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Heteroarm star copolymers as emulsifying agents in polymer blends

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We investigate the efficiency of heteroarm star copolymers of the type A_nB_n, synthesized by anionic polymerization, as compatibilizers of an A/B polymer blend. By measuring the size of the dispersed phase the star with $n = 6$ is found to be a better emulsifying agent than the diblock ($n = 1$) or the star with $n = 9$. These experimental observations agree with theoretical predictions. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

Polymer blends constitute one of the important topics of research in polymer science. The main goal of this research is to combine different properties and/or to produce new ones by mixing at least two polymeric species. The problem arises from the fact that mixing of polymers is a thermodynamically unfavorable process. In most of the cases the entropy of mixing is very small and cannot compensate the entropically unfavourable interactions between the unlike polymer segments. This leads to immiscible polymer blends with macroscopically phase-separated structures and very poor mechanical properties. In order to overcome the incompatibility between two immiscible homopolymers A and B, a small amount of a block copolymer is added to the system as a compatibilizing agent. The block copolymers migrate to the interface of the A and B microdomains of the blend, and reduce significantly the interfacial tension, provoking an efficient phase dispersion. Moreover, as each block of the copolymer is mixing with the corresponding homopolymers the adhesion between the A and B phases is strengthened, and therefore the mechanical properties of the blend are significantly improved.

The ability of the copolymers to compatibilize a polymer blend has received much attention in recent years both from experimental and theoretical points of view[1-10]. One of the important questions is, which are the optimum values of the molecular characteristics of the copolymer, like those of molecular weight, chemical composition and architecture, for the most efficient compatibilization of a given A/B polymer blend. Previous results have shown that in the case of diblock copolymers the more symmetrical the two blocks are and the higher their molecular weights, the more effective at reducing the interfacial tension at the A/B interface are[11]. Concerning the architecture, the diblock copolymers are more effective compatibilizers than the corresponding triblock, star or graft copolymers[12]. Very recently Balazs *et al.* have predicted by using self-consistent mean field methods and analytical theory, that comparing a diblock copolymer, a random copolymer, a four-armed star and various combs with fixed molecular weights and composition, the diblocks offer the best emulsifying activity[13].

In recent years, star-shaped block copolymers with a novel architecture named *heteroarm star copolymers* have been synthesized by anionic polymerization methods[14-16]. These polymeric species are star polymers of the general formula A_nB_n bearing two different chemical arms which emanate from a very dense poly(divinylbenzene) core, or other types of junction points[17,18]. The present communication aims to demonstrate our first results concerning the ability of the heteroarm star copolymers to act as emulsifying agents in an A/B polymer blend. We also compare the interfacial activity of a linear diblock copolymer AB with that of A_nB_n and we explore the influence of the number of arms n of the star copolymer. A first attempt in this field was reported very recently, showing that polystyrene-poly(ε-caprolactam) heteroarm star copolymers with a cyclotriphosphazene core act as effective compatibilizing agents in Poly(2,6-dimethyphenylene oxide)/nylon 6 blends[18]. Our efforts start from a simpler system as the different arms of the copolymer are of the same nature as the homopolymers of the blend, and specific interactions between the copolymer constituents with the corresponding homopolymers are absent.

Experimental

Materials. All the polymeric materials involved in this work were synthesized by anionic polymerization under an inert atmosphere. Polystyrene/poly(ethyl methacrylate) heteroarm star copolymers (PS_nPEMA_n) were prepared according to a three-step sequential 'living' copolymerization method established recently[14,15]. In the first step the polystyrene arms were synthesized using *sec*-butyl lithium as an initiator, at − 40°C in THF in the presence of LiCl. The salt was added to the reaction medium in order to prevent side reactions during the polymerization of ethyl methacrylate. In the second step a small amount of divinylbenzene was polymerized by living polystyril lithium, yielding star-shaped polystyrenes (PS_n). Due to the random character of this reaction the functionality of the obtained star polymers is an average value. These star polymers are still 'living', bearing a number of active sites equal to the

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Table 1 Molecular characteristics of PS_nPEMA_n copolymers

Sample	$M_w(LS) \times 10^{-3}$	$M_w(PSn) \times 10^{-3}$	N_{PS} (arm)	N^b_{PEMA} (arm)	n^c	$f_{PS}{}^d$	$W_{PS}{}^e$ (%)
$PS_1PEMA_1^a$	62		250	315	1	0.44	42
PS_6PEMA_6	291	135	230	245	5.6	0.48	46
PS_9PEMA_9	487	200	192	263	9	0.42	42

