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Phase Behavior of Heteroarm Star Copolymers by Differential Scanning Calorimetry

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New model polymers named "heteroarm star copolymers" have been synthesized recently using the anionic polymerization technique.[1,2] According to the synthetic method, a living polystyrene (PS) precursor was used to initiate a small amount of divinylbenzene (DVB). The copolymerization of DVB yields a small and very densely cross-linked core bearing a number of branches which is equal to the number of PS precursors involved in the initiation. The so-produced macromolecule can be viewed as a polystyrene–poly(divinylbenzene) star-shaped block copolymer. The interesting feature of these star polymers is that within the core there are now a number of active sites (equal to the number of branches) which can be used to initiate the polymerization of another suitable monomer such as *n*-butyl methacrylate (nBMA) or *tert*-butyl acrylate (tBA). During the polymerization of this monomer a new set of branches springs out from the core. Provided that no accidental deactivation has occurred, the resulting polymeric species are star copolymers bearing two kinds of branches of equal number. They can be described as a number of diblock copolymers which have been joined together at their A–B junction points (Scheme I).

The aim of this work is to give some preliminary results concerning the microphase behavior of these copolymers, having this novel architecture, in solid state. Differential scanning calorimetry (DSC) has been widely used in the study of the microphase separation in block copolymers,[3–5] and it is the main experimental tool in the present work.

Two kinds of heteroarm star copolymers have been investigated. The first sequence of branches for both copolymers is of the PS type such as amorphous glassy materials. The second sequence of the first copolymer is PnBMA, characterized by a rather low glass transition temperature, while the second copolymer has as a second sequence PtBA which can be easily hydrolyzed to yield ionic functions.

Experimental Part

All the samples used in this work have been synthesized via the anionic polymerization technique. The synthesis was performed under an argon atmosphere. *sec*-Butyllithium was the initiator for the polymerization of styrene at –40 °C in tetrahydrofuran (THF) yielding the PS precursor. Part of the precursor was sampled out for the characterization of the molecular weight of the PS branches. In the sequel, a chosen amount of DVB was added to the rest of the living PS solution, also at –40 °C, and the star PS precursor was formed. As before, part of this solution was sampled out in order to evaluate the number of branches. Finally the temperature of the reaction medium was lowered to –60 °C and an nBMA or tBA monomer was added dropwise. In order to avoid side reactions, diphenylethylene was added just before the addition of the acrylate monomers.[1,2] The color of the solution changed rapidly from deep red to faint yellow, showing that initiation had occurred. Once the polymerization of the last monomer was completed, the living sites were deactivated protonically and the heteroarm star copolymers were precipitated in a methanol–water mixture (85:15, v/v). Therefore, each synthesis yields three samples: the linear PS precursor (lPS), the star PS precursor (sPS), and one of the two types of the

Scheme I

AB　　　　　　A_nB_n
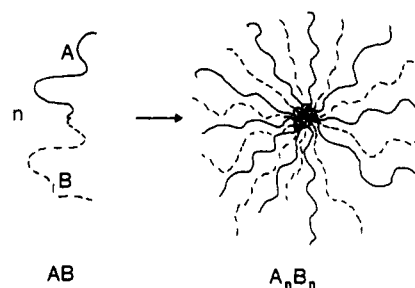
heteroarm star copolymers denoted by PS_nPnBMA_n, or PS_nPtBA_n as the case may be. The index *n* specifies the number of arms of each kind.

The weight-average molecular weights, $\bar{M}_w$, were determined by light scattering using a Fica apparatus fitted with a laser light source. The refractive index increments, dn/dc, were measured by means of a Brice Phenix instrument.

