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Some block copolymers illustrating the effects of siloxane and silane units on the properties of terephthalate–glycol thermoplastics

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

Modified poly(butylene terephthalate)–poly(tetramethylene glycol) multiblock copolymers were prepared by including either siloxane or silane units within the terephthalate hard blocks or the glycol soft blocks. These materials were characterized in terms of their dynamic-mechanical properties, glass transition temperatures T_g, and morphology (as obtained from small-angle X-ray scattering measurements). One interesting result was the finding that putting siloxane units into the terephthalate hard blocks significantly decreased the storage modulus, whereas placing them into the glycol soft blocks somewhat increased it. Other interesting results were the observation that the T_g of the soft segments increased if the siloxane units were placed into the hard blocks but slightly decreased if they were placed into the soft blocks, while the hard-segment T_g was not observed at all. Some of these results could be explained in terms of the phase separation suggested by the X-ray scattering results. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Thermoplastic elastomers are an important category of engineering materials because they frequently have extraordinary combinations of physical properties, such as elasticity, toughness, and low-temperature flexibility [1–6]. Traditionally, they consist of multi-block arrangements of two types of sequences, a soft block which is amorphous and rubbery, and a hard block which is crystalline or glassy. Various combinations of soft and hard blocks have already provided several good engineering-grade polymers, but there is always interest in improving these materials, for example, by modifying the chemical structures of one or both blocks

An interesting example of a block copolymer having good mechanical properties consists of the polyester poly(butylene terephthalate) (PBT) and the polyether poly(tetramethylene glycol) (PTMG). The PBT blocks provide hardness through their crystallinity, and the PTMG ones supply softness through the well-known flexibility of the polyethers [4,5]. On the contrary, siloxane (SO) units such as those occurring in poly(dimethylsiloxane) (PDMS) [–$Si(CH_3)_2O$–], exhibit what is probably the highest flexibility and mobility of any known polymer [7–10]. This is what gives them, for example, their superb mechanical properties. Silane (S) units, however, have backbones that differ from those in siloxane units by the absence of the oxygen atoms, and generally have much less flexibility and mobility [7–9,11]. It is therefore of interest to introduce either type of silicon-containing units into the PBT hard sequences in the basic PBT/PTMG structures, or even into the PTMG soft sequences. The hope is that at least some arrangements will improve properties of importance in a particular application without detrimental changes in other properties, or to restrict any such changes to properties of less significance.

2. Experimental

2.1. Basic building blocks

The structures of the various sequences are given in Scheme 1 (Hard and soft segments used in the block copolymers, in which n was 14 and m was approximately 5–10), and the combinations investigated are listed in Table 1. Details of their syntheses [12] and some preliminary

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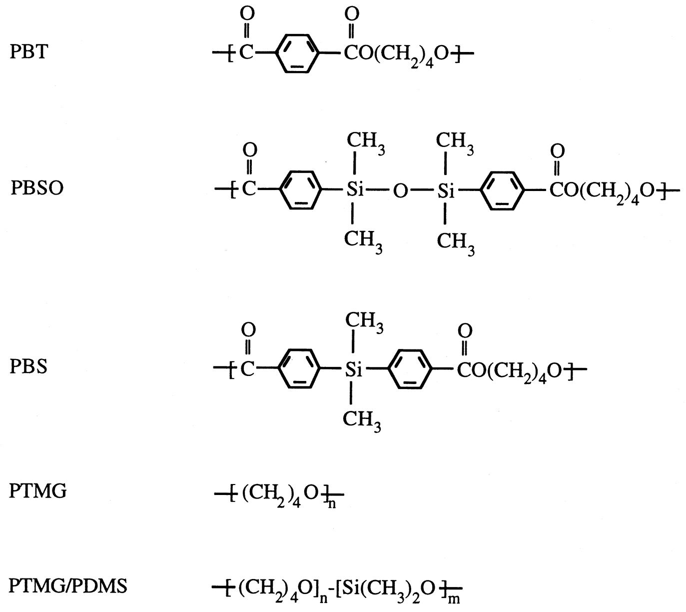


Scheme 1.

characterization [12,13] information is given elsewhere. The following sections summarize the synthetic approaches, and then describe the techniques used to further characterize these copolymers with regard to some of their physical properties.