[a] Diblock copolymer. The notation is for sake of uniformity

[b] From $M_w(PEMA_{arm}) = M_w(PS_n).(1 - W_{PS})/n.W_{PS}$

[c] Average number of each kind of arms, calculated by the formula $n = M_w(PS_n)/\{(M_w(PS_{arm}) + m_o[DVB]/[LE]\}$, ref. [16]

[d] $f_{PS} = N_{PS}/N_{PS} + N_{PEMA}$

[e] by i.r.

number of their arms. In the third step these active sites are used to polymerize the ethyl methacrylate. This step is carried out at −60°C. The second set of arms are growing from the PS_n cores. After deactivation of the sites by degassed methanol the heteroarm star copolymers were isolated by precipitation in a methanol/water mixture (80/20), dried, redissolved in benzene and freeze-dried. In all steps a small part of the reaction solution was sampled out and the polymeric species were isolated for the purpose of characterization.

A PS-*b*-PEMA diblock copolymer was also prepared by the above method, subtracting the intermediate step (DVB polymerization). All the samples were characterized by gel permeation chromatography, light scattering and Fourier transform infra-red spectroscopy (*FT*i.r.), and their characterization data are gathered in *Table 1*. The homopolymers PS and PEMA were designed as to have lower molecular masses than those of the corresponding blocks and/or arms of the compatibilizers. Their molecular weights M_w, are 17 000 ($M_w/M_n = 1.09$) and 26 000 ($M_w/M_n = 1.12$) respectively.

Differential scanning calorimetry. Differential scanning calorimetry (d.s.c.) was performed using a Du Pont 910 calorimeter equipped with a 99 thermal analyser. The heating rate was 10°C min^{-1}, and the experiments were carried out under a nitrogen atmosphere. For each sample the d.s.c. run was repeated three times, the first of which was always discarded, as it is affected by the sample thermal history.

Microscopy. Micrographs of the blends were obtained by means of a JEOL filtered scanning electron microscopy model 6320 F.

Blend preparation. The PS/PEMA (1/3 ratio) blends were prepared by solvent casting from a common good solvent (tetrahydrofuran, THF). The emulsifying agents were always 10 wt% of the blend. After prolonged drying under vacuum the specimens were etched for 18 h with cyclohexane which is a selective solvent for PS. The etched specimens were dried adequately before the microscopic observation.

Results and discussion

The compatibilizing effect of AB block copolymers in A/B blends is strongly dependent on the molecular weights of the individual blocks of the copolymers. As has been demonstrated, the most efficient compatibilizer should have equal or higher block molecular weights than those of the corresponding homopolymers of the blend[19].

Another aspect that should be considered is the phase behaviour of the A_nB_n star-shaped copolymers, which has been described by the theoretical predictions of Olvera de la Cruz and Sanchez[20]. Assuming that the A_nB_n star copolymers can be considered as n identical diblock copolymers joined together at their A–B junction points, the critical value χN remains 10.5 as in the case of diblock copolymers independent of the number of arms n. χ is the Flory–Huggins interaction parameter, and $N = N_A + N_B$ is the sum of the degree of polymerization of the A and B arms. This implies that the microphase separation of nearly symmetrical heteroarm star copolymers depends solely on the molecular weight of the arms and not that of the whole star polymer. Taking into account the above, the samples prepared for the present work were designed so as to have nearly the same arm molecular weight, about the same chemical composition (50 wt% styrene) but differing in the number of arms.