Gel permeation chromatography (GPC) was performed using a Waters Associates Model 201 instrument equipped with a differential refractometer as detector and a set of μStyragel columns (10^3, 10^4, and 10^5 Å). The elution solvent was THF at a flow rate of 1 mL/min. The data processing treatment was computerized. A deconvolution program[1] was used to determine precisely the amount of precursor polymer left in the samples of sPS and of heteroarm star copolymers. In the latter case the differences in the dn/dc values of the copolymer and of the lPS were taken into account.[1] All the molecular characteristics of the samples are summarized in Table I.

It is noted that the samples have been used without further purification. Nevertheless, the presence of the small amount of the lPS precursor has been taken into account in the characterization of the samples and the values of Table I are corrected values.

Details on the synthesis and characterization of the samples are reported elsewhere.[1,2]

Two diblock copolymers have also been used in this work: PS–PnBMA, $\bar{M}_w$ = 146 000, 51% PS, and PS–PtBA, $\bar{M}_w$ = 48 000, 54% PS.

DSC measurements were performed using a Du Pont 910 calorimeter equipped with a 99 thermal analyzer. The instrument was calibrated with a sapphire (Al_2O_3) standard. The samples were heated up to 140 °C at a heating rate of 20 °C/min, under a N_2 atmosphere, and then quenched to –40 °C using liquid N_2. This circle was repeated two or three times for each sample. The first run was always discarded. The reproducibility of the measurements concerning the glass transition temperature, T_g, was controlled by measurig 10 different pans of the same linear PS sample (no. 68); i.e., T_g = 381 ± 1 K. T_g is defined at half of the C_p change, and ΔT_g, the width of the glass transition, is the difference in temperature between the points where the tangent to the inflection intersects the extrapolated base lines below and above T_g.

Results and Discussion

Some characteristic DSC thermograms of the heteroarm star and diblock copolymers are depicted in Figure 1. One group of the samples displays one rather broad T_g (e.g., Figure 1c), another group displays two T_g's (e.g., Figure 1a), and there is a group exhibiting a third T_g at intermediate positions between the two T_g's of the copolymer components (e.g., Figure 1b).

Evidently the appearance of two distinct T_g's, when the system is microphase separated, is attributed to the PS-rich phase and the PnBMA- or PtBA-rich phase, respectively. The two rich phases are formed from star-shaped macromolecules having a common central core. Thus, in order to study the properties of the styrene microphases, the behavior of the star precursor is needed to be investigated first.

**Table I. Molecular Characterization Data of Heteroarm
Star Copolymers**

	sPS Precursor		
sample	$(M_n)_{br} \times 10^{-3}$ [a]	$M_n \times 10^{-3}$ [b]	n [c]
62	48.7	181	4
67	29.0	122	4
68	25.0	122	5
72	5.9	59	10
73	5.8	64	12
74	23.6	165	7
75	10.2	114	11
77	9.8	147	15
81	11.0	120	11
82	12.2	147	12
85a	11.5	195	17
85b	11.5	195	17
86a	3.0	45	15
86b	3.0	45	15

	Heteroarm Star Copolymer		
sample	$M_w \times 10^{-3}$ [d]	Sty (wt %) [e]	lPS left (%) [f]
	PS_nPnBMA_n		
62	295	59.8	12.5
67	245	51.6	7.7
68	237	48.3	8.5
72	96	57.7	0.7
73	125	63.0	0.8
74	362	51.1	3.1
75	213	63.4	2.1
	PS_nPtBA_n		
77	265	65.8	7.8
81	208	53.6	3.7
82	318	50.8	4.2
85a	289	72.0	0
85b	452	44.0	0
86a	78.5	73.0	0
86b	218	30.0	0

[a] By GPC using calibration with PS standards. [b] By GPC using
the universal calibration. [c] Average number of branches of sPS. [d] By
light scattering. [e] By differential refractometer. [f] From the GPC
chromatograms.

