

Synthesis and Thermal Analysis of Styrene and α -Methylstyrene Multiblock Copolymers

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Summary

Multiblock copolymers of styrene and α -methylstyrene ($M_n \leq 70.000 \text{ g.mole}^{-1}$) with various α -methylstyrene contents were synthesized by anionic polymerization. The glass transition temperatures (T_g) of these copolymers have been measured by D.T.A. A single T_g was observed over the whole composition range. This T_g obeys the derived GORDON and TAYLOR equation. Moreover these copolymers are heat resistant up to temperatures of at least 280°C .

INTRODUCTION

Copolymers of styrene (St) and α -methylstyrene (α MSt) have been much studied since BAER (1) discovered that triblock copolymers (poly styrene-block-poly α -methylstyrene-block-polystyrene or poly α -methylstyrene-block-polystyrene-block-poly α -methylstyrene) have a single glass transition temperature intermediate between the T_g 's of the homopolymers. This behavior was unusual for block copolymers and BAER suggested that the reason of this single T_g was due to compatibility of the polymers giving a one-phase system.

ROBESON et al. (2) studied anionic diblocks and their blends with homopolymers. They found that one-phase behavior is observed for diblock copolymers having molecular weights up to 200.000 for each block. Samples containing 50 mole percent of each constituent have a single T_g between 130 and 138°C according to the molecular weights and the type of copolymer, the higher T_g being relative to a random copolymer. In the case of blends with homopolymers, the authors found that poly α -MSt exhibits a single T_g in blends with its block copolymers while they observed two T_g 's in the case of blends with poly St.

More recently, WORSFOLD et al. (3) confirmed the existence of a one-phase behavior for block copolymers of styrene and α -methylstyrene.

This phenomenon has given rise to more detailed studies. It was found that compatibility in the case of these copolymers or of blends depends on the molecular weights, the percentage of each constituent and also on the techniques used.

From a D.S.C. study performed on films made by solvent casting SAEKI et al. (4) concluded that blends of homopolySt and homopoly α MSt display a range of miscibility which is a function of molecular weights and composition of the blends and also of the nature of the casting solvent. When toluene was used a single T_g was observed when the respective molecular weights of the components were lower than $70\ 000 \text{ g.mole}^{-1}$. This limit decreased down to $50\ 000$ when propylene oxide was used as solvent.

Solubility parameters of polySt and poly α MSt are very similar and KRAUSE (5) predicted that blends of these homopolymers (50:50 mixture) should be homogeneous when the respective molecular weights are both lower than 10^5

and that diblocks or triblocks should give one phase up to molecular weights respectively equal to 8×10^5 and 1.2×10^6 . The results of BAER (1) and of ROBESON (2) are in agreement with these assumptions. Later KRAUSE et al. (6) observed that diblock copolymers of St and α MSt are homogeneous up to a higher molecular weight range than blends of homopolymers. This author predicted that as the number of blocks increases in block copolymers of equal composition and molecular weight, microphase separation becomes more and more difficult (7).

Recently, WUNDERLICH et al. (8) reexamined St and α MSt copolymers by D.S.C. and electronic spectroscopy. They found that a triblock copolymer ($M_n = 4 \times 10^5$) who was considered homogeneous i.e. having a single Tg by KRAUSE was in fact phase separated. The very broad Tg signal was assumed to be the end of the poly St glass transition extending to higher temperatures and the beginning of the poly α MSt glass transition extending to lower temperatures.

The problem of compatibility between poly St and poly α MSt is complex and the molecular weight seems to be of great importance. In this paper we shall describe our results concerning multiblock St and α MSt copolymers of various compositions.

