Cationic Polymerization of α-Methyl Styrene from Polydienes. II. Tensile Properties of Poly(butadiene-g-α-Methyl Styrene) and Poly(styrene-b-Butadiene-g-α-Methyl Styrene) Copolymers

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Synopsis

Tensile properties of poly(butadiene-g-α-methyl styrene) copolymers have been investigated on molded samples. These graft copolymers show thermoplastic elastomer behavior because of their graft copolymer structure. Both modulus and strength increase with increasing α-methyl styrene content and tensile strength is highest at the 45–50% by weight α-methyl styrene level. Tensile strength at elevated test temperatures is considerably higher for these poly(butadiene-g-α-methyl styrene) copolymers than for styrene-butadiene-styrene triblock polymers. This is attributed to the higher glass transition temperature for poly(α-methyl styrene) segments compared to polystyrene segments. The oil acceptance of these graft copolymers appears to depend on the number of loose polybutadiene chain ends. Thus, the tensile strength of oil-extended poly(butadiene-g-α-methyl styrene) copolymers was considerably lower than oil-extended poly(styrene-b-butadiene-g-α-methyl styrene) copolymers even though both copolymers contained equal hard segment contents.

INTRODUCTION

Thermoplastic elastomers have been investigated widely because of their unique combination of properties and processability.[1,2] The primary structure utilized as a thermoplastic elastomer in these early investigations was the A—B—A triblock polymer in which A represents a rigid segment such as polystyrene and B represents an elastomeric segment such as polybutadiene.[3] More recently, a number of investigators have shown that thermoplastic elastomers can also be obtained from graft copolymer structures.[4,5] In both triblock and graft copolymer structures the hard segments migrate into domains which impart both physical crosslinks and reinforcement to the elastomeric matrix. In spite of this basic similarity, however, there are subtle differences between the triblock and graft copolymer structures that can influence the mechanical properties of these materials. Most notably, the molecular weight between physical tie points is constant in A—B—A triblock polymers but variable in graft copolymers, depending on position and number of grafts per chain. In addition, triblock polymers have no loose or dangling elastomeric chain ends, while this is rarely the case with graft copolymers. In principle, a graft copolymer should have at least two rigid grafts per chain in order for the copolymer to possess thermoplastic elastomer characteristics. Even then the grafts must be reasonably well spaced or a uniform network will not result.

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In an earlier report,[6] we described the preparation of poly(butadiene-*g*-*α*-methyl styrene) (PBd-*g*-MS) copolymers. It was shown that under the proper grafting conditions, the grafting efficiency was 100% and no homopolymer was present. It was also pointed out that these copolymers, with elastomeric backbones and rigid grafted side chains, have the structure necessary for possessing thermoplastic elastomer behavior.

The present study is concerned with the effect of graft copolymer structure on the tensile properties of PBd-*g*-MS and poly(styrene-*b*-butadiene-*g*-*α*-methyl styrene) (PS-*b*-PBd-*g*-MS) copolymers. We have molded these copolymers with and without oil and measured the tensile properties of the molded samples. The effects of various structural parameters on tensile properties, including copolymer composition and grafting frequency, were then investigated.

EXPERIMENTAL

Polymerizations. All graft copolymers were prepared according to procedures described previously.[6] For those copolymers having a styrene-*b*-butadiene diblock backbone, the backbone was prepared anionically in cyclohexane using butyllithium initiator at room temperature.

Compounding and Molding. The only compounding ingredient employed was a naphthenic oil obtained from the Shell Chemical Co. (Shellflex 371-N) and used without further purification. The oil was added to the copolymers on a mill at 85°C at the 45 parts per hundred (phr) polybutadiene level. All samples were compression molded at 160°C for 10 min and cooled under pressure.

Mechanical Property Measurements. Tensile strength, modulus, and elongation were measured on elastomers according to ASTM Method D-412.

