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End-functionalized block copolymers of styrene and isoprene. A d.s.c. study

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The influence of the end groups on the glass transition temperature, T_g, of the polyisoprene block of styrene–isoprene diblocks was studied by differential scanning calorimetry. The end-functionalized styrene–isoprene diblock samples used have dimethylamino and sulfobetaine groups attached on the polyisoprene chain end. An increase in the low temperature (polyisoprene-type) T_g value was observed for the lower molecular weight zwitterion capped polymers. This effect is attributed to restricted segmental mobility of the polyisoprene chains found in the proximity of the ionic aggregates. Copyright © 1996 Elsevier Science Ltd.

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Introduction

The incorporation of a small amount of ionic groups in a nonpolar polymeric chain changes dramatically the thermorheological properties of the material[1]. The thermal properties of random ionomers have been studied extensively[2]. Much work has also been done on the thermal and thermomechanical properties of halatotelechelic polymers[3-8]. These polymers, where salt groups are attached on each end of the polymeric chain, are considered to be model compounds for the study of the structure–properties relationships of the more complicated random ionomers. However, the case where the end group is a zwitterion (inner salt) has received little attention as far as the solid properties of these materials are concerned[9-11]. Some work concerning the thermal properties of random copolymers containing zwitterionic groups has also been published[12,13].

In this work we used differential scanning calorimetry (d.s.c.) to investigate, for the first time, the influence of the nature of the end group on the thermal behaviour of ω-functionalized zwitterionic diblock copolymers. These polymers are comprised of polystyrene and polyisoprene blocks and bear dimethylamino and sulfobetaine groups at the polyisoprene end. We are also interested in the existence of interrelations between ionic aggregation and phase separation of the incompatible blocks and their impact on the glass transition temperature of the block directly connected to the ionic groups. The study of these model systems, which unify the concepts of block copolymers and end-functionalized nonpolar polymers with ionic end groups, will eventually lead to the design of new polymeric materials with the properties tailored for specific applications.

Experimental

The synthesis and characterization of the styrene–isoprene diblock copolymers used in this work have been reported earlier[14,15]. The dimethylamino group was introduced at the polyisoprene chain end by polymerizing isoprene with the anionic functional initiator [3-(dimethylamino)propyl]lithium. Styrene was then polymerized in the presence of a small amount of tetrahydrofuran. The tertiary amine group was converted to sulfobetaine by reaction with cyclopropanesultone. The architecture of the copolymers is shown in *Scheme 1*. The molecular characteristics of the ω-functionalized diblocks are given in *Table 1*.

The d.s.c. measurements were performed on a Mettler Toledo model TA8000 thermal analyser under a continuous flow of nitrogen. The instrument was calibrated with heptane (melting point $-90.6^{\circ}C$, low temperature region) and indium (melting point $156.6^{\circ}C$, high temperature region). Vacuum dried samples, precipitated from methanol or acetone, were placed in the sample cell at room temperature and cooled down to $-150^{\circ}C$ at a rate of $15^{\circ}C\,min^{-1}$, where they were kept for 10 min. Subsequently the temperature was raised to $150^{\circ}C$ at a rate of $15^{\circ}C\,min^{-1}$ and the first thermogram was obtained. The sample temperature was kept at this value for 10 min and then it was lowered to $-150^{\circ}C$ at a cooling rate of $10^{\circ}C\,min^{-1}$. After another 10 min the samples were heated to $150^{\circ}C$ at a heating rate of $10^{\circ}C\,min^{-1}$ and the second thermogram was obtained. The glass transition temperature (T_g) was determined as the temperature at which the heat capacity of the sample was the mean between that of the glassy and rubber like states.

The glass transition region for the polyisoprene block was well-defined and at the low temperature range of the thermograms, whereas the T_g region for polystyrene was less well-defined and broad due to the low molecular weights of the samples. Measurements of T_g were

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reproducible within 2°C based on independent analyses of the same sample.

