

MOLECULAR-WEIGHT DEPENDENCE OF THE GLASS TRANSITION TEMPERATURES OF RIGID SIS TRIBLOCK COPOLYMERS STUDIED BY DSC

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Differential scanning calorimetry (DSC) measurements have been carried out on a series of ABA poly(styrene-*b*-isoprene) triblock copolymers with 30% polyisoprene content and various molecular weights. The DSC data show an inward shift for the glass transition temperatures (T_g) of the blocks compared to the corresponding homopolymers. As a function of the molecular weight, one to three transitions were found. The additional third T_g gives some further evidence of the existence of an interphase between the microdomains.

Numerous studies [1, 2] on multicomponent polymer systems have established the occurrence of phase segregation and microdomain formation when two or more polymers are combined. In block copolymers, the factors governing the size of the domains depend on the number and length of the blocks and on their chemical nature.

Meier [3] was the first to develop a theory about microphase formation for styrene-butadiene di- and triblock copolymers [4]. He showed that above a certain molecular weight, phase segregation takes place. Williams [5] and later Helfand [6] investigated the formation of an interphase: between the two pure phases, a region of mixed phases exists. These authors evaluated the influence of molecular weight and composition of the different blocks on the size of the pure phases and of the interphase. Particularly, the volume of the interphase increases with decreasing molecular weight. Toporowski and Roovers [7] as also Kraus and Rollmann [8] concluded that some low molecular weight block copolymers form a single phase. Through these investigations, block copolymers may exist in the solid state with morphologies going from a single phase to a completely organized two-phase structure.

Glass transition temperatures (T_g) are commonly used to detect phase changes in copolymers. Two distinct T_g 's corresponding roughly to those of the parent homopolymers appear when two well segregated phases exist in a copolymer. On the other hand, random copolymers known to exist as a single phase, show only one T_g , the value of which depends on its phase content. Thus, the number of transitions and the temperature at which they occur, provide information about the morphology of SIS copolymers.

In the present note, we report results obtained for rigid ABA poly(styrene-*b*-isoprene) block copolymers with various total molecular weights. These SIS copolymers have all the same composition, about 30% polyisoprene by weight. Their T_g 's have been determined by differential scanning calorimetry (DSC).

Experimental

Material and characterization

SIS block copolymers were prepared in benzene by a three-step anionic polymerization described in detail elsewhere [9]. Homopolymer controls also used in these experiments were obtained as follows: the polystyrene samples were the "parent" homopolymers removed after the first step in the SIS synthesis. Polyisoprene was prepared by anionic synthesis in benzene, which yields mainly 1,4 microstructure.

Block molecular weights were determined by gel permeation chromatography using a universal calibration curve [10]. The molecular characteristics, total molecular weight (M_{tot}) and polyisoprene content are shown in Table 1.

Table 1
Molecular characteristics of the SIS triblock copolymers

Sample code	Block molecular weights, g/mol	M_{tot}	Polyisoprene, wt-%
SIS-1	32 000—25 000—32 000	89 000	28.1
SIS-2	28 000—21 000—28 000	77 000	27.7
SIS-3	21 000—17 500—21 000	59 500	29.9
SIS-4	16 000—13 500—16 000	45 500	29.7
SIS-5	11 000—9 000—11 000	31 000	29.9
SIS-6	8 500—7 500—8 500	24 500	30.1
SIS-7	6 500—6 000—6 500	19 000	30.9
SIS-8	4 600—4 200—4 600	13 400	31.3
SIS-9	3 600—3 300—3 600	10 500	31.4
SIS-10	2 000—1 800—2 000	5 800	31.0

DSC measurements

The T_g values were determined with a Perkin-Elmer DSC-1B calorimeter. Preceding the first measurement, the samples were annealed for 10 min at 147° and brought back to the starting temperature at a rate of 4°/min. As T_g depends strongly on the rate of heating, we operated at various heating rates ($v = 4, 8, 16, 32^\circ/\text{min}$). For each rate, three measurements were carried out with less than 1° deviation between these three values. As there are numerous—but all open to criticism—methods [11, 12] to obtain zero-heating-rate transition temperatures, we only

report here the results rounded to the nearest half-degree for a heating speed of 8°/min, which are a good reflexion of the behavior of the copolymers studied. The rise in heat capacity, ΔC_p , at T_g was evaluated by measuring the difference in height between the extrapolated base lines recorded before and after the transition.

