Polymer Bulletin 19, 573–578 (1988)

Polymer Bulletin

Structural modifications of segmented poly(hydroxyether-siloxane) copolymers

J.L. Hedrick[1], D.C. Hofer[1], T.P. Russell[1], and B. Haidar[2]

[1]IBM Almaden Research Center, 650 Harry Road, San Jose, CA-95120-6099, USA
[2]CNRS, F-68100 Muhlhouse, France

Summary

Hydroxyether linked copolymers were synthesized from α,ω-bis(aminopropyl)polydimethyl diphenylsiloxane oligomers and diglydicylether of bisphenol-A (DGEBA). The siloxane oligomers were synthesized by the bulk coequilibration of the various weight percents cyclic dimethylsiloxane tetramer (D_4) with cyclic diphenylsiloxane tetramer (D_4'') using a basic catalyst. The molecular weight and functionality was controlled by the incorporation of 1,3-bis(aminopropyl)-tetramethyldisiloxane end blocker. The copolymers containing low diphenylsiloxane compositions have two T_g's suggesting a microphase separation. Networks containing higher diphenylsiloxane compositions show a single phase morphology. The mechanical behavior of these copolymers is influenced by the composition changes.

Introduction

We have recently published (1) the synthesis and mechanical properties of segmented poly(hydroxyether-siloxane) copolymers from the reaction of diglycidylether of bisphenol-A (DGEBA) and α,ω-bis(aminopropyl) terminated polydimethylsiloxane oligomers. In this monomer-oligomer synthetic approach, a hydroxyether linkage is formed between the blocks or segments. Initially, DGEBA was employed as both a chain extender and crosslinker. However, the DSC scans showed two T_g's (−120 and ~20°C) suggesting a two phase morphology. We believe that the large solubility parameter difference between the siloxane and hydroxyether (7.3 and ~9.5) components together with the strong intermolecular interactions within the hard segment provides the microphase separation. The mechanical properties of these materials varied depending on the molecular weight of the siloxane oligomer used. The moduli ranged from 1 to 150 MPa, and the ultimate elongations were ca. 50%.

One major problem associated with this monomer-oligomer synthetic approach involves processing. Conventionally, in the synthesis of epoxy resins, it is desirable to have a two component miscible system which can be cured to form a network. In our case, there is a significant difference in solubility parameter between the DGEBA and siloxane oligomer which prevents mixing, and chloroform is required to facilitate the miscibility and promote the initial chemical reaction. In this communication, we will discuss structural modifications in the siloxane oligomers which will decrease the solubility parameter difference between the two components, thereby approaching the desired miscibility while maintaining the blocky nature of the copolymer. The synthetic approach used was the coequilibration of various concentrations of cyclic diphenylsiloxane tetramer with cyclic dimethylsiloxane tetramer, producing a random copolymer. The solubility parameter of the diphenylsiloxane has been estimated as 9.5 which is similar to the hydroxyether hard block used in this study.

Experimental

Octamethylcyclotetrasiloxane (D_4), octaphenylcyclotetrasiloxane (D_4'') and 1,3-Bis(aminopropyl) tetramethyldisiloxane were purchased from Petrarch. D.E.R. 332 (diglycidylether of bisphenol-A (DGEBA)) was purchased from Dow Chemical Company and had a titrated molecular weight of 342 g/mol. The tetramethylammonium hydroxide pentahydrate was purchased from Aldrich and used without further purification.

The α,ω-bis(aminopropyl) polydimethylsiloxane oligomers of various molecular weights were synthesized by base (tetramethylammonium hydroxide pentahydrate) catalyzed-bulk equilibration reaction of D_4 with 1,3-bis(aminopropyl)tetramethyldisiloxane end blocker (2,3). The equilibration was maintained at 80°C for 48 hours and then increased to 150°C to decompose the catalyst. The mixed cyclics remaining in the oligomers were removed by vacuum distillation (150°C).

The aminopropyl terminated dimethylsiloxane and dimethyldiphenylsiloxane oligomers containing 25 wt.% diphenylsiloxane were allowed to react with DGEBA at 50°C for 24 hours in chloroform (~35 wt.% solids). The solution was cast into films and cured at 100°C (1 hour), then post cured at 120°C (1 hour). The oligomers with higher diphenylsiloxane compositions were mixed with the DGEBA at 80°C and poured into a mold (100°C) and cured as described above. Each network contained less then 3 wt.% sol fraction after swelling in chloroform for 7 days.