In Figure 2 the T_g's of the lPS and sPS precursors are
plotted as a function of the molecular weight, $\bar{M}_n$. As
shown the points corresponding to star molecules lie
approximately on the solid line drawn for the linear
molecules. This means that the T_g's of the sPS have about
the same T_g compared to the lPS of equal molecular weight.
Two effects may be observed on the T_g of the star-branched
macromolecules: the chain-end effect which provokes a
T_g depression and the core effect which could provoke a
T_g increase analogous to that observed in polymer net-
works.[6] Of course these phenomena should be observed
for star molecules with high functionality and low branch
lengths. In our case it seems that the chain-end effect and
the core effect partially compensate. This is corroborated
by the fact that there is a small broadening of the T_g region
for the star molecules, as is implied from the inspection
of the ΔT_g. The average ΔT_g value of the sPS is 9.8 K,
whereas for the lPS it is 7.5 K. There are two exceptions:
for sample no. 86 ($(M_n)_{br}$ = 3.0 × 10³, n = 15) the chain-
end effect predominates, showing a T_g depression, while
for sample no. 72 ($(M_n)_{br}$ = 5.9 × 10³, n = 10) the core
effect provokes a noticeable T_g increase. We must note
here that the latter effect is not observed for sample no.
73 ($(M_n)_{br}$ = 5.8 × 10³, n = 12) with a slightly lower branch
length and higher functionality.

In Figure 2 the T_g's of the styrene (sS) microphases of
the heteroarm star copolymers which show microphase
separation are also depicted. A remarkable decrease of
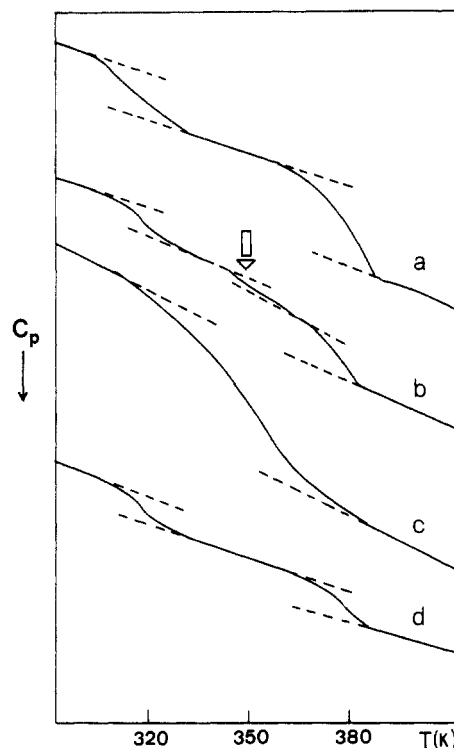the T_g of the styrene microphases with respect to the

Figure 1. DSC thermograms of PS_nPnBMA_n heteroarm star
copolymers: (a) no. 62, (b) no. 74, (c), no. 75, (d) PS–PnBMA
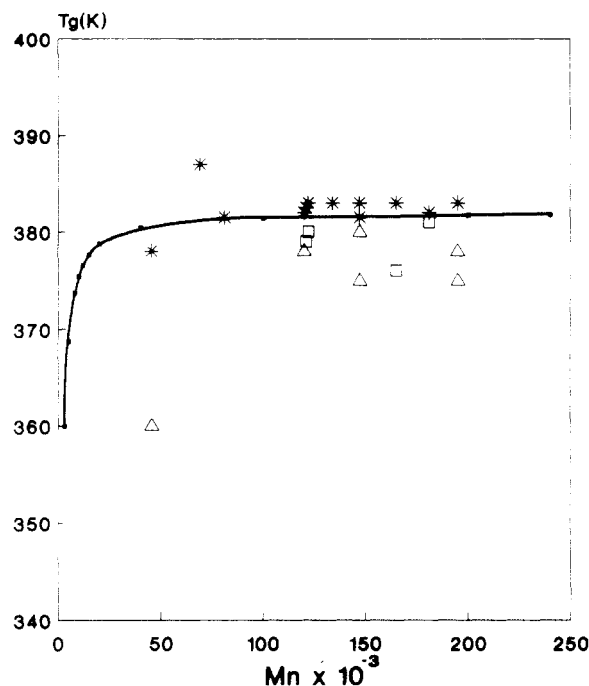diblock copolymer.