2.2. Preparation of organosilicon monomers

Two organosilicon monomers, [1,1,3,3-tetramethyl-1,3-bis(*p*-carbomethoxyphenyl)disiloxane] (I) and dimethyl-bis(*p*-carbomethoxyphenyl)silane (II), were synthesized by Grignard reactions using *p*-bromotoluene and dimethyldichlorosilane as starting materials. $KMnO_4$/pyridine was used as oxidizing agent, and CH_3I as esterifying agent. The reactions involved are illustrated in Scheme 2 (The synthetic procedures for monomers [1,1,3,3-tetramethyl-1,3-bis(*p*-carbomethoxyphenyl) disiloxane] (I) and dimethyl bis(*p*-carbomethoxyphenyl)silane (II)).

2.3. Synthesis of the Si-containing polyester–polyether multiblock copolymers

Monomer I or II obtained from the process described earlier was mixed with dimethyl terephthalate (DMT), 1,4-butanediol, and PTMG or PTMG/PDMS. Proper amounts of the reactants were used so as to produce copolymers having a weight ratio of hard segments to soft segments of 30:70. Transesterification and polycondensation were carried out for the mixture at 200–220°C and 250°C sequentially, as shown in Scheme 3 (The synthetic procedure for silicone-embedding multi-block copolymers). The resulting polymers were purified by re-precipitation using $CHCl_3$ as solvent and CH_3OH as precipitant.

Table 1
Segment combinations in the block copolymer samples

Sample	Hard segment	Soft segment	Sample structure
1	PBT	PTMG	PBT–PTMG
2	PBT and PBSO (PBT:PBSO = 4:1)	PTMG	PBT/PBSO–PTMG
3	PBT and PBS (PBT:PBS = 4:1)	PTMG	PBT/PBS–PTMG
4	PBT	PTMG/PDMS	PBT–PTMG/PDMS

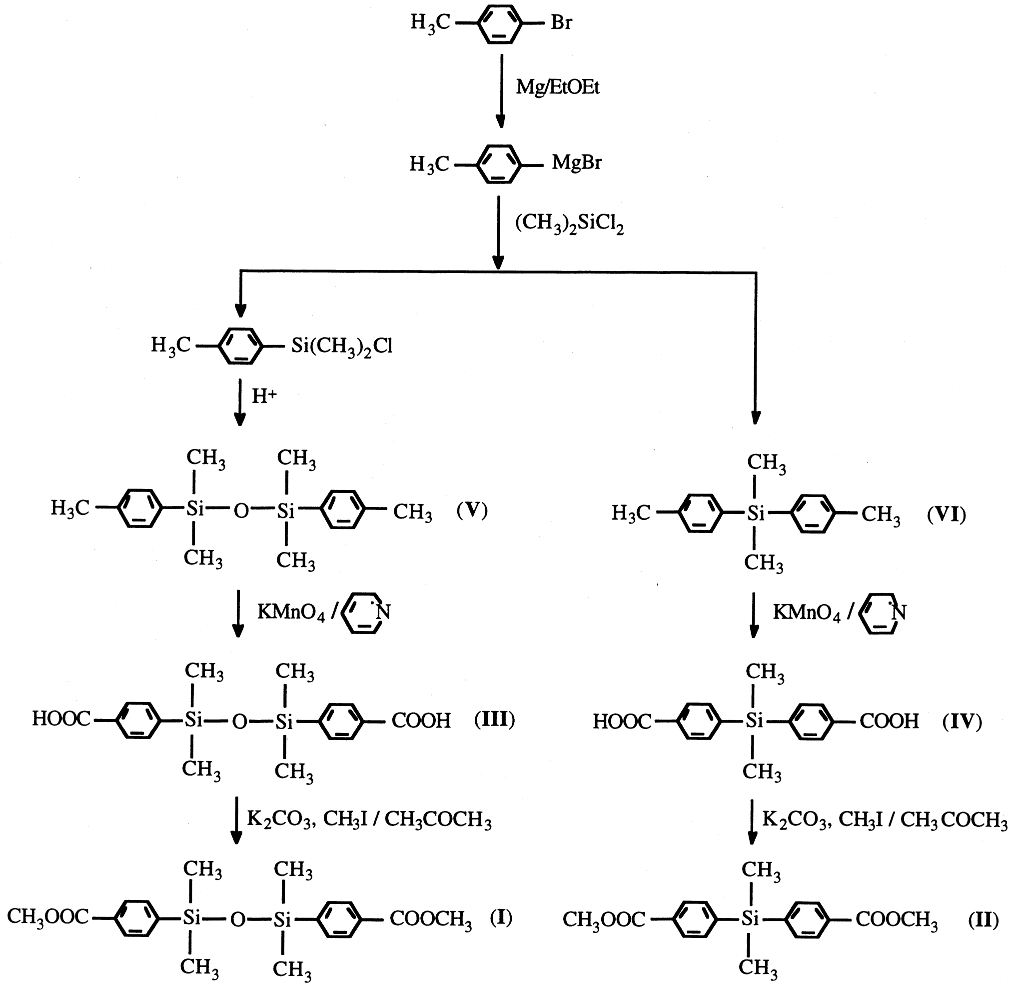
Intrinsic viscosities obtained on the polymers in *m*-cresol at 30°C [12] could be used to obtain rough estimates of molecular weights, as no micellarization occurred in any of the solutions. In this regard, the number of repeat units in the hard segments is about 2. The molecular weight of the soft segments is about 1000 for PTMG, and 350–800 for PDMS, and the values of the intrinsic viscosities were 1.2–1.4 dl g^{-1}. This suggests that the molecular weights were at least several tens of thousands.