Results and discussion

DSC curves for several SIS are shown in Fig. 1. It can be seen, as the total molecular weight M_{tot} decreases, a substantial decrease of ΔC_p and a broadening of the transition zone for both phases. Progressively, the upper and lower T_g 's corresponding to the hard and soft blocks disappear, whereas an intermediate T_g appears. Copolymers SIS-1 and SIS-4 have two distinct transition steps which indicate a sharp phase separation. SIS-5 yields 3 T_g 's: there is a third phase which can only originate from a mixing of PS and PI phases. For still smaller molecular weights only one relative sharp glass transition is visible, that indicates a rather well-defined phase. As ΔC_p for homopolymers does not change with molecular weight and if one assumes that the magnitude of ΔC_p is a measure of the weight fraction of the pure phase, one can conclude that there is a significant mutual solubility of both phases rather than partial solubility of the soft domains in the glassy matrix as M_{tot} decreases.

The glass transition temperatures of the copolymers are given in Table 2. The T_g of the hard phase decreases with M_{tot} and disappears for SIS with M_{tot} less than

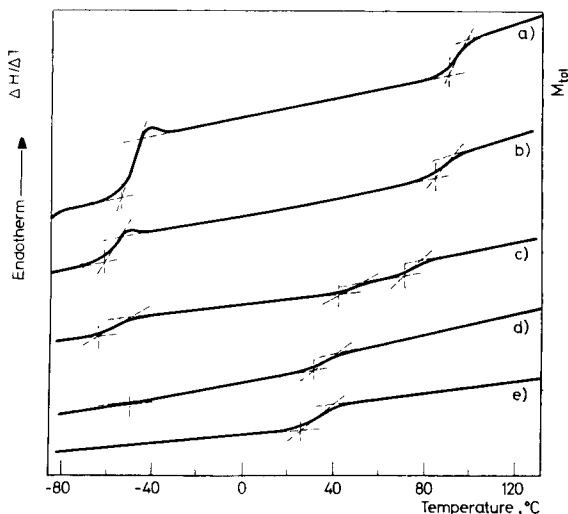


Fig. 1. Typical DSC curves of SIS block copolymers with various total molecular weight (a) 89000; (b) 45500; (c) 31000; (d) 19000; (e) 10500

Table 2

DSC results of the SIS triblock copolymers at a heating rate of 8°/min

Sample code	Lower T_g , °C	Medium T_g , °C	Upper T_g , °C
SIS-1	-52		92.5
SIS-2	-44		89.5
SIS-3	-55.5		89
SIS-4	-59.5		84
SIS-5	-60	41.5	76
SIS-6	-54	38	60.5
SIS-7		31.5	
SIS-8		35	
SIS-9		28.5	
SIS-10		14	

about 25 000. The lower T_g corresponding to the soft phase is irregularly dispersed around -57° . When an intermediate or single T_g appears, it varies with M_{tot} . In any case, it may be clearly distinguished from the pure homopolymer transition zones as shown in Fig. 2. The upper scale gives the molecular weight of the PS block, the lower one that of the corresponding PI block. The variable, M_{tot} , appears also on both scales.

As can be seen, the T_g of homopolystyrene decreases with molecular weight, according to Fox and Flory's general expression [13]. On the contrary, T_g 's of homopolyisoprene are all near -70° and their variation with molecular weight is slight and irregular. We examined this problem elsewhere [14] and it will not be discussed here.

In Fig. 2, the T_g 's of the copolymer and the homopolymers with a molecular weight corresponding to that of each block, appear on the same vertical. With respect to the T_g 's of homopolymers, an inward shift is always observed for those of the copolymers. Hence, there is an additional effect due to structure, namely covalently bonded blocks of different chemical nature. For the upper T_g , this effect becomes more pronounced when M_{tot} decreases. Thus for high molecular weights, over 60 000, the difference is small and one can safely conclude that two distinct phases exist with few or no interdiffusion at their boundaries. As M_{tot} decreases, the domain becomes smaller. For lower M_{tot} , the chain ends also tend to increase the free volume. Under these conditions, phase mixing easily occurs: depending on its volume fraction, an intermediate T_g first appears, followed by a single transition.

Several authors [8, 15] have reported an abnormal lowering of T_g of the hard phase in polystyrene-polydiene di- and triblock copolymers and particularly controversial has been the assumption of pure phases and mixed interdomain region [16, 17]. To our knowledge the existence of a third mixed phase which coexists with the pure phases or which dominates for very low molecular weight block copolymers has not yet been detected experimentally.

