Chemistry of Crystalline, Well-Phase-Separated Poly(siloxane)–Poly(pivalolactone) Copolymers

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ABSTRACT: A broad range of compositions of poly(siloxane)-*graft*-poly(pivalolactone) copolymers can be synthesized via heterogeneous techniques using crown ether mediated chemistry. Copolymers of dichlorodimethylsilane and (dichloromethyl)(3-cyanopropyl)silane can be prepared by known procedures during which the cyano group is hydrolyzed to an acid group. The potassium salt of this acid group is used as an initiator to graft pivalolactone onto the poly(siloxane) backbone. No grafting occurs in the absence of 18-crown-6. However, various lengths of poly(pivalolactone) can be grafted in the presence of the crown ether, and the grafting reaction proceeds even in the heterogeneous state, which is rare. No homopoly(pivalolactone) is formed. The copolymers are high in molecular weight, exhibit excellent phase separation, and possess high melting points. The glass transition temperature of the poly(siloxane) phase is essentially the same as that of homopoly(siloxane) and remains unchanged regardless of the mole percentage of the polysiloxane phase in the copolymer. This indicates excellent phase separation of the two segments.

Introduction

Well-phase-separated copolymer systems can display elasticity without requiring chemical cross-linking if one of the phases, often called the hard phase, is capable of a thermally reversible change of state. These copolymers have become known as thermoplastic elastomers and a large number of such polymers exist.[1] Examples are (a) poly(styrene–diene–styrene)s and their blends,[2,3] (b) poly(olefin)s and their blends,[4] (c) poly(urethane–ether)s,[5] (d) poly(amide) copolymers,[6] (e) poly(ester) copolymers including those containing poly(pivalolactone);[7,8] (f) ionomeric systems,[9,10] (g) acrylics,[11] and (h) poly(siloxane) copolymers. Several poly(siloxane) copolymers have been reported in the past[12–16] and have the advantage that they can be used as elastomers at very low temperatures. Copoly(siloxane)s reported include (a) poly(siloxane)–poly(urethane)s,[12] (b) poly(siloxane)–poly(carbonate)s,[13] (c) poly(siloxane)–poly(methacrylate)s,[14] (d) poly(siloxane)–poly(amide)s,[15] (e) poly(siloxane)–poly(methylstyrene) block compolymers,[15] and (f) poly(siloxane)–polypeptide block copolymers.[16]

Very few of these poly(siloxane) copolymers possess a semicrystalline phase, however, and in many respects the crystalline state is preferred for thermally induced changes in state. The crystalline state also enhances physical properties such as solvent resistance and ultimate strength. Consequently, with the goal of synthesizing semicrystalline siloxane copolymers, we have grafted poly(pivalolactone) onto a poly(siloxane) backbone using crown ether mediated chemistry under heterogeneous reaction conditions. This paper describes the polymerization chemistry, characterization of the copolymers, their thermal behavior, and surface characteristics.

Experimental Section

Polymer Synthesis. Synthesis of the random copoly(siloxane), I, has been reported previously.[17] In a typical preparation, I (4.5 g) in diethyl ether (450 mL) was shaken with 10 M aqueous KOH (14 mL) for 5 min, and the ether layer was washed with water until it was neutral. The ether extract was evaporated, and the residue was dried under vacuum (yield 92%). In order to prepare a poly(siloxane)–poly(pivalolactone) copolymer containing 50% poly(pivalolactone), the residue (2 g) was placed in a three-necked flask fitted with a mechanical stirrer, which was also connected to an argon supply and a vacuum pump. After evacuating the contents overnight, dry THF (8 mL) and 18-crown-6 (.01 g) were added under argon, and the contents were stirred to obtain a homogeneous solution. Freshly distilled pivalolactone (2 g) was added under argon, and the contents were stirred further. The homogeneous solution became heterogeneous in 20 min, and at this time stirring was stopped. The reaction mixture was kept unstirred for 1 day. The product was washed with diethyl ether to remove any unreacted pivalolactone, filtered, and dried under vacuum at room temperature. This method was also used to prepare a wide range of copolymer compositions containing 30, 40, 60, and to 70% poly(pivalolactone).

Polymer Characterization. Gel permeation chromatography (GPC) was done by Betec Laboratories under the following conditions: columns, PL-Gel, 1×10^6, 1×10^5, and 1×10^4 Å; solvent, methylene chloride/hexafluoroisopropyl alcohol (90:10); flow rate, 1 mL/min. ^{13}C NMR, 50 MHz, and 200-MHz ^{1}H NMR were obtained on a Varian 200 XL Series superconducting spectrometer system. Elemental analyses were done by Galbraith Laboratories.