Polymer Characterization. NMR spectra were measured at 60 MHz in $CDCl_3$ at room temperature to investigate copolymer composition. Osmotic molecular weights were measured in toluene with a Mechrolab model 502 osmometer. Grafting efficiencies were determined by the method described previously.[6] The chlorine content of the polymer backbones was determined according to the method of Altenau and co-workers.[7]

RESULTS AND DISCUSSION

Polymer Characterization

The compositions, backbone molecular weights, grafting efficiencies (GEs), and backbone allylic chlorine concentrations [Allylic Cl] of the copolymers examined are presented in Tables I and II. Grafting efficiencies were high in all of the copolymers listed. The allylic chlorine concentrations of the polymer backbones are included because we showed earlier[6] that the number of grafts per chain (*f*) increases as the allylic chlorine concentration increases. While we did not actually measure *f* for the copolymers listed in Tables I and II, we expect a value for *f* of 1.7 for samples 1 through 6 and a value of 3.0 for sample 7 based on their respective allylic chlorine concentrations.[6]

TABLE I
Characterization of PBd-g-MS Copolymers

Sample No.	MS in Copolymer (wt %)	GE (%)	[Allylic Cl] (wt %)	$\overline{M}_n$ PBd backbone (g/mol × 10⁻⁵)
1	30	88	0.50	1.16
2	41	86	0.50	1.16
3	46	98	0.47	1.14
4	46	94	0.46	1.14
5	50	92	0.47	1.14

Polymer Evaluation

Figure 1 illustrates the effect of copolymer composition on tensile properties measured on a series of PBd-g-MS copolymers. The stress levels at any given extension show a dependence on the α-methyl styrene content as might be expected. The ultimate strength appears to be maximized at the 45–50% α-methyl styrene level. Since these PBd-g-MS copolymers are thermoplastic or uncured, they presumably owe their strength to domain formation arising from the graft copolymer structure. One interesting feature of these copolymers is that they have relatively low tensile strengths at the 30% α-methyl styrene level. In fact, it is only at >35% α-methyl styrene contents that we observed high tensile strengths. This is in contrast to the A—B—A triblock polymers mentioned earlier which have high strengths at the 25–30% styrene level.[3] Perhaps the differences in polymer structures, i.e., block versus graft contribute to these differences in tensile strength behavior.

TABLE II
Characterization of PS-b-PBd-g-MS Copolymers

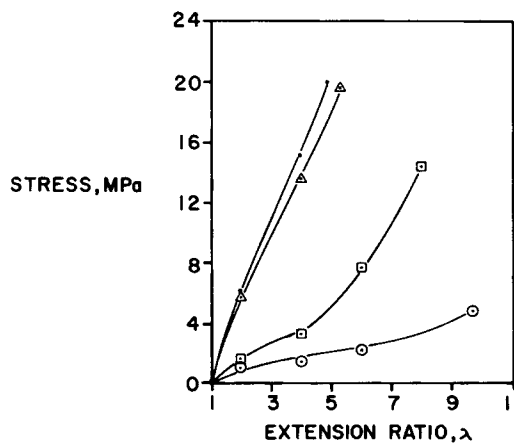| Sample No.	MS in Copolymer (wt%)	Styrene in Copolymer (wt%)	GE (%)	[Allylic Cl] (wt%)	$\overline{M}_n$ PS-b-PBd backbone (g/mole × 10⁻⁵)
6	32	14	100	0.41	1.15
7	32	14	100	1.54	1.15

Fig. 1. Effect of MS content on stress–strain properties for PBd-g-MS copolymers: (⊙) sample 1, 30% MS; (▫) sample 2, 41% MS; (△) sample 4, 46% MS; (●) sample 5, 50% MS.

In Figure 2, the tensile strengths of two PBd-*g*-MS copolymers at elevated test temperatures are compared with those of a styrene-butadiene-styrene (SBS) block polymer. The SBS copolymer is made commercially by the Shell Chemical Company and contains 32% styrene by weight. It can be seen that the SBS copolymer loses tensile strength most rapidly as test temperature is increased. Both of the PBd-*g*-MS copolymers retain their tensile strength much more effectively than the SBS control. Sample 5, which has the highest α-methyl styrene content, has the highest tensile strength at all temperatures. These results are not surprising when one considers the glass transition temperatures of both the poly(styrene) and poly(α-methyl styrene) segments. The polystyrene segments tend to soften at 60–80°C because of their low glass-transition temperature of 100°C.[8] This softening causes a loss in tensile strength such that at 80°C the SBS copolymer has lost essentially all of its strength. The poly(α-methyl styrene) segments have a high glass transition temperature of 170°C.[8] Thus, the glassy domains made up of the poly(α-methyl styrene) segments remain fairly well intact even at 100°C. The result is the retention of a considerable amount of tensile strength in these PBd-*g*-MS copolymers at elevated test temperatures.