The number average molecular weights of the aminopropyl terminated siloxane oligomers were determined by titration using a Fisher Computer Aided Titrimeter. The oligomers were dissolved in isopropanol and titrated with O.1N HCL (4). Glass transition temperature and kinetic measurements were performed on a Dupont DSC 910 instrument at a 10°C/min heating rate.

Stress-strain properties were measured on an Instron Tensile Testing Machine at a strain rate of 10 mm/min (22°C). The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at 10 Hz and a heating rate of 3°C/min.

Small angle x-ray scattering measurements were performed on a Kratky slit collimated camera using Ni filtered Cu radiation from a standard focus sealed tube operated at 40 kV and 2 mA. Scattered radiation was collected with a TEC 205 position sensitive proportional counter and stored in a Tracor Northern 1705 multichannel analyzer. The scattering profiles were desmeared in the usual manner taking into account the geometries of the incident beam and detector.

Results and Discussions

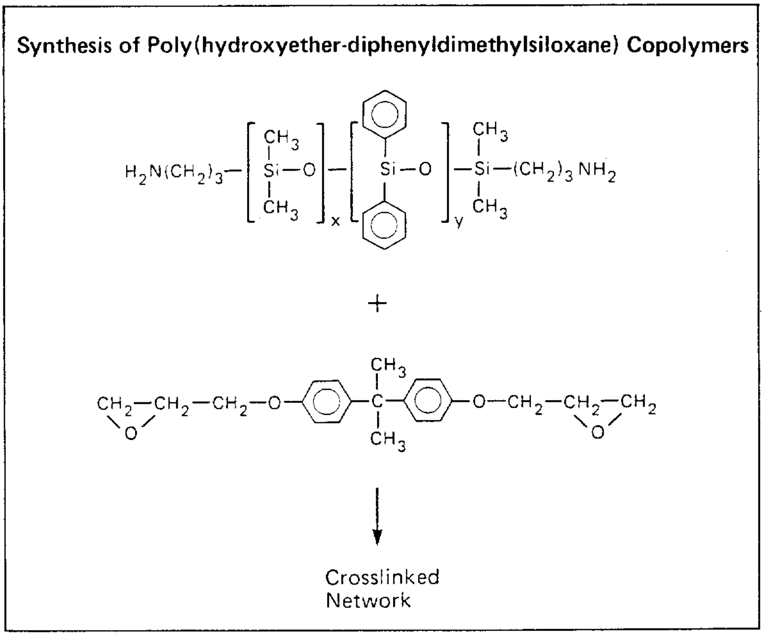
Table 1 contains the aminopropyl terminated polydimethyldiphenylsiloxane oligomers synthesized by a bulk coequilibration reaction using a base catalyst (2,3,5). The different reactivities of the two cyclic tetramers required extended reaction times (48 hours) to avoid block structures. In each case, a single T_g was observed, which increases with diphenylsiloxane content. The addition of the diphenylsiloxane sufficiently disrupts the chain packing to prevent thermal recrystallization.

Table I. Characteristics of α,w-bis(aminopropyl)polydimethyldiphenylsiloxane copolymers

Sample Number	wt.% Diphenyl	<Mn>, g/mol[a]	T_g[b] °C
1	0	5,400	-121,-42[c]
2	25	4,800	-109
3	50	5,400	-71
4	75	5,700	-26

[a] Titration with standard HCL
[b] DSC 10°C/min
[c] Melting point

The aminopropyl siloxane oligomers with the lower diphenylsiloxane compositions were reacted with DGEBA in chloroform for 36 hours, then cast and cured as described previously (Scheme 1). In contrast, the networks containing 50 wt.% diphenylsiloxane or higher could be reacted in the bulk or neat. The DGEBA and siloxane oligomer which homogenized at temperatures above 80°C were poured into a hot mold (100°C) and cured as described previously. In this monomer-oligomer synthetic approach, a hydroxyether linkage is formed between the siloxane blocks. Table II contains the thermal analysis of the networks synthesized. Two T_g's were observed for those samples containing up to 50 wt.% diphenylsiloxane. However, the low temperature transitions are somewhat higher than the starting oligomers indicating at least partial phase mixing.