Differential scanning calorimetry (DSC) data were obtained by using a Perkin-Elmer 7 Series thermal analysis system equipped with a data analysis station. For subambient operations, the instrument was calibrated by a two-point method using *n*-decane and indium. For operations at room temperature it was calibrated with indium. A scan rate of 20 °C/min was used in all runs. The samples used were the reaction products before removing any unreacted poly(siloxane). The air and water contact angles were measured by the captive air bubble method using a Ram-Hart contact angle goniometer.

Results and Discussion

Figure 1 displays the complete scheme for the synthesis of poly(siloxane)–poly(pivalolactone) copolymers. A high molecular weight fraction of I was prepared according to the method of Katayana[17] and was rendered free of cyclics by dissolving the crude copoly(siloxane) in ether and precipitating in methanol. The siloxane ratio in I, determined by ^{1}H NMR, depended on the time of reaction between the two chlorosiloxanes. In this particular case, the reaction time used (20 h) was such that the feed siloxane ratio was equal to the siloxane ratio of I.

Concentrated aqueous KOH converted I to the copoly(siloxane–carboxylate anion) II under two-phase reaction conditions, and the reaction was monitored using IR and GPC. Figure 2 shows the IR spectra of I and II. The conversion of the COOH group to the carboxylate anion was evident from the disappearance of the peak at 1700 cm^{-1}, while all other peaks in the two spectra were the same. The peaks at 3690 and 860 cm^{-1} in both spectra are due to the OH stretch in the free Si–OH end groups,[18]

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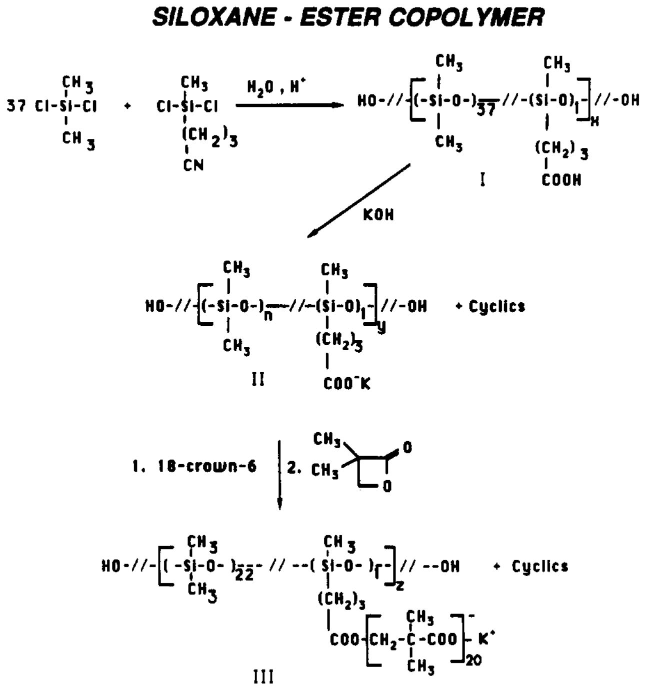

Figure 1. Synthetic scheme for poly(siloxane)-poly(pivalolactone) thermoplastic elastomers.

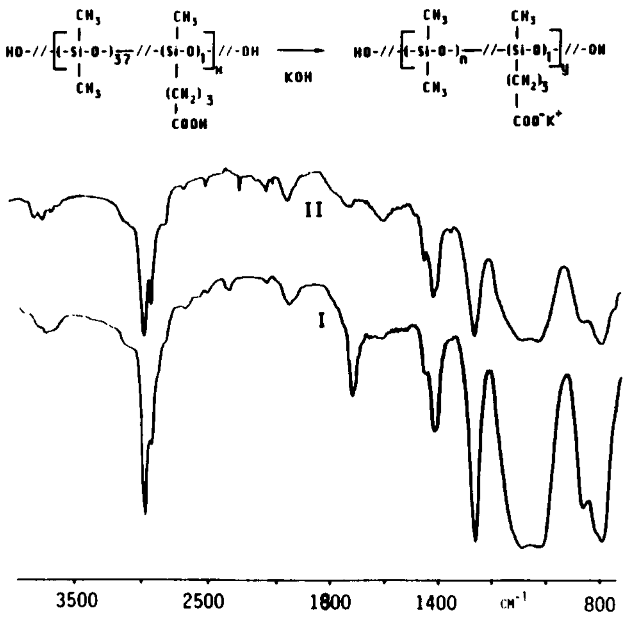

Figure 2. IR spectra of I and II.

