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Multiblock Copolymers of Polyethylene and Polydimethyl Siloxane

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SUMMARY

It has been demonstrated that multiblock $(AB)_n$ copolymers of silane terminated poly(dimethylsiloxane) and hydroxyl terminated polyethylene can be prepared by coupling in the presence of stannous octanoate. Values of n from 3 to 10 have been obtained. Compositions were varied by using different block lengths and potentially useful elastoplastics can be prepared when the weight % of both components is comparable. The complex modulus for one such structure varied from $1.5 \times 10^8 Nm^{-2}$ to $4 \times 10^7 Nm^{-2}$ in the temperature range 150K to 390K.

INTRODUCTION

Polydimethylsiloxane (PDMS) has been used extensively as a component in di-, tri- and multiblock copolymers, in combination with a wide range of polymers forming the second block (PLUMB and ATHERTON 1973). In the majority of cases the construction of the copolymer has been achieved by anionic polymerization which leads to well characterized materials. An alternative method involves step growth coupling of preformed blocks with reactive terminal groups and this has extended the number of possible block combinations. NOSHAY et alia (1973) coupled blocks of dihydroxyl terminated poly(α-methyl styrene) oligomers with bis-dimethylamino terminated PDMS to form $(AB)_n$ structures, and similarly end capped oligomers were used by O'MALLEY et alia (1977) to form multiblock copolymers of PDMS and poly(hexamethylene sebacate). In the former the low glass transition temperature (Tg), of ∿143K for the PDMS blocks is combined with the high Tg (∿350-400K) of the poly(α-methyl styrene) component, while in the latter the elastoplastic range is extended to the melting point of the highly crystalline polyester (Tm = 340K).

Short polyethylene chains with terminal carboxyl units can now be prepared by the acid degradation of polyethylene crystals (BALLARD and DAWKINS, 1973). This

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technique eventually produces polyethylene blocks (PE) with Mn$\sim$1200-1400 (centuric acid) which can be chain extended to yield longer bifunctional blocks. Coupling with other functionalized chains should then produce structures similar to those mentioned above. This report describes our preliminary studies on the preparation and properties of multiblock copolymers of PE and PDMS.

EXPERIMENTAL

Samples: Specimens of centuric acid used were kindly donated by I.C.I. or produced from high density polyethylene using the method outlined by MELBY 1978. The terminal carboxyl units were converted to terminal hydroxyls by end capping with either 2,3 butane diol or cyclohexane diol. Two samples of PDMS oligomers with silane (-Si-H) end groups were used. One (SI-1) was generously supplied by Dr J.B. Plumb, I.C.I. and the other (SI-2) was prepared by reacting octamethylcyclotetrasiloxane with dimethyl chlorosilane (mole ratio 11/8) in the presence of 1% sulphuric acid. Fractionation of SI-2, using butanol-methanol mixtures yielded four fractions. The Mn of each was measured by vapour pressure osmometry (V.P.O.) and compared with the value estimated from analysis of the silane end group. This was achieved by comparing the ratio of the optical densities of the Si-H stretching (2140cm^{-1}) with the C-H bending (1460cm^{-1}) in the infrared spectrum. Values of Mn estimated from end group analysis were always larger than those from VPO, by an amount outside reasonable experimental error. This suggests that not all the chains were terminated in Si-H units and that samples contained either cyclic species or Si-OH terminal units, although there is no evidence of the latter in the infrared spectrum.

Copolymerisation: The condensation of the OH-terminated PE with the silane units in PDMS was effected by refluxing a stoichiometric mixture of the two blocks in xylene in the presence of stannous octanoate as catalyst (0.3% wt/v). A reaction time of 24 hours is sufficient, but because of the uncertainty in estimating the exact concentration of silane units, the reaction was carried out in stages. Four or five successive additions of the block component found to be deficient at each stage, led to the formation of block copolymers with useful molecular weights. The resulting polymer was extracted by precipitation with methanol and freed from any contaminating starting material by repeated dissolution and reprecipitation. This was followed by a soxhlet extraction using the sequence petrol ether, toluene and xylene, which gave fractions with slightly varying compositions.

Characterization: Examination of the products by infrared yielded spectra consistent with copolymers of PE and PDMS (Figure 1). Copolymer compositions were estimated from elemental analysis and the consistency of the materials was found to range from waxy substances (rich in PDMS) through elastomeric solids, to powders which had high PE contents. Determination of copolymer Mn by membrane osmometry showed values lying between 1.4×10^4 and 3.2×10^4. A Perkin Elmer DSC-2 differential scanning calorimeter (dsc) was used to determine Tg and the melting points, Tm. Dynamic thermomechanical behaviour was investigated by means of a torsional braid analyser (tba) and a rheovibron viscoelastometer (rv).

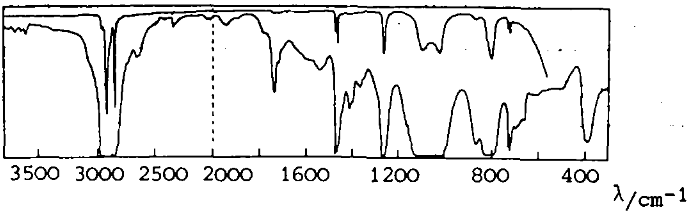

Figure 1. Infrared spectrum of sample PESI/3/3 as (a) a thick film (lower spectrum) and (b) thin film on rock salt (upper spectrum).

RESULTS

Three copolymers, with a spread of composition were selected for more detailed study. These were prepared from a PDMS block, Mn~3200, and PE blocks of Mn~1200 (PESI/1/6), Mn~2400 (PESI/3/3) and Mn~6500 (PESI/4/2). Their characteristics are shown in Table 1. Analysis suggests that $(AB)_n$ multiblock structures are formed with $n \sim 6$ or 7 for PESI/1/6 and $n \sim 9$ or 10 for PESI/3/3. Sample PESI/4/2, in which the PE block size was largest, had a much lower value of n and is most probably a PE/PDMS/PE triblock structure.