Figure 2. T_g as a function of the molecular weight, $\bar{M}_n$, of the
following samples: (*) sPS precursor, (□) sS microphase of
PS_nPnBMA_n, (△) sS microphase of PS_nPtBA_n, (—) lPS precursor,
$T_g = 382 - 66.463/M_n$ (in K).

corresponding sPS homopolymers can be observed. More-
over, an increase of the ΔT_g mean value from 9.7 K of the
sPS homopolymer to 12.7 K of the sS microphases, when
the second copolymer component is nBMA, is observed.
This ΔT_g enhancement arises from a T_g broadening toward
intermediate temperatures between the two T_g's. If the
second component is tBA, the above effect is very weak,
as the ΔT_g mean value is 10.2 (no. 86 not included). Sample
no. 86 shows a different behavior. ΔT_g increases dra-
matically to 19 K accompanied by a dramatic shift of T_g

toward lower temperatures. The different behavior in the T_g broadening of the sS microphases between the copolymers of different nature could be attributed to the interactions between the unlike segments reflected in the values of the Flory–Huggins interaction parameters χ_{AB}.

In the case where experimental values are not available, χ_{AB} can be calculated from the well-known formula[7]

$$\chi_{AB} = V_r(\delta_A - \delta_B)^2/RT \qquad (1)$$

where δ_A and δ_B are the Hildebrand solubility parameters and V_r is the reference volume, conveniently taken to be 100 cm^3/mol. The solubility parameter of polymers can be estimated from the structural formula using the molar attraction constants, F_i, and their densities, ρ.[7] Taken for PS $\delta = 9.25$ cal$^{1/2}$ cm$^{-3/2}$ mol^{-1} ($\rho = 1.05$ g/cm^3), for PnBMA $\delta = 8.7$ cal$^{1/2}$ cm$^{-3/2}$ mol^{-1} ($\rho = 1.055$ g/cm^3), and for PtBA $\delta = 8.0$ cal$^{1/2}$ cm$^{-3/2}$ mol^{-1} ($\rho = 1.0$ g/cm^3) (the F_i values were obtained from Hoy tables[8]), we found $\chi_{PS,PnBMA} = 0.052$ and $\chi_{PS,PtBA} = 0.264$, showing that miscibility is favored in the former case.

In order to have a better insight of the phase behavior of the heteroarm star copolymers, the variation of ΔT_g as a function of the number of each kind of arms, n (functionality of the heteroarm star is $2n$), is depicted in Figure 3. For the samples PS$_n$PnBMA$_n$ with high functionality ($n > 10$), one, rather broad T_g is evidenced, implying macroscopically one-phase behavior. This is not observed in the case of PS$_n$PtBA$_n$ even for the samples bearing 34 arms ($n = 17$) of both kinds. This means that the functionality itself is not the determining factor of the phase behavior of these polymeric species.

To describe the phase behavior of such systems, de la Cruz and Sanchez[9] have proposed a theory for the microphase separation in graft and star copolymers which is an extension of the Leibler theory for block copolymers.[10] For the case of the heteroarm star copolymers, their theory predicts a very surprising result. Assuming that the A$_n$B$_n$ type star copolymers can be considered as n identical diblock copolymers joined together at their A–B junction points (Scheme I), the critical value (χN_0) equals 10.5, which is the case of block copolymers, independent of the number of arms n. It is mentioned that N_0 is the degree of polymerization of the corresponding diblock A$_1$B$_1$ and not of the A$_n$B$_n$ star.

The χN_0 values for all the samples have been calculated and are summarized in Table II. $N_0 = N_1 + N_2$ where N_1 is the degree of polymerization of the lPS precursor while N_2 is an average value calculated from the overall molecular weight of the A$_n$B$_n$ star copolymer minus the molecular weight of the sPS precursor and divided by n.