Results and discussion

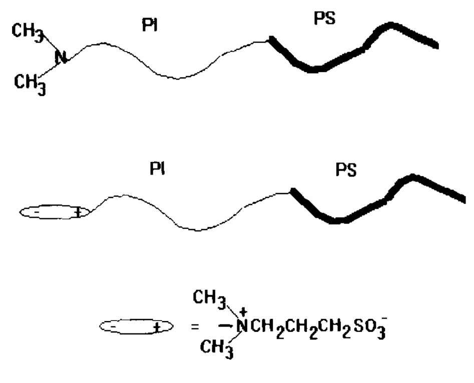
The results from d.s.c. are shown in *Table 2*. In this table the glass transition temperatures of the polyisoprene block of each sample are given, along with the width of the transition, defined as the difference between the onset and the endset temperatures.

In the case of the amine capped polymers the T_g values correlate rather well with the expected variation of T_g from the change in the polyisoprene microstructure[16] (*Table 1*). This change is due to the presence of the dimethylamino group on the initiator segment which acts as a polar modifier. The behaviour of the tertiary amine end-functionalized polymers does not differ from that of *s*-BuLi initiated (unfunctionalized) diblocks[17,18]. So the amine precursors can be used as reference materials for the zwitterion capped copolymers as far as the effects of diblock structure on the thermal behaviour of the samples are concerned. In this way we can isolate the effects on T_g connected with the presence of the more polar zwitterion group (see below).

The results for the diblock samples with the sulfozwitterionic group are more interesting. For the higher molecular weight polymers ($M_n > 12000$) the T_g values are the same as the ones obtained for the amine precursors (the ΔT_g values are the same within experimental error). For the two samples with the lower molecular weights an increase in the T_g of the polyisoprene block is observed (*Table 2*). The increase is larger than the experimental error. This is expected since the ionic content in the material increases as the molecular weight decreases. Furthermore, the width of the transition is the same for the amine and the zwitterion capped polymers indicating that the degree of mixing of the polymeric phases remains the same and no change is observed because of the change in the end group (the width for sample ZwIS-8 on the first heating cycle may be an exception as will be discussed below).

This phenomenon must be attributed to the ionic character of the sulfobetaine groups which tend to aggregate in the nonpolar hydrocarbon matrix of the copolymeric chains. These aggregates, whose concentration increases as the molecular weight of the chain decreases, act as crosslinks and decrease the mobility of the isoprene segments directly connected to them[1,2]. The decrease in mobility must be enhanced, compared to the case of halatotelechelic polymers[3,6,7], because of the tendency of the zwitterions to self assemble in an antiparallel fashion[17] (*Scheme 2*). This preference decreases the number of different placements of the ionic heads possible, in order to relax the restrictions on the tail segments. The portion of the chain that is hindered by the ionic associations may be the same irrespective of the molecular weight of the main chain if the size of the multiplets is constant, but as M_n decreases an increasing fraction of the tail is restricted in mobility giving rise to a higher T_g. An increase in the size of the multiplets by decreasing M_n would have the same effect[1]. Apparently, in the amine capped samples the dimethylamino groups, which are of much lower polarity, are unable to form aggregates. We can assume that even at the lowest molecular weights studied, the size of the ionic aggregates must be small (smaller than 100 Å, the typical resolution of d.s.c.) since no separate T_g could be observed, in the temperature range studied, that can be attributed to the ionic phase.

Another point that deserves mentioning is that the ΔT_g value of sample ZwIS-8 decreases from 11°C at the first heating run to 5°C at the second. On the other hand



Scheme 1

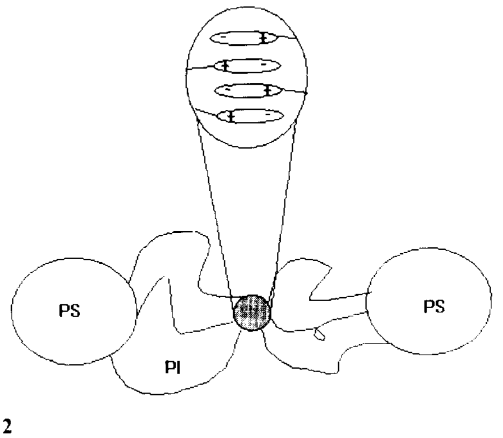
Table 1 Molecular characteristics of end-functionalized diblock copolymers