Synthesis of Poly(hydroxyether-diphenyldimethylsiloxane) Copolymers

Scheme 1

Table 2. Characteristics of poly(hydroxyether-dimethyldiphenylsiloxane) networks

wt.% Diphenyl	<Mn>, g/mol PSX	Thermal Analysis of Networks, °C	
		T_g^a	T_g^b
0	5,400	-120	10
25	4,800	-102	20
50	5,400	-55	17
75	5,700	-5	--

[a] Soft segment
[b] Hard segment

Figure 1 contains the dynamic mechanical thermal analyses of the networks. As can be seen for networks containing the pure dimethylsiloxane or 25 wt.% diphenylsiloxane, two distinct, sharp T_g's are evident. However, incorporation of 50 wt.% diphenylsiloxane significantly broadens both glass transitions. Increasing the diphenylsiloxane content to 75 wt.% produces a network with only one sharp tanδ relaxation. Consequently, the increased diphenylsiloxane content in the network has produced a single phase system.

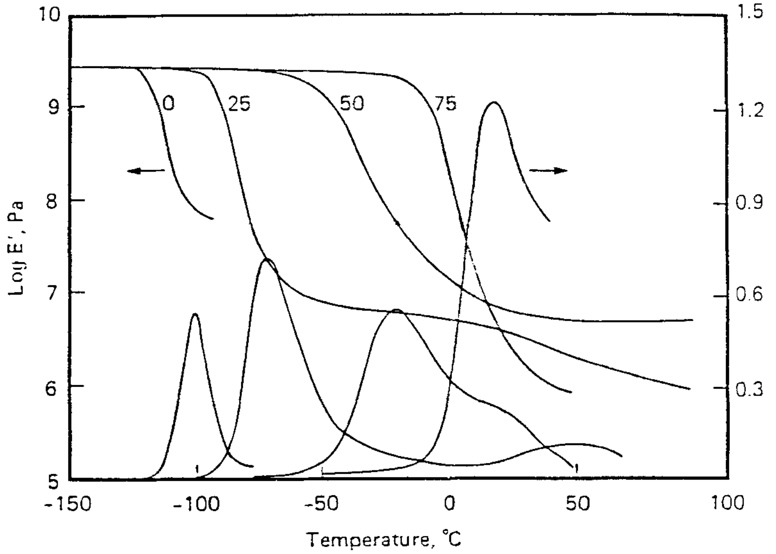


Figure 1. DMTA results for the networks with varying diphenylsiloxane compositions ranging from 0 to 75 wt.%.

Small angle x-ray scattering (SAXS) profiles for the 0% and 25% diphenyl copolymer are typified by a weak diffuse maximum occurring at ca. 100Å. The SAXS for the 25% diphenyl copolymer is shown in Figure 3. The maximum characterizes the separation distance between the hard and soft segment phases and clearly reflects that a microphase separated morphology. For these two copolymers, the scattering was exceptionally weak and it was too difficult to quantitatively analyze the scattering profiles. However, it was evident that as the concentration of the diphenyl units increased, the SAXS reflections became broader and more diffuse. SAXS profiles for the 50% and 75% diphenyl copolymers were monotonically decreasing functions of the scattering angle. There was no evidence of a maximum in the profile which strongly suggests that these copolymers are homogeneously dispersed rather than microphase separated. More than likely, the morphology of the 50% diphenyl copolymer is too diffuse and the spatial arrangement of the phases is disordered enough so that a scattering maximum would not be evident. It is evident form these results that incorporation of the diphenyl units enhances phase mixing.