EXPERIMENTAL

Homopolymers and block copolymers were synthesized by anionic polymerization in a vacuum system ($< 10^{-5}$ torr). Toluene was used as the solvent and sec-BuLi ($2 \sim 3 \cdot 10^{-3}$ M) as initiator. In the case of copolymers a small quantity of St was first initiated at room temperature. Then the solution was cooled at -78°C in order to introduce the whole amount of α MSt by cryo-distillation. The mixture was then warmed up to -30°C , temperature of copolymerization. In order to increase the yields of poly α MSt, THF in amounts of 10 % in volume was added as an accelerator (as in the case of homopoly α MSt synthesis). When the small amount of St was consumed the orange solution turned red indicating the polymerization of α MSt. After polymerization of some α MSt an identical new small amount of St was added to the mixture through a Rotaflo^R stopcock. The process was renewed at regular intervals the solution being alternatively red or orange. These intervals were chosen arbitrarily in function of St polymerization (change from orange to red). For instance St polymerized in 15 to 30 min. and α MSt was allowed to polymerize during 30 to 45 min. As the kinetics of the α MSt polymerization in toluene-THF mixture is not known it is difficult to be sure of the length of the respective poly α MSt blocks. The last poly α MSt block, which was formed during a whole night might have an higher molecular weight than the first ones. However for this block the monomer concentration is very low and the polymerization rate is lower than for the formation of the previous α MSt blocks. In order to prevent depolymerization at temperatures higher than 230°C (9) the ultimate block of the copolymers was always a poly St block. Molecular weights were measured by osmometry (MECHROLAB osmometer) and the molecular weight distributions were determined by G.P.C. (WATERS chromatograph equipped with five μ styragel columns with THF as eluant at $1 \text{ ml} \cdot \text{min}^{-1}$). α MSt content and microstructure were determined by ^1H NMR spectroscopy (90 MHz VARIAN or 250 MHz BRUCKER). Tg's were measured by D.T.A. on a DUPONT 990 instrument. The samples were annealed before measurement. The Tg was determined at the inflexion point of the curve at a heating rate of $5^\circ\text{C} \cdot \text{min}^{-1}$.

RESULTS AND DISCUSSION

The characteristics of the homopolymers and copolymers are summarized in table I. As may be seen, the Tg of homopoly α MSt are very dependent on mo-

lular weight for molecular weights lower than 20.000 g.mole⁻¹. This agrees very well with the results of COWIE et al.(10) and of MALHOTRA et al.(11).

TABLE 1 : Characterization of homopoly α -methylstyrenes and styrene and α -methylstyrene multiblock copolymers.

	% weight α MeSt	\overline{M}_n osmo	$\overline{M}_w/\overline{M}_n$ (G.P.C.)	Total number of blocks	Tg (°C)	T _{decomp.} (°C)
Homopolymers						
α MSt	100 1)	5000	1,2		123	
	100 2)	11000	1,9		165	
	100 3)	14000	1,23		169	
	100 4)	20000	1,11		176	230
St	0	190000			107	340
Copolymers						
	43	24000	1,11	5	133	300
	50	19800	1,13	11	135	300
	63	70000	1,08	7	151	280
	76	27000	1,15	17	158	300
	85	26000	1,08	7	161	280

Conditions of syntheses : Homopolymers of α MSt : in toluene with polar additives. 1) anisole : 40 % vol, - 17°C. 2) THF : 28 % vol, - 17°C 3) THF : 12 % vol, - 30°C 4) THF : 5 % vol, - 30°C ; HomopolySt : THF - 78°C ; copolymers : in toluene with 10 % in volume of THF ; initiator : sec-BuLi \approx 2 to 3 x 10⁻³ M ; time of polymerization \sim 20 to 22 h.

COWIE et al.(12) also found that syndiotactic polymers have an higher Tg than atactic polymers. In our case, our polymers have approximately the same microstructure (i \approx 10 ; h \approx 40 ; s \approx 50 %). Our Tg values are higher than those found by COWIE but this difference may be due to the method of Tg measurement (beginning of transition in COWIE's case and inflexion point of the curve in our case). Our values are closer to those of MALHOTRA determined at a heating rate of 1°C.min⁻¹ and slightly higher probably because our samples are more mono disperse. Moreover, for a \overline{M}_n equal to 20000, the observed Tg is nearly the same as that of high polymers described in the litterature (from 172°C (10) to 180°C (11)). For block copolymers, only one Tg is observed. The values and the temperature of decomposition are given in table 1. The Tg increases with α MSt content. The variation of Tg versus weight percentage of α MSt is shown in fig. 1. On this plot we added ROBESON's value (2) and SHULTZ's value (13) respectively for a block copolymer and a statistical copolymer having both nearly 50 % of α MSt. Their values are in good agreement with our's. The GORDON and TAYLOR equation (14) established for random copolymers and verified for poly(ester 1-co-ester 2) block copolymers (15) was applied to our values. In figure 2 we plotted (Tg-Tg₁)/(Tg-Tg₂) versus ω_2/ω_1 where ω_1 and ω_2 are weight fractions of St and α MSt units ; Tg₁ and Tg₂ the Tg's of homopolySt and homopoly α MSt respectively and Tg of the block copolymer. Tg₁ and Tg₂ were values determined on our samples. As may be seen on this plot, the derived GORDON and TAYLOR equation is verified within experimen-