indicating that the end silanol groups of I were not converted to the potassium salt, which is an important reaction to avoid in the synthetic procedure at hand. The GPC chromatograms of I and II indicate some depolymerization of I and the formation of some cyclics during the conversion, yet the molecular weight of II as determined by a polystyrene calibration was still high, exhibiting a value $M_{GPC} = 112000$. The yield of II was 92%, less than 100% since the cyclics formed evaporated under vacuum while drying, and this is to be expected since siloxane bonds in the linear polymer and the cyclic species have similar reactivities, meaning that the formation of cyclic compounds is difficult to avoid. Similar situations, called "redistribution" or "equilibration reactions", have been reported in the past, and these reactions depend on a number of parameters that can be controlled.[19]

Compound II was converted to the poly(siloxane)-*graft*-poly(pivalolactone) III under anhydrous conditions, wherein the conversion of pivalolactone to poly(pivalolactone) grafts was greater than 90%. The reaction became heterogeneous even before 10% conversion of pivalolactone, yet the pivalolactone polymerization continued, and a 24-h period was sufficient to produce conversions of greater than 90%. Heterogeneous graft copolymerizations of this nature are rare, and in this case the grafting of pivalolactone took place only in the presence of 18-crown-6. Crowns are known to complex with the potassium counterion and thus render the carboxylate anion an efficient initiator for lactone polymerization. Note, however, that in control experiments it was shown that the crown ether by itself did not polymerize pivalolactone. In another control experiment, it was shown that poly(dimethylsiloxane) possessing end silanol groups did not polymerize the lactone, indicating that the end silanol groups in II did not act as an initiator. This evidence confirms that hydroxy groups and water are much slower initiators than carboxylate anions for poly(pivalolactone) polymerization.[20]

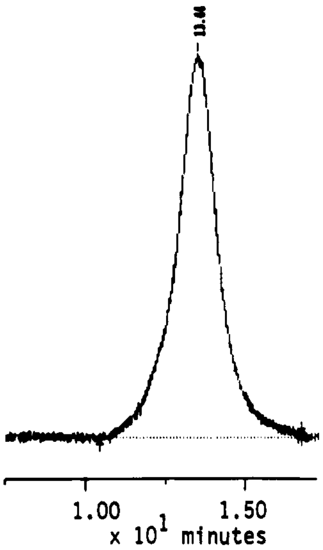

Figure 3. GPC curve of III (in methylene chloride/hexafluoroisopropyl alcohol (90:10): 25 °C; flow rate, 1 mL/min; columns, 1×10^6 Å, 1×10^5 Å, and 1×10^4 Å PL-GEL columns.

The product obtained after pivalolactone polymerization was extracted alternatively with *m*-cresol, a good solvent for homopoly(pivalolactone) and CH_2Cl_2, a good solvent for poly(siloxane). While no homopoly(pivalolactone) was extracted by *m*-cresol, about 5% low molecular weight siloxanes were extracted by CH_2Cl_2, yet the ^1H NMR of the extracted siloxanes showed that they did not contain any carboxy propyl groups. Therefore, it was evident that (a) any unreacted poly(siloxane) I was not extracted into CH_2Cl_2, (b) the extract consisted of cyclics, and (c) these cyclics did not contain any carboxypropyl-containing siloxane units. When the product obtained after pivalolactone polymerization was dissolved in a mixture of CH_2Cl_2 and hexafluoroisopropyl alcohol (90:10) and precipitated in ether, about 15% of the product dissolved in the ether layer and another 15% was extracted when the precipitation was repeated. In view of the "equilibration" or "redistribution" reactions mentioned previously, an estimate of the percent unreacted copolysiloxane is not possible.

After precipitation of the product from CH_2Cl_2/hexafluoroisopropyl alcohol, GPC analysis showed the presence of only one peak (Figure 3), indicating that grafting occurred and that the precipitate was not a polymer blend. The precipitate is the poly(siloxane)-poly(pivalolactone) graft copolymer III, whose molecular weight, M_{GPC}, cal-

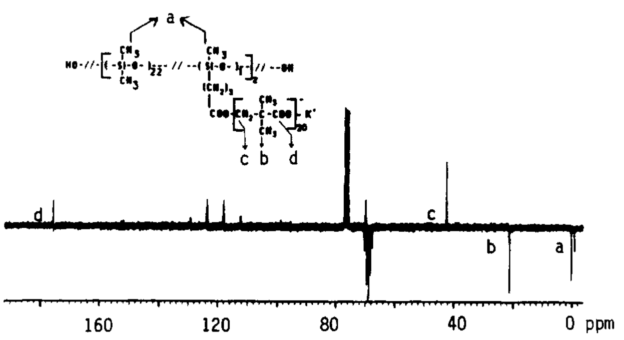

Figure 4. 50-MHz ^{13}C NMR spectrum of poly(siloxane)-*graft*-poly(pivalolactone) III, using attached proton test sequence (CH, CH_3, pos; CH_2, C, neg) in deuterated chloroform/hexafluoroisopropyl alcohol (90:10).