2.4. Film preparation

Films of the copolymers synthesized were made by the following procedure: 8 g of copolymer was dissolved in 100 ml $CHCl_3$. The resulting solutions were poured into glass molds, and the solvent was allowed to evaporate slowly at room temperature. The films were taken from the glass plates and were then dried under vacuum at 50°C for 8 h. They were approximately 0.5 mm thick.

2.5. Measurements of dynamic-mechanical properties

Sample sheets were cut into strips having the lateral dimensions $20 \times 4\ mm^2$. Some of their dynamic-mechanical



Scheme 2.

properties [14–16] were measured using a Solid Analyzer RSA II (from Rheometrics, Inc.). First a static-strain scan was made for every sample strip to determine pre-tension; this was followed by both a frequency sweep and temperature sweep. To establish the reproducibility of the data, duplicate experiments were carried out with two sample strips from each sample sheet. Sample data as ASCII files were then processed using standard software.

2.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements [4,17,18] were performed on a Polymer Laboratories (PL) Thermal Science DSC system with nitrogen as the purging gas. Base-line calibrations were performed with sapphire, while second-stage calibrations employed indium, silicon, and zinc references. This permitted the temperature readings to be within 0.5°C. The heating rate was 10°C min^{-1}, and values of the glass transition temperature T_g were obtained by identifying deflection points on the DSC curves with the software package provided with the apparatus.

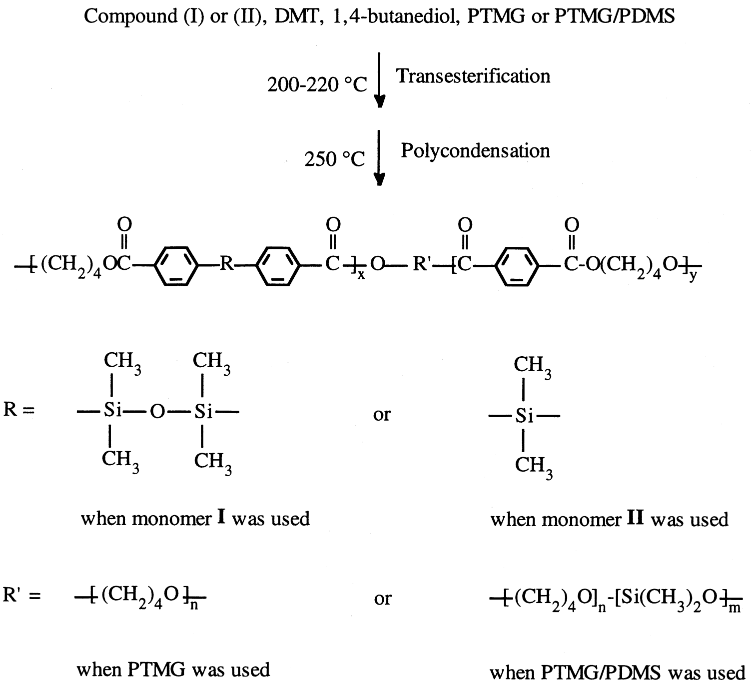
2.7. Small-angle X-ray scattering (SAXS)

Small-angle X-ray scattering (SAXS) experiments [19–23] were conducted on the 10-m pinhole camera at the Oak Ridge National Laboratory. The incident X-ray was Cu K_α, with a wavelength of 1.54 Å. The scattering data were corrected to absolute intensities by measurements of sample thickness, and through comparisons with results on secondary standards.