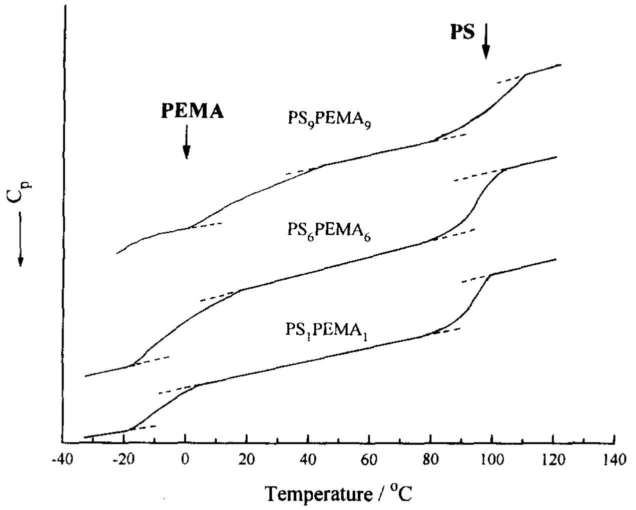


Figure 1 D.s.c. thermograms of PSnPEMAn block copolymers

The phase behaviour of the block copolymers used as compatibilizers was first investigated by means of differential scanning calorimetry, and their thermograms are presented in *Figure 1*. For all three samples two distinct glass transition temperatures (T_gs) can be observed, revealing a microphase separation in accordance with the theoretical predictions[20] and experimental findings[21–24]. The higher T_gs are attributed to the PS-rich phase and the lower ones to the PEMA-rich phase. Although the position of T_gs for the PS_1PEMA_1 and PS_6PEMA_6 is the same, the T_g of the PEMA-rich phase for the PS_9PEMA_9 is about 20°C higher and broader than those of the two other samples. This broadening is also observed on the PEMA homopolymer, and could be attributed to the different microstructure (tacticity) of the PEMA chains[25].

In order to investigate the compatibilizing activity of the

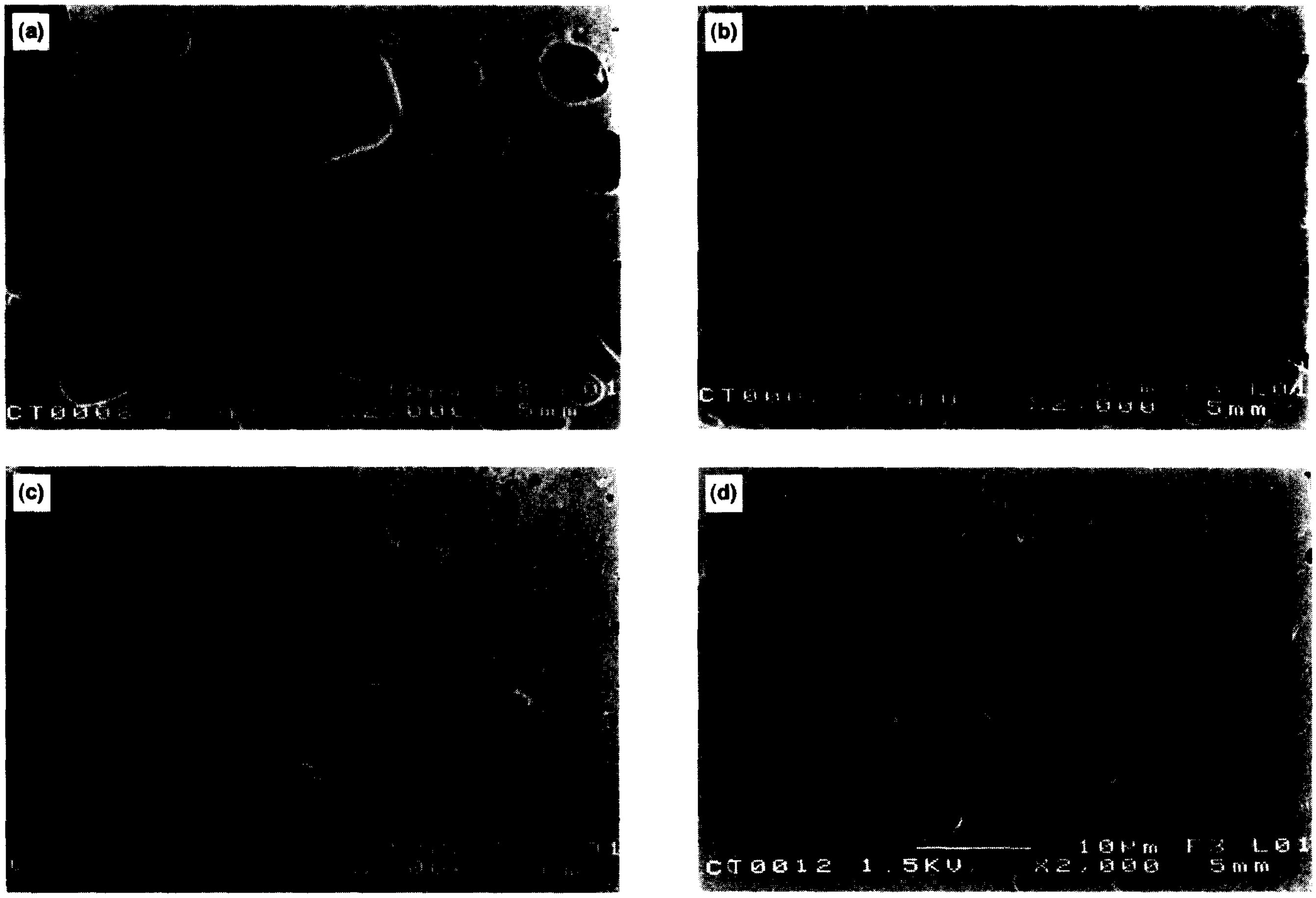
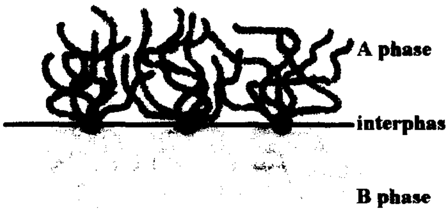