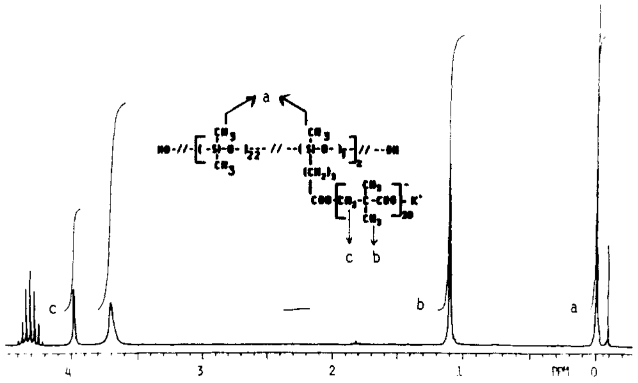

Figure 5. 200-MHz ^1H NMR spectrum of poly(siloxane)-*graft*-poly(pivalolactone) III.

culated by a polystyrene calibration, was 177 000.

The ^{13}C NMR of III (Figure 4) is an attached proton test spectrum, wherein the primary and tertiary carbons appear as downward signals and the secondary and quaternary carbons appear as upward signals. The downward signal at 0 ppm is due to methyl groups a in the polysiloxane and the downward signal at 21.4 ppm and the upward signals at 42.2 and 176.5 ppm are due to b, c, and d carbons in the poly(pivalolactone) graft. The other signals are due to the solvent, which is a mixture of $CDCl_3$ and hexafluoroisopropyl alcohol (90:10). The ^1H NMR of III (Figure 5) is in agreement with the above assignments. Whereas the signal at 0 ppm is due to protons a in the poly(siloxane) backbone, the signals at 1.2 and 4.0 ppm are due to protons b and c in the poly(pivalolactone) grafts.

The ratio of poly(siloxane) to poly(pivalolactone) in III was calculated by ^1H NMR, and the percent atomic concentrations, calculated on this basis, are the following: C, 47.15; Si, 16.98; H, 8.02. As compared to experimentally observed values: C, 47.30; Si, 17.49; H, 8.24.

Differential scanning calorimetry gave evidence for the thermoplastic behavior of these materials (Figure 6). The samples used were the reaction product after pivalolactone polymerization and before removing any unreacted poly(siloxane). No homopoly(pivalolactone) was present in these samples. Curve a was obtained by heating a sample of poly(siloxane)–poly(pivalolactone) containing 40% poly(pivalolactone) at 20 °C/min without any prior treatment and shows a melting temperature of 201 °C for the poly(pivalolactone) segment. Curve b was obtained by cooling that sample at 20 °C/min, and crystallization of the poly(pivalolactone) segment occurred just below 100 °C. When the sample was subjected to four heating cycles at 20 °C/min from 50 to 310 °C and then heated at 20 °C/min, curve c was obtained. The endotherm around 200 °C due to the poly(pivalolactone) segment was still evident in curve c; however, the endotherm was slightly shifted to a lower temperature.

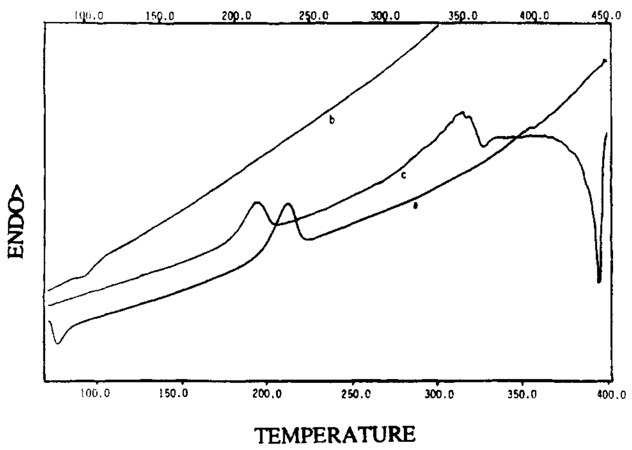

Figure 6. Thermograms for poly(siloxane)–poly(pivalolactone) containing 50 wt % poly(pivalolactone): (a) first hearing curve at 40 °C/min; (b) cooling curve at 20 °C/min after first heating (top scale); (c) heating curve at 40 °C/min, after four heating cycles from 50 to 310 °C.