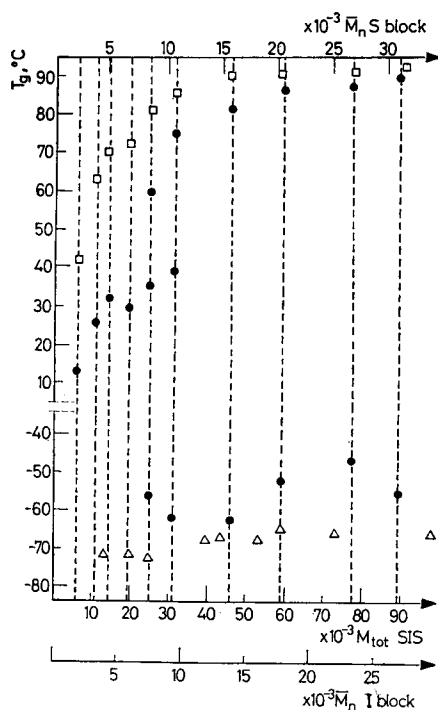


Fig. 2. Experimental glass transition temperatures, T_g , as a function of molecular weights, M_{tot} or M_n : (●): SIS block copolymer; (□): bulk polystyrene; (△): bulk polyisoprene

Comparison of observed and predicted values of the glass transition temperature may be of complementary usefulness. In recent publications, Couchman [18, 19] has reported a general thermodynamic theory to predict T_g in compatible blends from pure-component properties, i. e. glass transition temperature and heat capacity increment. By making several approximations, one will find the following classical empirical expressions elaborated for a binary mixture of homopolymers A and B:

$$\frac{1}{T_g(AB)} \approx \frac{x_A}{T_g(A)} + \frac{x_B}{T_g(B)} \quad (1)$$

which is identical to Fox's [20] model based on free volume considerations;

$$T_g(AB) \approx \frac{\Phi_A \cdot T_g(A) + k \cdot \Phi_B \cdot T_g(B)}{\Phi_A + k\Phi_B} \quad (2)$$

which is similar to Dimarzio-Gibbs [21] expression derived from configurational entropy hypothesis or Wood [22] equation for random copolymers;

$$\ln T_g(AB) \approx \Phi_A \cdot \ln T_g(A) + \Phi_B \cdot \ln T_g(B) \quad (3)$$

which is a logarithmic relationship formally empirically established by Pochan, Beatty and Pochan [23]. In these equations x and Φ are the weight and volume fraction, respectively and k a constant approximately equal to unity.

The values calculated according to the above equations are coded T_{g_1} , T_{g_2} and T_{g_s} in Table 3 where they are compared with the intermediate or single T_g found

Table 3
Predicted and observed values of the glass transition temperature for the polystyrene/polyisoprene mixed phase

Sample code	Glass transition temperature			
	experimental data T_g	calculated data ^a		
		T_{g_1}	T_{g_2}	T_{g_s}
SIS-5	41.5	18.8	34.3	24.6
SIS-6	38	17.3	32	22.8
SIS-7	31.5	11.3	24.3	15.9
SIS-8	35	9.7	22.5	14.2
SIS-9	28.5	5.8	17.1	9.6
SIS-10	14	-4.2	3.4	-2.0

a) T_{g_1} , T_{g_2} and T_{g_s} according to references [20], [21] and [23], respectively.

experimentally. As may be expected, they do not actually coincide with the experimental T_g , but are satisfactorily close to it, especially less than 10° for T_{g_s} which may be due to heatin grate effects. This indicates a definite phase mixing for some SIS, but also that their structure in blocks still differentiates them from a simple polymer blend.

Conclusions

In these experiments, we examined the glass transition behavior of a series of glassy SIS block copolymers with nearly 30% polyisoprene. Depending on their molecular weight, two, three or one single T_g were detected by DSC measurements. Three T_g 's are shown by SIS having a total molecular weight of approximately 30000 g/mol: two pure phases coexist with a rather well defined third phase which results from some mutual phase mixing. Such copolymers may be regarded as the boundary between single phase and dual phase copolymers.

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ZUSAMMENFASSUNG — DSC wurden an einer Reihe von ABA Poly(styrol-*b*-isopren) Dreiblock-Kopolymeren mit 30% Polyisoprengehalt und verschiedenen Molekulargewichten durchgeführt. Die DSC-Daten zeigen eine innere Verschiebung der Glas-Übergangstemperaturen (T_g) der Blöcke im Vergleich zu den entsprechenden Homopolymeren. Als Funktion des Molekulargewichts wurden ein bis drei Übergänge gefunden. Die zusätzliche dritte T_g erbringt weitere Beweise bezüglich der Existenz einer Interphase zwischen den Mikrodomänen.

Резюме — Проведены ДСК-измерения ряда АБА поли(стирол-*b*-изопрен) трехблочных сополимеров с различным молекулярным весом и содержащих 30% полиизопрена. Данные ДСК показали внутренний сдвиг температуры стеклообразования (T_g) блочных сополимеров по сравнению с соответствующими гомополимерами. В зависимости от молекулярного веса полимеров было найдено от одного до трех переходов. Наличие дополнительного третьего T_g перехода служит дальнейшим доказательством существования какого-либо межфазного состояния между микродоменами.