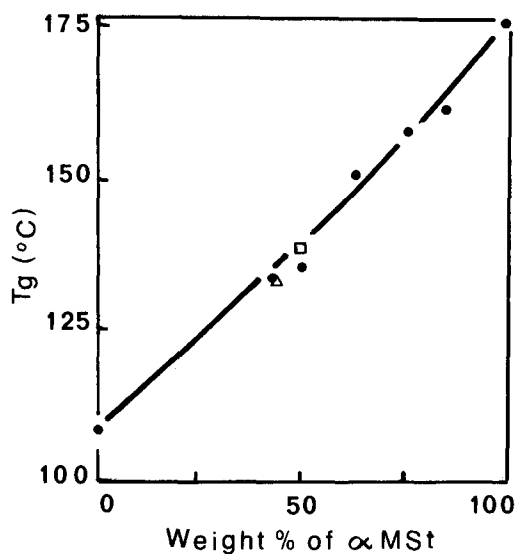


Fig. 1 : Dependence of T_g on weight percentage of α -methylstyrene for styrene and α -methylstyrene multiblock copolymers

- our results
- Robeson (2)
- △ Shultz (13)

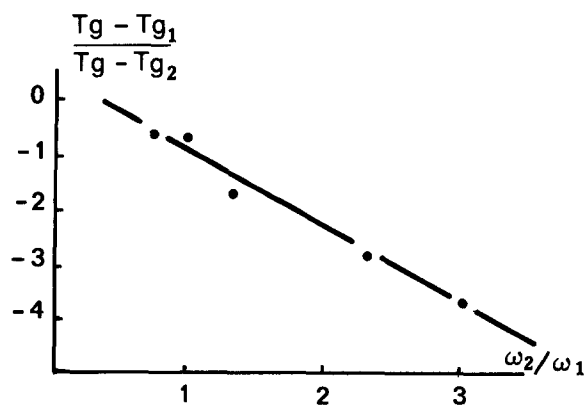


Fig. 2 : Verification of Gordon and Taylor equation for styrene and α -methylstyrene multiblock copolymers.

tal errors (that may occur in the determination of weight fractions or T_g values).

Whereas it was known that diblock or triblock copolymers of St and α MSt have a single T_g intermediate between the T_gs of homopolymers, the GORDON and TAYLOR equation has not been applied yet to this type of copolymer. This relationship was verified only for polySt and poly α MSt blends of various compositions with molecular weights lower than 9×10^4 (16) or for poly (St-stat- α MSt) (13) copolymers.

An increase in the number of blocks seems also to improve the heat resistance of the copolymers. For an α MSt content of approximately 50 % degradation begins at about 300°C (poly α MSt decomposes at 230°C), while ROBESON (2) observed it at 230°C for triblocks, and this even for copolymers having polySt end blocks as for our samples. The increase of T_g with α MSt content for multiblock copolymers of St and α MSt and the absence of degradation around 230°C may be of interest for plastic materials processability i.e. for molding at high rate.

CONCLUSION

Monodisperse low molecular weights poly α -methylstyrene were synthesized by anionic polymerization in mixed solvents (toluene/anisole or toluene/THF) at low temperature with sec-BuLi as initiator. For a sample with a molecular weight of 20000 g.mole⁻¹, the T_g is nearly the same as for high polymers.

Multiblock copolymers of styrene and α -methylstyrene ($M_n \leq 70000$) of various compositions were obtained in toluene containing 10 % in volume of tetrahydrofuran at -30°C with sec-BuLi as initiator. These copolymers are monodisperse and exhibit a single glass transition temperature which follows the derived GORDON and TAYLOR equation. The increase of T_g with α -methylstyrene content and a thermal stability up to about 280°C may be of interest for the manufacturing of heat resistant plastic materials.

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