Figure 2 SEM micrographs of the blends: (a) PS/PEMA; (b) PS/PEMA/PS_1PEMA_1; (c) PS/PEMA/PS_6PEMA_6; (d) PS/PEMA/PS_9PEMA_9

heteroarm star copolymers, blends 75%PEMA/25%PS were modified by always adding 10 wt% of the compatibilizing agent. In *Figure 2* scanning electron micrographs (SEM) of the unmodified and modified blends are illustrated. The minor phase (i.e. PS) has been extracted by selective solvation, and the holes correspond to the PS dispersed phase. All the micrographs concerning the modified blends show emulsion behaviour, since a significant decrease of the microdomain size of the dispersed phase is evident. It seems that the heteroarm star copolymers, although exhibiting a complex architecture, migrate easily to the PS/PEMA interface[26] (*Scheme 1*). They reduce the interfacial tension, eventually provoking a much better dispersion of the minor phase. This emulsification activity is different for the three copolymers investigated. It appears that the heteroarm star copolymer bearing six of each kind of arms provokes a finer dispersion of the PS phase with an average microdomain size of the order of 1 μm (Figure 2*c*) and therefore it acts as a better emulsifying agent even with respect to the diblock copolymer (PS_1PEMA_1), which was considered to be the best combatibilizer among other types of block copolymers[13]. We must note here that the M_w of the arms of the star is slightly lower than those of the blocks of the linear homologue, and therefore less favourable with respect to molecular weights[11]. The above results are very promising, however a more detailed study is needed (complete emulsifications curves) to deduce a final conclusion.



Scheme 1

In an effort to explain the different effectiveness of the heteroarm star copolymers as compatibizers observed experimentally, we can employ the theoretical model of ref. [27]. It furnishes equilibrium density profiles perpendicular to the interface of the two different phases, and it can explain the behaviour of systems at or close to equilibrium, like the system of polymers which we have. The three heteroarm stars, PS_nPEMA_n, contain the same number, *n*, of arms of PS and PEMA, and show increased densities at the interface of the two phases of PS and PEMA. The density profile of the cores of heteroarm stars in number of macromolecules per volume along the interface of the two phases is given by section 4.5 of ref. [27]. The two different kinds of arms made of PS or PEMA being in the two different phases of PS or PEMA can have four different sizes, which we denote using two different indices as R_{kind}(phase). In the present experiment the mass *m* of compatibilizers is kept constant, and the number of macromolecules goes as the ratio of *m* to the molecular weights of the macromolecules. Of interest is the density of monomers m(*z*), which is related to the compatibility effectiveness of these macromolecules and can be found by multiplying the number of coils with the molecular mass of

Table 2 The four sizes Rkind(phase) in Å for each of the three copolymers

Sample	R_{PS}(PS)	R_{PS}(PEMA)	R_{PEMA}(PS)	R_{PEMA}(PEMA)
PS_1PEMA_1	300.39	45.85	51.46	266.25
PS_6PEMA_6	288.23	44.00	45.39	234.75
PS_9PEMA_9	263.34	40.19	47.04	243.30