3. Results and discussion

3.1. Dynamic-mechanical properties

Figs. 1 and 2 show the frequency dependence and temperature dependence, respectively, of the storage moduli E' obtained for some of the copolymers. It can be seen that the addition of silicone to the PBT–PTMG copolymer does not have much effect on these dependencies. But it is interesting to note that the silicon-containing sequences have



Scheme 3.

different effects on the modulus itself, depending on whether they are placed in the soft blocks (PBT–PTMG/PDMS) or the hard blocks (PBT/PBSO–PTMG and PBT/PBS–PTMG). Specifically, the modulus was increased in the PBT–PTMG/PDMS copolymers, while it was decreased in both the PBT/PBSO–PTMG and the PBT/PBS–PTMG materials. Similar differences were found in the loss moduli (not shown), and may result from PBSO, PBS, and PDMS having different compatibilities with the two blocks of the PBT–PTMG system. Another important factor could be the low glass transition temperature of PDMS [7–10,24]; this flexibility could perhaps lead to an increase in crystallinity in the block copolymer, and this increased crystallinity would give a higher modulus. This would be consistent with the observed marked decreases in E' with increase in the temperature, as shown in Fig. 2.

There may well be miscibility problems between the silicon-containing units and the PBT hard blocks, because of the large differences in chemical structure. This is in fact suggested by the loss-tangent–temperature relationships,

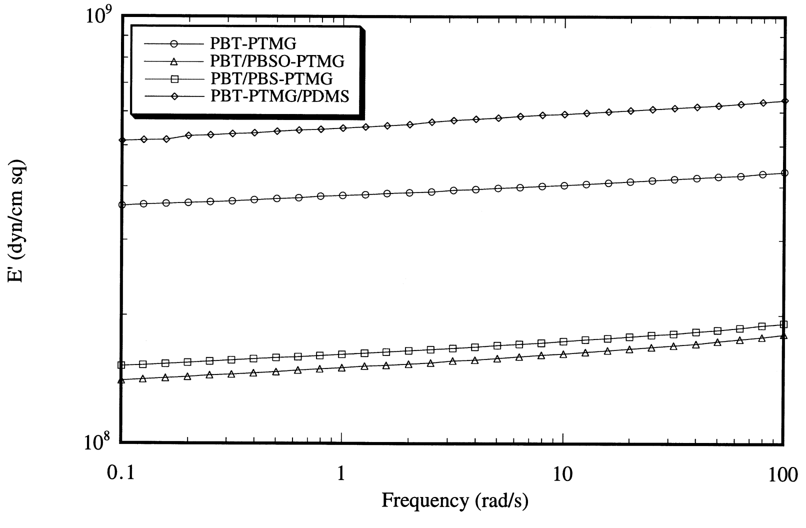


Fig. 1. Storage-modulus–frequency relationships for the block copolymers at room temperature.

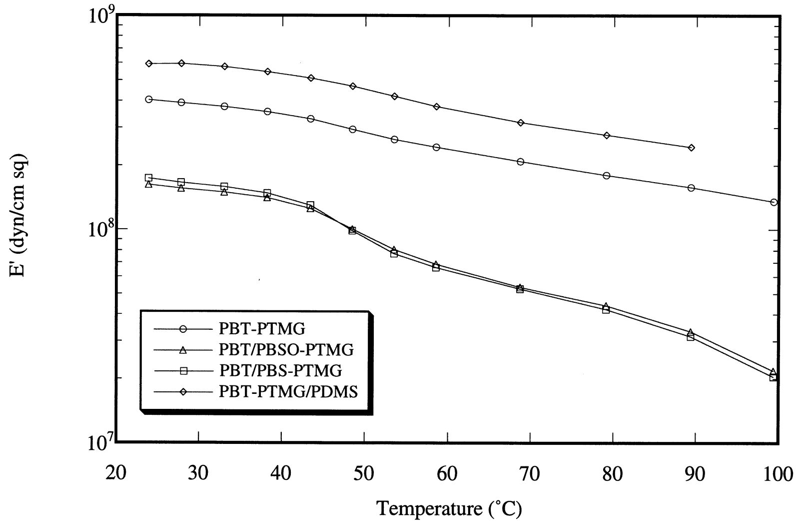


Fig. 2. Storage-modulus–temperature relationships at a frequency of 10 rad s^{-1}.

