non-phase separated, miscible structure requires a critical PSU segment molecular weight. In case of the BCP investigated, the segments have to exceed the M_e value two times. In blends of PSU with BCP

containing immiscible segments of LCP and PSU oligomers the segment length necessary to achieve partial miscibility of the PSU phases (PSU in the BCP and PSU blend component) was found to be higher than $3M_e$ [6]. The difference between the two blend systems can be explained by the behavior of the PTMO/PSU and LCP/PSU block copolymers. Whereas the former represents a non-phase separated, more or less "random" material, the latter is a strongly phase separated block copolymer. In the first case, the whole BCP chain mixes with the PSU blend partner. In case of the LCP/PSU block copolymers, only the PSU segments mix with the PSU blend partner and have to entangle into the PSU phase which requires a higher molecular weight of PSU segments.

Summarizing, it can be stated that PSU multiblock copolymers are useful for compatibilization of immiscible polymer blends containing PSU. Further results of other blend systems will be presented soon.

References

[1] C. Koning, M. van Duin, C. Pagnoulle, R. Jerome, Progr. Polym. Sci. 23 (1998) 707.
[2] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953.

[3] L.A. Utracki, Commercial Polymer Blends, Chapman & Hall, London, 1998.

[4] A.A. Adedeij, A.M. Jamieson, Compos. Interf. 3 (1995) 51.

[5] J. Noolandi, Makromol. Theory Simul. 1 (1992) 295.

[6] L. Häußler, D. Pospiech, K. Eckstein, A. Janke, R. Vogel, J. Appl. Polym. Sci. 66 (1997) 2293.

[7] L.J. Fetters, D.J. Lohse, D. Richter, T.A. Witten, A. Zirkel, Macromolecules 27 (1994) 4641.

[8] Ch. Friedrich, unpublished results.

[9] O.H. Schönherr, A. Schneller, A.M. Seifert, M. Soliman, J.H. Wendorff, Makromol. Chem. 193 (1992) 1955.

[10] D. Jehnichen, P. Friedel, S. Kummer, L. Häußler, K. Eckstein, D. Pospiech, Materials Science Forum, accepted, November 1998.

[11] D. Pospiech, L. Häußler, B. Voit, F. Böhme, H.R. Kricheldorf, Synthesis of LC multiblock copolymers, Solvent-Free Polymerization and Processes, ch. 2, ACS Symposium Series Nr. 713, 1999.

[12] D. Pospiech, K. Eckstein, L. Häußler, H. Komber, D. Jehnichen, K. Grundke, F. Simon, Macromol. Chem. Phys. 200 (1999) 1311.

[13] D. Pospiech, L. Häußler, A. Gottwald, D. Jehnichen, P. Friedel, Ch. Kunert, in preparation.

[14] C.A. Dai, B.J. Dair, K.H. Dai, C.K. Ober, E.J. Kramer, C.Y. Hui, L.Y. Jelinski, Phys. Rev. Lett. 73 (1994) 2472.

[15] T.G. Fox, Bull. Am. Phys. Soc. 1 (1956) 123.