Sample	M_n[a] $\times 10^4$	M_n PI[a] $\times 10^4$	M_w/M_n[b]	% PS[c] (wt)	% 3,4[c] vinyl	% 1,2[c] vinyl
NIS-4	1.57	1.15	1.07	29	18.5	
NIS-5	1.22	0.88[d]	1.06	28	20	
NIS-8	0.83[d]	0.60[d]	1.10	27	28	
NIS-6	0.51[d]	0.43[d]	1.19	16	38	3

[a] By membrane osmometry
[b] By size exclusion chromatography
[c] By ^{1}H n.m.r.
[d] By vapour pressure osmometry

Table 2 D.s.c. results for end-functionalized diblock copolymers (polyisoprene-type glass transition region)

Sample	T_g^{15} (°C) (1st run)	Width (°C)	T_g^{10} (°C) (2nd run)	Width (°C)	ΔT_g^{15} (°C)	ΔT_g^{10} (°C)
NIS-4	−47	13	−51	10		
NIS-5	−48	14	−50	11		
NIS-8	−44	12	−45	14		
NIS-6	−30	12	−32	11		
ZwIS-4	−49	12	−53	12	−2	−2
ZwIS-5	−46	13	−50	11	2	0
ZwIS-8	−33	16	−40	14	11	5
ZwIS-6	−24	12	−26	11	6	6



Scheme 2

the ΔT_g value for sample ZwIS-6 remains constant in both runs. However, there are two distinct differences between the two samples. First, the molecular weight of the polystyrene block, and consequently the polystyrene content, is lower in sample ZwIS-6. Second, due to the lower overall molecular weight the ionic content is larger for ZwIS-6. Additionally, no second T_g, in the high temperature region is clearly observed for ZwIS-6 (or NIS-6), whereas for ZwIS-8 the width of the transition seems a little bit larger on the first heating run, where effects of sample history after precipitation can be observed. Sample NIS-6, and consequently ZwIS-6, can be considered to be in the disordered state at room temperature and presumably in thermodynamic equilibrium as far as the non-polar polymeric matrix is concerned. Thus the measured T_g value is independent of the thermal history and arises from the presence of the ionic domains (virtual crosslinks) in the sample. For sample ZwIS-8, and NIS-8, two separate T_gs could be observed suggesting that polyisoprene and polystyrene separate phases exist. Annealing at room temperature for several months after precipitation, is not enough to drive this polymeric system to equilibrium. After annealing at 150°C some constraints are relaxed for the polyisoprene segments close to the polystyrene phase since this temperature is higher than the T_g of the polystyrene phase.

In the phase separated copolymers under investigation the polyisoprene chain is forming a bridge between the ionic aggregates and the polystyrene hard phase (*Scheme 2*). Annealing can enhance the mobility in either of the two hard phases, if the annealing temperature is high enough for the ionic interactions to be decreased. This would permit some relaxation to take place in the polyisoprene segments closer to the hard phases. Annealing at 150°C surely produces movement in the polystyrene phase, since this temperature is much higher than the polystyrene T_g in all cases. The question that remains is whether the ionic multiplets remain intact at this temperature. Zwitterionic homopolymers are known to have fairly high T_gs judging from the behaviour of sample ZwIS-6, in relation to that of sample ZwIS-8, it seems that when the bridging chains are not restricted from one end no annealing effects are evident. Thus, the zwitterionic aggregates must be stable at the highest temperature studied and over the time period used for the annealing. The behaviour of sample ZwIS-8 implies that in these three phase systems organization in each phase is interrelated with processes taking place in the other phases and each process contributes to the thermal history and behaviour of the whole sample.

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