The samples PS$_n$PnBMA$_n$ exhibiting one-phase morphology have indeed χN_0 values lower than the critical value 10.5. From the theoretical universal phase diagram[10] arises that for $0.25 < f = N_1/N_0 < 0.75$, and for $n > 4$ the critical values of χN_0 are lower than 16. Therefore, all of the other samples should exhibit microphase separation, which is confirmed from the experimental results.

There is an exception of the sample no. 86a which may be attributed to the fact that the χ values in the above calculation have been obtained from eq 1 and they do not correspond to actual experimental data. Moreover, the estimation of N_2 and therefore of N_0 relies on two assumptions. The first assumption demands the number of arms of both kinds to be equal. This means that no accidental deactivation of the active sites located within the core has occurred during the addition of the second monomer. This can be secured by very careful purification of the reagent. The second assumption asks for a low
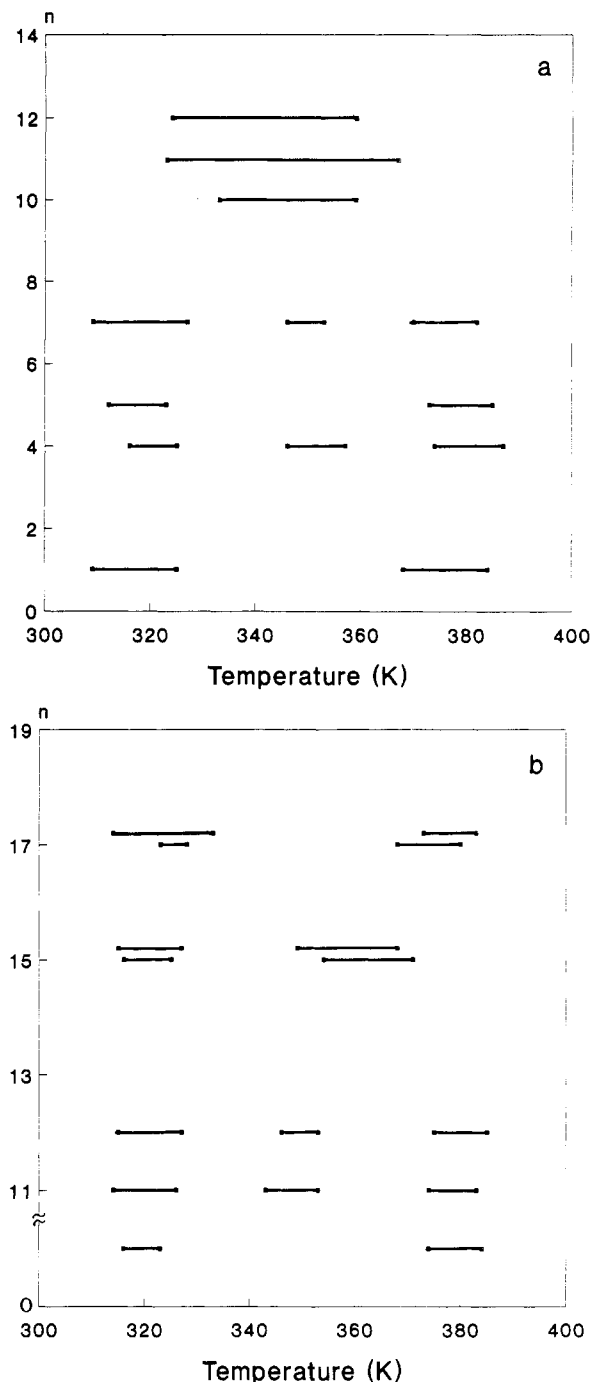