TABLE 1

Compositions and molecular weights for PE/PDMS multiblock copolymers.

Copolymer	10^{-4}Mn	PE content		n	Soxhlet Extraction Solvent
		Wt%	Mole %		
PESI/1/6	1.7	25.0	46.8	6-7	100/120 Pet.Ether
PESI/3/3	3.2	57.5	78.1	9-10	Toluene
PESI/4/2	1.6	76.2	89.4	2	Toluene

Thermal properties: Dsc thermograms were obtained between 110K and 430K at a scan rate of 20K min^{-1}. Samples were cooled rapidly prior to measurement, and recycling gave reproducible results. Four distinct features were observed: a Tg, a cold crystallization exotherm, Tc, and a melting endotherm, Tm, arising from the PDMS block, and at much higher temperatures a Tm for the PE block. These are listed in Table 2 together with the corresponding data derived from the dynamic mechanical measurements. In sample PESI/4/2, both Tc and Tm for the PDMS block were undetectable, but in general the relative sizes of the Tg inflexions and the Tm endotherms were consistent with the compositions quoted in Table 1.

TABLE 2

Transition temperatures for PE/PDMS block copolymers, obtained from dsc, tba and rv measurements.

Copolymer / Technique	Tg/K (PDMS)	Tc/K (PDMS)	Tm/K (PDMS)	Tm/K (PE)
PESI/1/6				
dsc	146	173	228,240	392
tba (1Hz)	157	203	233	388
PESI/3/3				
dsc	138	165	233	397
tba (1Hz)	148	202	221	395
rv (11Hz)	153	185	225	390
PESI/4/2				
dsc	145	-	-	395

Dynamic mechanical response: In the non-absolute tba measurements (Figure 2) on samples PESI/1/6 and PESI/3/3, damping peaks are observed which correspond to Tg, Tc, Tm (PDMS) and Tm(PE) detected in the dsc. Absolute measurements of the complex modulus E^* as a function of temperature for sample PESI/3/3 were made at a frequency of 11Hz on the rv, using compression moulded rectangular bars prepared at 453K. This sample appears to be the most promising elastoplastic material, exhibiting a complex modulus ranging from $1.5\text{x}10^{8}\text{Nm}^{-2}$ at 150K to $4\text{x}10^{7}\text{Nm}^{-2}$ at 390K, see Figure 3. These values, which are well within the range measured for commercial Kraton G samples (COWIE et al. 1979) suggest that sample PESI/3/3 is a useful, tough, elastomeric material within these temperature limits.

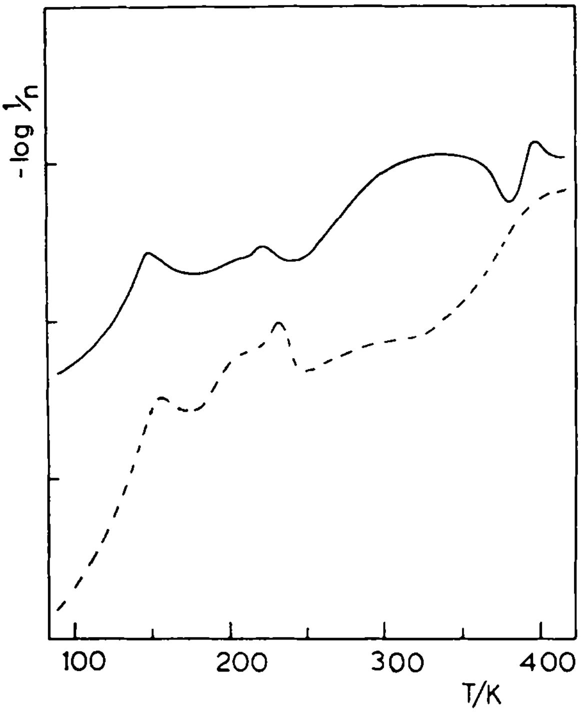

Figure 2. T.b.a. damping spectra for sample PESI/3/3 (solid line) and sample PESI/1/6 (dashed line).

CONCLUSION

The data indicate that useful block copolymers of PE and PDMS can be prepared, which make use of the PE crystallinity to introduce thermo-reversible cross-links for the PDMS segments and impart toughness to the polymer. Further work is aimed at improving the block linking process and to examine the effect of block length on tensile strength and melt flow characteristics.

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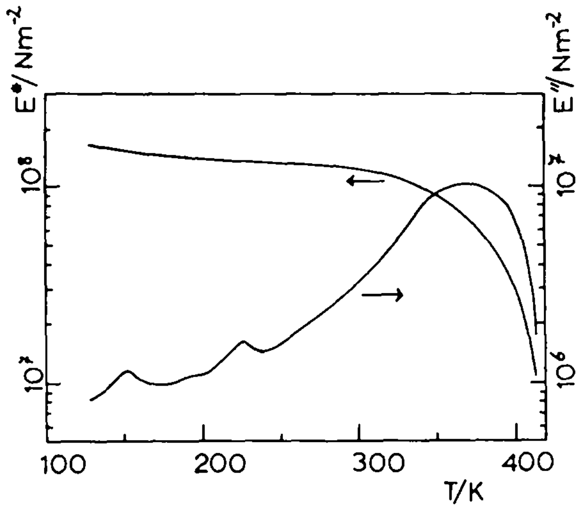

Figure 3. Logarithmic tensile complex modulus (log E*) and loss modulus (log E") as a function of temperature for sample PESI/3/3 measured on the rheovibron at 11Hz.

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