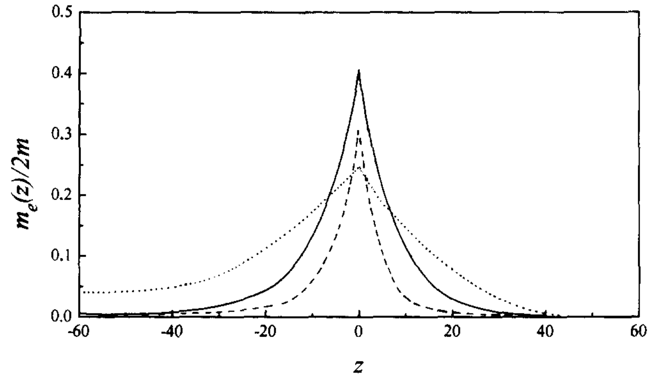


Figure 3 The ratios $m_e(z)/2m$ of the excess density profiles of the mass of the monomers at a distance z from the interface ($z = 0$) to the total mass m added for these copolymers: PS_6PEMA_6 (—), PS_9PEMA_9 (- - -), PS_1PEMA_1 (· · ·). The PS phase is at the left, $z < 0$, and the PEMA phase is at the right, $z \geq 0$

each one. This leads to the expression

$$m(z) = \frac{2m r_{PS}^{(n/2)\mathrm{erfc}[\sqrt{3}z/\sqrt{2}R_{PS}(z)]} r_{PEMA}^{(n/2)\mathrm{erfc}[\sqrt{3}z/\sqrt{2}R_{PEMA}(z)]}}{1 + r_{PS}^{n} r_{PEMA}^{n}}$$

where $r_{PS} = R_{PS}(PS)/R_{PS}(PEMA)$ is the ratio of the two sizes of a PS arm in the PS and PEMA phases while $r_{PEMA} = R_{PEMA}(PS)/R_{PEMA}(PEMA)$ is the ratio of the sizes of the PEMA arm in the PS and PEMA phases respectively. The size $R_{kind}(z)$ of each arm depends on the phase where the density profile is drawn. If we take that the phase of polystyrene is in the left half space with $z < 0$ while that of PEMA at the right with $z \geq 0$, then we have that $R_{kind}(z < 0) = R_{kind}(PS)$ and $R_{kind}(z \geq 0) = R_{kind}(PEMA)$. It is expressed by means of the end to end square distance given by $R_{kind}(phase) = l_{kind}(phase)N^{1/2}$ where N is the number of segments given in *Table 1* for each case and l_{kind}(phase) is the Kuhn length expressing the size of each segment considered to take different values for the two different kinds of arms in the two different phases. The Kuhn lengths of the PS and PEMA arms in the phases of their homopolymers are given by the values $l_{PS}(PS) = 19$ and $l_{PEMA}(PEMA) = 15$ Å[28]. Because of the immiscibility of the arms in the dissimilar phases, smaller sizes of R_{kind}(phase) are necessary in this case. A choice in the model to ensure this shrinkage is to keep the values and the dependence on N of an arm the same in the two phases but to reduce the value of l_{kind}(phase) in the dissimilar phases. Though a broad range of a smaller values can be used, we choose for both of them the value $l_{PEMA}(PS) = l_{PS}(PEMA) = 2.9$ Å, which is larger than the minimum possible value of 2.5 Å of the length of a monomer. This set of values determines both the sizes of the PS and PEMA arms for the three kinds of heteroarm stars in the two different phases written in *Table 2*, together with their ratios $r_{PS} = 19/2.9 = 6.55$ and $r_{PEMA} = 2.9/15 = 0.19$ being common for all three macromolecules.

After these the plot of the excess density profiles $m_e(z)/2m$ can be drawn, and these appear in *Figure 3*. A gathering of all three copolymers is seen at the interface of the two phases with a maximum value at $z = 0$ and a weak broad minimum at the right phase of PEMA. This minimum is followed by a slight increase of the density profile of the stars in the PEMA phase far from the interphase which indicates the presence of tiny amount of compatibilizers in the PEMA phase far from the interphase. Of importance to the extend of the compatibility is the relative amount of compatibilizers at $z = 0$ with respect to this minimum given by the difference of m(z) and the minimum value for each star. This excess density $m_e(z)$ is drawn in *Figure 3*, and the three graphs clearly show that the heteroarm PS_6PEMA_6 has the biggest excess density profile at the interface, while the other two have smaller ones. This explains the largest compatibilizability of the middle star in accordance with the experimental observations.

In conclusion, our preliminary results show that the heteroarm star copolymers of the type A_nB_n can act as emulsification agents in immiscible A/B polymer blends. In comparison with a diblock copolymer a star polymer bearing 6A and 6B arms seems to be more effective. Further work is in progress in order to support this first promising result.

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