Oil Acceptance versus Polymer Structure

Figure 3 illustrates the tensile behavior of three copolymer structures containing oil. Sample 3 is a PBd-*g*-MS copolymer while samples 6 and 7 are PS-*b*-PBd-*g*-MS copolymers. All three copolymers contain the same hard segment content (46% by weight). Samples 3 and 6 were prepared from backbones having the same [Allylic Cl] and therefore contain the same number of hard segment grafts per chain. Sample 7 was prepared from a backbone having a high [Allylic Cl] and therefore is expected to have a higher number of hard segment grafts per chain than samples 3 and 6.[6] It can be seen that the PBd-*g*-MS copolymer has very low tensile strength. This was typical behavior for all PBd-*g*-MS copolymers when compounded with oil. Sample 6, which has a styrene-butadiene diblock backbone, has a much higher tensile strength than the PBd-*g*-MS sample
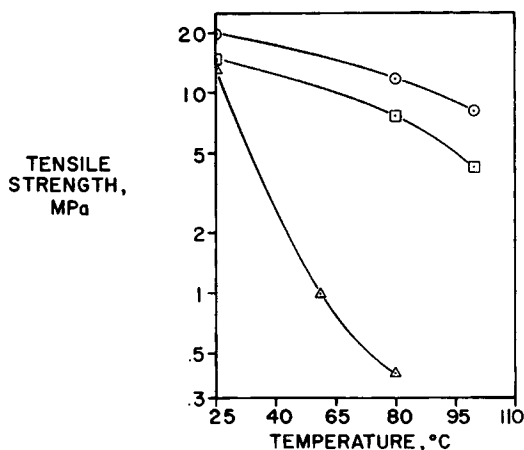

Fig. 2. Effect of test temperature on tensile strength of PBd-*g*-MS copolymers: (▲) SBS control contains 32% styrene; (□) sample 2, 41% MS; (⊙) sample 5, 50% MS.
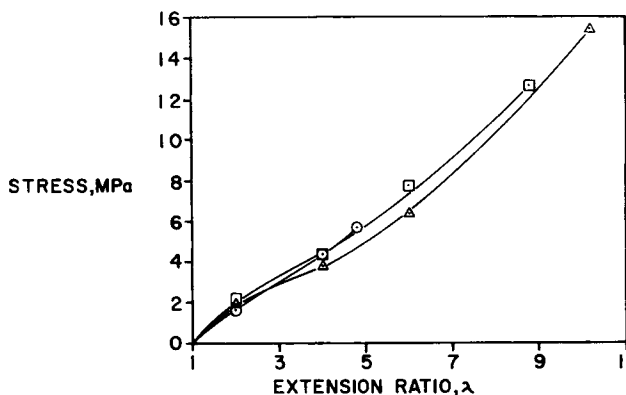
Fig. 3. Effect of polymer structure on the tensile properties of oil-filled copolymers: (⊙) sample 3, oil extended; (□) sample 6, oil extended; (△) sample 7, oil extended.

even though both copolymers have the same hard segment content. We interpret this in terms of the number of loose polybutadiene chain ends present in these copolymers. The PBd-g-MS copolymers are expected to have a considerably greater number of loose polybutadiene chain ends than the PS-b-PBd-g-MS copolymers, provided both copolymers have the same number of grafts per chain. The fact that the oil-extended PS-b-PBd-g-MS copolymers have considerably higher tensile strengths than their PBd-g-MS counterparts indicates that loose polybutadiene chain ends are detrimental to the tensile strength of these oil-extended graft copolymers. By increasing the number of grafts per chain as we did in sample 7 of Figure 3, the tensile strength was increased still further. Statistically, one expects the number of free polybutadiene chain ends to decrease as the number of hard segment grafts is increased. The fact that the tensile strength increased with increasing number of grafts per chain also supports the contention that loose polybutadiene chain ends are detrimental to the tensile strength of these oil-extended copolymers.

CONCLUSIONS

PBd-g-MS copolymers show thermoplastic elastomer behavior presumably because of domain formation arising from their graft copolymer structure. Tensile strength was maximized at the 45–50% by weight α-methyl styrene level. Tensile strength at elevated test temperatures is considerably better for these PBd-g-MS copolymers compared with SBS triblock polymers. This is attributed to the higher glass transition temperature of poly(α-methyl styrene) compared with polystyrene. The tensile strength of oil-extended PS-b-PBd-g-MS copolymers is considerably higher than oil-extended PBd-g-MS copolymers at the same hard segment content levels. It is believed that loose polybutadiene chain ends, which are present in greater quantity in the PBd-g-MS copolymers, are detrimental to the tensile strength of these oil-extended graft copolymers. Further evidence for this is the fact that the tensile strength of oil-extended PS-b-PBd-g-MS copolymers can be increased by increasing the number of grafts per chain.

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