Glass Transitions of Some Block Copolymers

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Synopsis

A number of block and graft copolymers have been prepared from several vinyl monomers, and their glass transition temperatures measured. The series included polar, nonpolar and polar-nonpolar pairs. It was found in all cases except one that the glass transition temperatures were close to those found for the individual homopolymers. The exception was a block copolymer of styrene and α-methylstyrene, the only pair whose homopolymers would give clear mixed solutions in a mutual solvent.

INTRODUCTION

Reports in the literature on the glass transition (T_g) of block and graft copolymers show that frequently the copolymers have two separate glass transitions,[1] each one close to the glass transitions of the parent homopolymers. Block and graft copolymers with T_g values at intermediate temperatures have also been reported.[2] As yet the behavior appears rather unpredictable.

The occurrence of mutual solubility in homopolymer pairs is rare,[3] and the block copolymers of such pairs would be expected to show only one transition. For other pairs to show only one T_g in their block copolymers, when each block is of reasonable size, the single link between them would have to be sufficient to overcome their mutual incompatibility.

Most reports are of only one or two polymer pairs, and different methods of measurement are used in different reports. This paper describes a larger series of block and graft copolymers, with T_g values all measured by the same technique. The polymers are all of the vinyl addition type, but cover polar–polar, polar–nonpolar, and nonpolar–nonpolar pairs.

EXPERIMENTAL

Where suitable, the polymers were prepared by sequential anionic polymerization. Others were prepared from polystyrene or poly(α-methylstyrene) containing styryl endgroups, as described before.[4] Two were prepared by grafting onto a base polymer of poly(methyl methacrylate) containing styryl endgroups. This base polymer was formed by anionic polymerization in THF, using as initiator butyllithium to which had been added, in rapid succession, two equivalents of p-divinylbenzene and an

excess of diphenylethylene. This gave as an initiator a diphenylmethyl-lithium substituted with one or two styryl groups.

The polymers were checked by GPC to detect the presence of homo-polymers; and, if necessary, they were treated by solvent extraction to be essentially free of homopolymer. The blocks were all over 20,000 in molecular weight.

The T_g values were measured on a Perkin-Elmer thermomechanical analyzer TMS1. The expansion mode was used, with a temperature rise of 5°/min and a load of 3 g. Some confirmatory runs were made on a differential scanning calorimeter, and some by a density gradient method.

RESULTS

The T_g values are shown in Table I. In this series, with only one excep-tion, the polymers show the presence of glass transitions in the region of those of the parent polymers. The polystyrene–poly(methyl methacry-late) block copolymer shows only one transition. But as the T_g's of the homopolymers measured by this technique were 101° and 106°C, respec-tively, it would be difficult to separate them. The random copolymer of this pair shows only a small decrease in T_g at this composition,[5] so little can be said about this system. The polystyrene–poly(ethylene oxide) block copolymer also showed the crystal melting point of poly(ethylene oxide) as well as the two T_g's.

The only real exception is the block copolymer of styrene and α-methyl-styrene, which only showed one transition at 127°C between those of the homopolymers. This was found also by Baer.[1] The homopolymers are not fully compatible, however, because when the two polymers are copre-cipitated, the mixture shows two transition points (Fig. 1). There must

TABLE I
Glass Transitions of Block and Graft Copolymers

| M_1	M_2	$\%M_1$	Total MW	Lower T_g	Upper T_g
α-Methylstyrene	vinyl acetate	18	103,000	35	182
α-Methylstyrene	vinyl chloride	67	39,000	−8	182
α-Methylstyrene	styrene	45	61,000	127°	
Styrene	methyl methacrylate	40	70,000		98°
Styrene	butyl acrylate	46	104,000	−55	99
Styrene	ethylene oxide	50	40,000	−72	100
Styrene	isoprene	50	1,000,000	−75	101
Styrene	isobutylene	40	141,000	−69	102
Methyl methacrylate	ethyl acrylate	56	162,000	−23	115
Methyl methacrylate	vinyl acetate	50	96,000	38	98
Methyl methacrylate	ethyl methacrylate	50	104,000	69	106
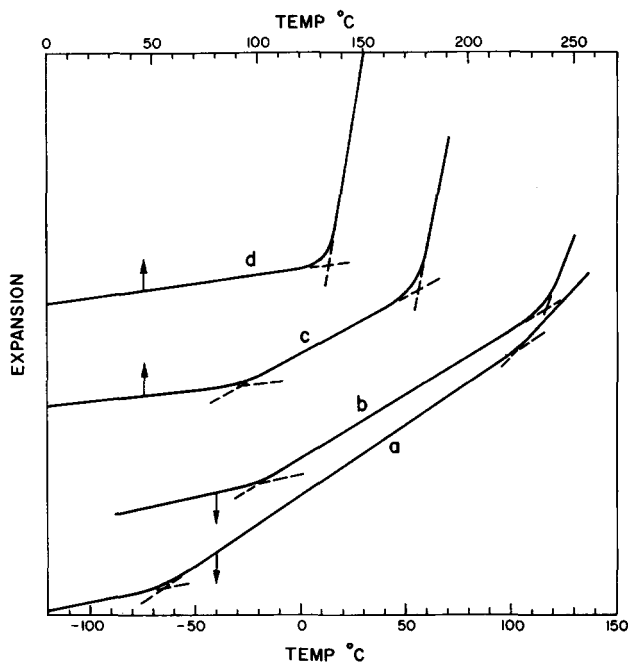
Fig. 1. Expansion curves for (a) styrene–isoprene block copolymer, (b) methyl methacrylate–ethyl acrylate block copolymer, (c) a coprecipitated mixture of polystyrene and poly(α-methylstyrene), and (d) styrene–α-methylstyrene block copolymer. Expansion scale is in arbitrary units.

be some degree of compatibility between the homopolymers, however, because it was found possible to prepare a 30% solution of the mixed polymers in benzene which showed no turbidity, even in transverse illumination.

The isomeric pair ethyl acrylate and poly(methyl methacrylate) gave two T_g's. One was near that of poly(ethyl acrylate), but the other was somewhat anomalous, at 115°, which is 9° higher than the parent poly-(methyl methacrylate). These two homopolymers showed slight turbidity in transverse illumination, even at 10% concentration in benzene. The block copolymer of methyl methacrylate with ethyl methacrylate gave the normal T_g's. But in the block copolymer with vinyl acetate, the T_g of the PMMA block was slightly lower than normal, and that of PVAc was rather higher than normal.

It appears, as a general rule, that separation of the two phases will occur, even in polar pairs with such small differences as in the case of PMMA and PEMA or PEA, where mutual attraction might occur. Where sufficient compatibility of homopolymers does exist to give a single T_g, this may be indicated by their ability to give clear concentrated solutions in a mutual solvent.

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