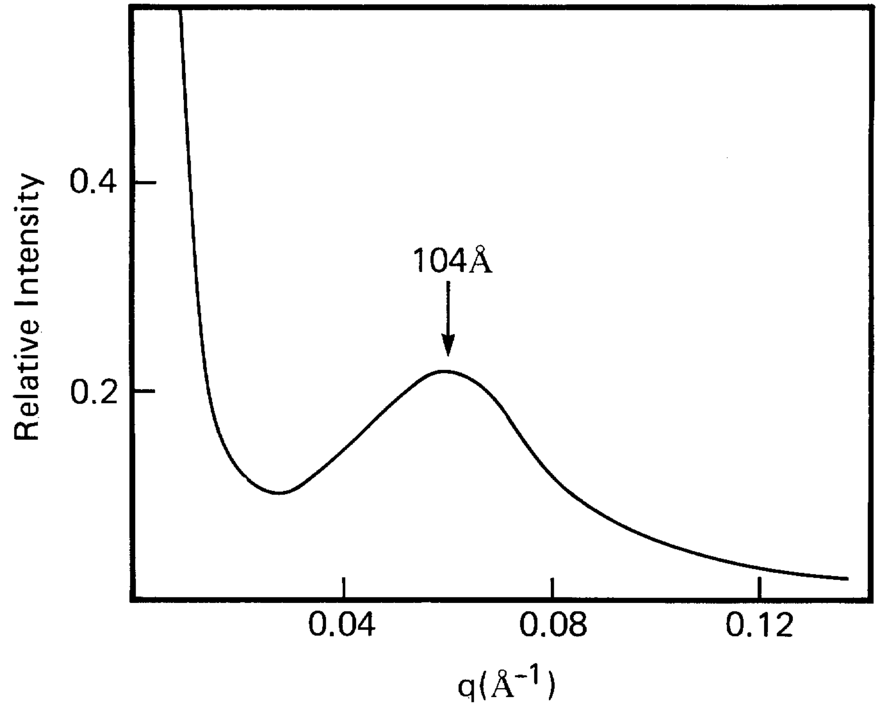


Figure 2. Small angle x-ray scattering profile for a 25% diphenylsiloxane network. Here, the relative intensity is shown as a function of the scattering vector $q = (4\pi/\lambda) \sin(\theta/2)$ where λ is the wavelength and 2θ is the scattering angle.

The mechanical behavior of the networks vary with the introduction of the diphenylsiloxane as illustrated in Figure 3. Both the modulus and tensile strength decrease with increasing diphenylsiloxane content. The well-defined morphology associated with the network containing the pure dimethylsiloxane is believed to afford the best mechanical properties. The incorporation of the diphenylsiloxane allows a significant amount of phase mixing and this mixing is believed to be detrimental to the mechanical properties.

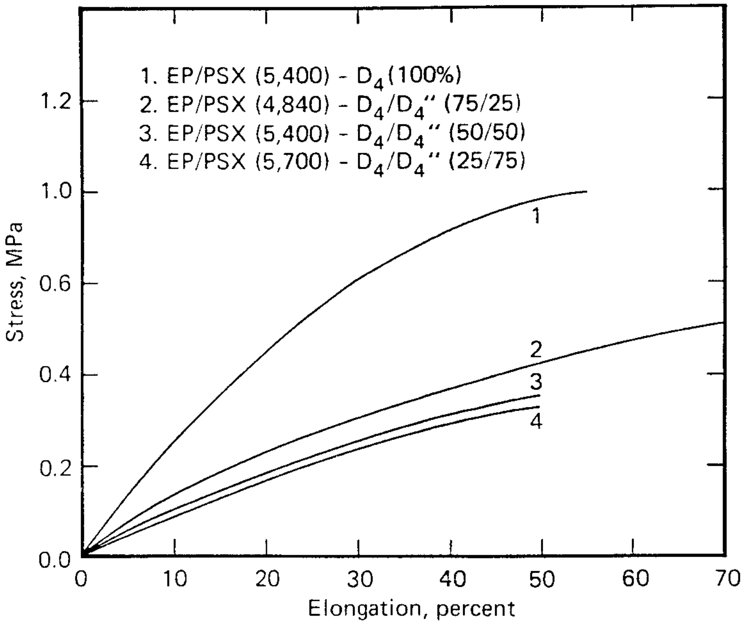


Figure 3. Stress *versus* elongation plots for the poly(hydroxether-siloxane) networks.

Conclusions

We have synthesized aminopropyl terminated dimethyldiphenylsiloxane oligomers which were reacted with DGEBA. The addition of the polar diphenylsiloxane decreases the solubility parameter difference between the oligomer and DGEBA allowing bulk polymerizations. In this monomer-oligomer synthetic route, a hydroxyether linkage is formed between the siloxane blocks. These materials are both chemically crosslinked as well as microphase separated. However, at 75 wt.% or higher diphenylsiloxane compositions, a single tanδ relaxation is observed indicating phase mixing. The mechanical behavior of the networks is somewhat influenced by the compositional changes.

References

1. Hedrick, J.L., Haidar, B., Hofer, D.C., Tran, C., McGrath, J.E., Polym. Preprints, submitted (1986).
2. McGrath, J.E., *et al.*, "Epoxy Resin - II," ed. by R.S. Bauer, ACS Symposium Series (1983).
3. Kantor, S.W., Grubb, W.T., Osthoff, R.C., J. Amer. Chem. Soc., 76, 5190 (1954)..
4. Wnuk, A.J., Davidson, T.F., McGrath, J.E., J. Appl. Polym. Sci., Appl. Polym. Sym., 34, 89 (1978).
5. Brandt, P.J.A., Webster, D.C., McGrath, J.E., Polym. Preprints, 25(2), 91 (1984).

Accepted March 23, 1988 K