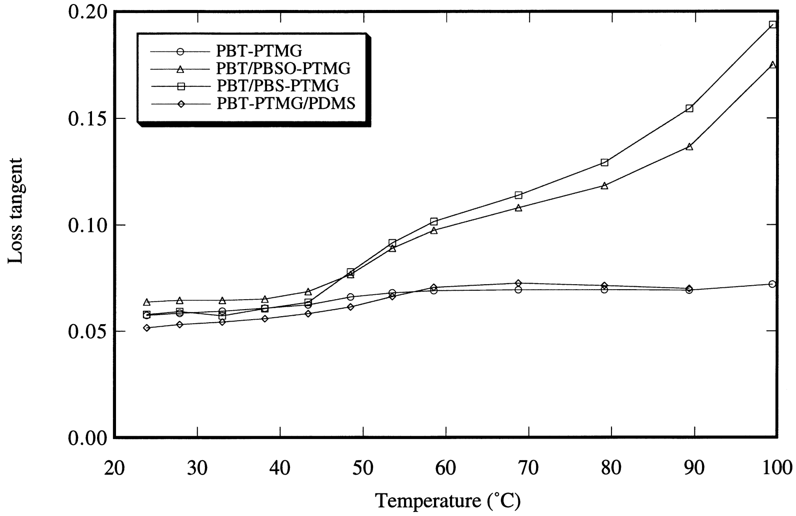


Fig. 3. Loss-tangent–temperature relationships at a frequency of 10 rad s^{-1}.

illustrated in Fig. 3. It is obvious that the loss tangent increases markedly beyond approximately 45°C for the hard-block modified PBT/PBSO–PTMG and PBT/PBS–PTMG, but is quite insensitive to temperature for the unmodified PBT–PTMG and the soft-block modified PBT–PTMG/PDMS. Similar differences were found in the loss-tangent–frequency relationships (not shown).

3.2. Glass transition temperatures

Within the test temperature range, the DSC curves of the copolymer samples show only one glass transition, near −80°C. Table 2 lists the T_g values obtained from DSC for the copolymer samples, along with some reference values for the parent homopolymers. By comparing the experimental T_g values with the reference values, it can be concluded that the observed glass transition is soft-segment related. Although the observed changes in T_g are not very large, it is interesting that inserting the silicon-containing units into the PBT hard blocks causes a discernible increase in T_g. However, inserting them into the PTMG soft block causes

Table 2
Glass transition temperatures T_g for the block copolymer samples and their parent homopolymers

Sample	Measured values (°C)	Literature values [4,5,24,25] (°C)
PBT		22
PTMG		−84
PDMS		−127
PBT–PTMG	−80	
PBT/PBSO–PTMG	−74	
PBT/PBS–PTMG	−75	
PBT–PTMG/PDMS	−82	

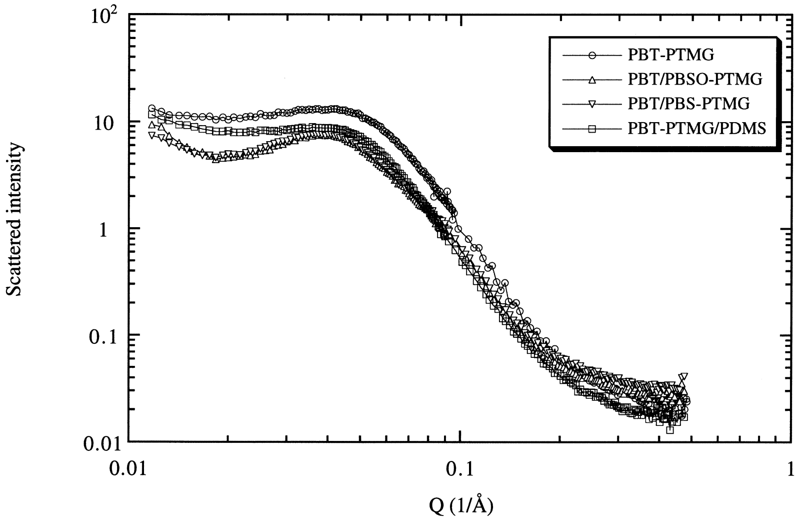


Fig. 4. Scattered X-ray intensities as a function of the scattering vector.

a slight decrease, which again suggests less of a miscibility problem in the case of insertions into the soft blocks.

3.3. Morphologies

The X-ray scattering results are shown in Fig. 4. It can be seen that the scattering plots for PBT–PTMG and PBT–PTMG/PDMS are almost identical, indicating that the PDMS does not cause much morphological change in the PBT–PTMG blocks. The scattering plots for the hard-block modified PBT–PTMG have significant intensity minima at low values of the scattering vector Q that are not present in the unmodified PBT–PTMG. This could be an indication of the phase separation mentioned earlier in the case of these two modified copolymers.

4. Conclusions

Previous characterization work on these same materials [13] showed related improvements in physical properties upon insertion of the silicon-containing units. Specifically, there was increased hydrophobicity (from siloxane group migration to the sample surfaces), improved heat resistance, and increased permeabilities to oxygen and nitrogen. These earlier results, along with those reported here, suggest that this type of modification of PBT–PTMG copolymers could be very useful, at least for some potential applications of these materials, for example utilization as membranes or novel hydrophobic elastomers.

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