Figure 3. Variation of ΔT_g (horizontal bars) of the heteroarm star copolymer (A$_n$B$_n$) microphases with the number of arms n: (a) PS$_n$PnBMA$_n$, (b) PS$_n$PtBA$_n$. The bars in the bottom of the figures are referred to the diblock copolymers ($n = 1$).

polydispersity of the molecular weight of the second-generation arms. Provided that the polydispersity of the PS arms is very low, as measured by GPC of the lPS precursor, the compositional heterogeneity of the corresponding diblock copolymer from which the whole star copolymer is consisted is also bound to be low. Unfortunately, the polydispersity of the second-generation arms, or the compositional heterogeneity of the diblock copolymer constituents, cannot be measured by direct experiments. Nevertheless, it should be rather low because, as is implied by the rapid decoloration of the reaction media upon the addition of the second monomer,[1,2] its initiation is fast and quantitative.

Some of the microphase-separated samples exhibit a three-phase morphology as shown in Figure 3. Besides the two phases corresponding to the copolymer compo-

Table II. Calculation of χN_0 with Composition for the Corresponding Diblocks

sample	$N_1{}^a$	$N_2{}^b$	$N_0{}^c$	χN_0	f^d
		PS–PnBMA			
62	500	158	658	34.2	0.76
67	307	186	493	25.6	0.62
68	259	142	401	20.8	0.64
72	64	19	83	4.3	0.77
73	63	26	89	4.6	0.70
74	250	165	415	21.6	0.60
75	110	51	161	8.4	0.68
diblock	715	500	1215	63.2	0.59
		PS–PtBA			
77	104	48	152	40.1	0.68
81	115	55	170	44.9	0.67
82	132	90	222	58.6	0.59
85a	122	29	151	39.8	0.81
85b	122	103	225	59.4	0.54
86a	33	11	44	11.6	0.75
86b	33	83	116	30.6	0.29
diblock	249	172	421	111.0	0.59

^{a} N_1 = degree of polymerization of the PS block. ^{b} N_2 = degree of polymerization of the PnBMA or PtBA block. ^{c} $N_0 = N_1 + N_2$. ^{d} $f = N_1/N_0$.

Scheme II
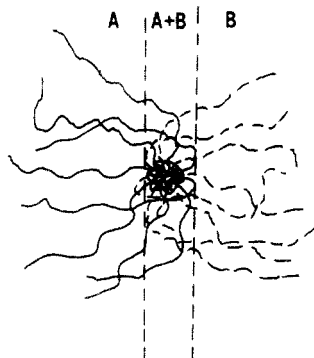
nents, a third phase is revealed by a third T_g region (see an example in Figure 1) lying at intermediate positions between the T_g's of the two other phases. This third phase should be attributed to a pronounced interphase, i.e., an A + B mixed phase, as the corresponding T_g region always appears at the middle of the two other T_g's irrespective of the composition of the star-shaped copolymer. This conclusion may be corroborated by inspecting the ΔC_p

values corresponding to the PS-rich phase. In fact, these values appear considerably lower than those of the sPS homopolymer precursor. This lowering should be attributed mainly to the fact that an amount of the PS segments is located in the mixed phase.

The effect of the three-phase morphology could be ascribed to structural constraints arising from the star-shaped architecture of the macromolecules (Scheme II). However, this effect does not always appear even for sample no. 85 having the highest functionality ($n = 17$). Probably there will be a combination of factors such as the molecular architecture (e.g., functionality, size of the core, molecular weights of the arms) and/or the interactions of unlike segments that could affect the phenomenon. At this stage of our investigation no definite explanations can be given.

Conclusions

Differential scanning calorimetry has been used for the investigation of the phase behavior of new model macromolecules named heteroarm star copolymers. The theory of de la Cruz and Sanchez for the microphase separation of such polymeric species seems to satisfactorily explain the experimental results.

In some cases the samples exhibit a three-phase morphology, i.e., phase A, phase B, and a pronounced interface, A + B mixed phase, which may be attributed to the influence of the molecular architecture.

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