Table I
DSC Data of Poly(siloxane)–Poly(pivalolactone)

poly(pivalolactone), wt %	T_g(PDMS), °C	T_m[poly(pivalolactone)], °C
10	−123	187.7
20	−123	191.1
30	−123	201.5
40	−123	202.1
50	−123	221.5

Table II
Contact Angle Measurements of Poly(siloxane)–Poly(pivalolactone)

poly(pivalolactone), wt %	underwater contact angle	poly(pivalolactone), wt %	underwater contact angle
0	91	40	89
10	90	50	89
20	86	70	50
30	90		

Table I shows the glass transition temperatures of poly(dimethylsiloxane) segments, T_g(PDMS), and the crystalline melting temperatures of poly(pivalolactone) segments, T_m[poly(pivalolactone)s], calculated from DSC data of copolymers containing different weight percentages of poly(pivalolactone). A broad use temperature range is evident for all the compositions. For instance, the composition containing 30% poly(pivalolactone), which appeared to show better elastic behavior than the other compositions, has a use temperature range from −125 °C to about 200 °C. The T_g(PDMS) was the same as that of homo-PDMS, and it did not vary with increasing poly(pivalolactone) content in the samples. Also, the melting temperatures observed for the poly(pivalolactone) segment in these compositions were very close to the melting temperatures of homopoly(pivalolactones) having comparable molecular weights. Therefore, it could be concluded that the phase separation in these systems is excellent. A quantitative study of phase separation will be carried out in the future, using a method used for poly(pivalolactone)-*block*-poly(ethylene oxide)-*block*-poly(pivalolactone) telechelomers.[21]

The surface morphology of poly(siloxane)–poly(pivalolactone) was investigated by contact angle measurements. Underwater contact angles, measured in water with air bubbles, are shown in Table II. Except for copolymers

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containing 70% poly(pivalolactone), all show a surface richer in poly(dimethylsiloxane). Annealing of the polymer samples should cause poly(pivalolactone) to better crystallize and cause more poly(dimethylsiloxane) to appear at the surface.

In conclusion, the chemistry that is described herein offers a new synthetic route to semicrystalline, high molecular weight poly(siloxane)–poly(ester) copolymers. These copolymers are very well phase separated and can be synthesized in a variety of compositions. All compositions exhibit a high melting point, yet offer the surface characteristics of siloxane copolymers. When the composition is rich in the siloxane phase, the copolymer is elastic in its behavior; when the composition is rich in the poly(ester) phase, the copolymer exhibits the properties of an engineering copolymer.

Our future work involves determining mechanical and rheological properties of these materials and expanding the synthesis to fluorinated siloxane copolymers.

Acknowledgment. We thank the Army Research Office for their financial support of this work (Contract DAAL 03-86-K-0050).

Registry No. 18-Crown-6, 17455-13-9.

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Hydrogen Bonding in Poly(amic acid)s

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Received April 22, 1988; Revised Manuscript Received March 14, 1989

ABSTRACT: Hydrogen bonding interactions in the poly(amic acid) precursors to polyimides are thought to significantly affect the curing process. Association models are applied to a calculation of the equilibrium distribution of hydrogen-bonded species. In the absence of a strongly hydrogen-bonding solvent, the principal types of interaction are between functional groups of the same type, i.e., acid/acid, amide/amide. These conclusions are supported by the infrared spectra of solvent-free amic acid and poly(amic acid) films.

Introduction

Numerous studies of the curing of polyimide precursors can be found in the literature. In much of this work the principal tool used to characterize the mechanism and the kinetics of the curing process has been infrared spectroscopy. The functional groups involved in the curing process, carboxylic acids and amides, have strong, easily identified absorption modes near 1700 and 1640 cm^{-1} and the technique is well-suited to the study of films. Upon curing, characteristic imide carbonyl stretching modes near 1780 and 1730 cm^{-1} appear, with the latter being far more intense than the former. (The vibrational character of these modes has been discussed by Matsuo[1] and Vanclef and Bouche.[2]) In many curing studies, however, only the weak 1780-cm^{-1} band is clearly resolved, very thin films being required to prevent "overabsorption" of the more intense mode near 1730 cm^{-1}. As a result, we believe some important information concerning competing reactions that can occur during curing has been lost. This forms the subject matter of these two papers. In this first paper we wish to consider what may at first seem to be a digression from the principal lines of our work: a consideration of hydrogen bonding in the poly(amic acid) precursors.

A number of authors have considered the hydrogen bonding of poly(amic acid)s to various solvents[3-9] and

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