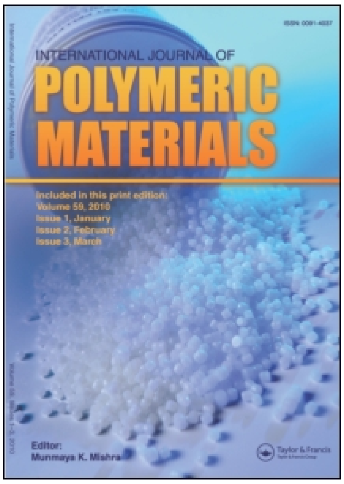

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Synthesis of Siloxane Graft Copolymers with Lactones and Lactams

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Synthesis of graft copolymers of siloxanes with pivalolactone, γ and δ-valerolactones and ε-caprolactam will be described. A carboxyl functionalized siloxane, previously prepared, promotes ring opening polymerization of the corresponding lactone or lactam, under conditions depending of the ring size, producing the graft copolymers. Products were characterized by spectroscopy, GPC, DSC, TGA. Surface composition was studied by XPS and water contact angle.

Keywords: Poly (siloxane); lactones; ε-caprolactam; graft copolymers

INTRODUCTION

Synthesis of graft copolymers Poly (siloxane-*g*-pivalolactone) with potential for thermoplastic elastomers was discussed in a previous paper [1]. Extension of this work to other lactones and to ε-caprolactam was undertaken looking again for compounds which could behave as thermoplastic elastomers [2].

Thermoplastic elastomers are materials with rubber-like behaviour that soften and can be reshaped upon heating. Their synthesis is based on the domain theory which considers that if a block or graft copolymer contains a hard phase (a crystalline or glassy segment) and a soft phase (an amorphous polymer with low glass transition temperature) the hard phase agglomerates and forms domains inducing microphase separation. These agglomerations act as strong, multifunctional junction points and the copolymers behave as though they are joined in a crosslinked network.

Poly(siloxane) copolymers can be used as elastomers at very low temperature due to the low glass transition temperature of the siloxane phase. Detailed information on siloxane copolymers can be found in the review by Yilgör and McGrath [3].

Differential scanning calorimetry of siloxane-pivalolactone graft copolymers confirms microphase separation of the two segments and their surface analysis indicates poly(siloxane) rich surface [1]. The low Tg (-123°C) of the soft poly(siloxane) segment and the high T_m (200°C) of the hard poly(pivalolactone) segment, permits a wide use range for different compositions of these copolymers.

Poly(siloxanes) are biocompatible and permeable to oxygen which would allow their use as biomaterials [3].

RESULTS AND DISCUSSION

Functionalized poly(siloxanes) were synthesized by a known method, [4] which consists in hydrolytic polymerization of a mixture of dimethyldichlorosilane and methyl, cyanopropyldichlorosilane or ring opening polymerization of their cyclic analogs (cyclosiloxanes), as shown in Figure 1. Hydrolysis of the cyano to the carboxyl group is necessary as this group promotes ring opening polymerization of the lactone or lactam under different conditions which are summarized in Table I. Poly(siloxane-*g*-pivalolactone) copolymers are very resistant to solvents and produce free standing films which have shown promising results in oxygen permeation tests [5].

The grafting reaction of δ-valerolactone on the siloxane (Mn 6500, GPC) afforded a copolymer, soluble in THF (Mn 15000, GPC), which did not produce free standing films. No grafting occured with γ-valerolactone, in agreement with previous studies [6, 7].

Poly (siloxane-*g*-ε-caprolactam) copolymers were obtained under similar conditions to nylon 6 synthesis [8]. The product was extracted successively with ether and dichloromethane, in order to eliminate unreacted siloxanes, and it was then crystallized from hexafluoroisopropanol/ether. The ^1H NMR spectrum allowed analysis of the siloxane-lactam ratio. By comparing the integration of the signals at $\delta = 0.00$ ppm (CH_3—Si) and $\delta = 2.2$ ppm (CH_2—CO), a siloxane content in weight %, of 2–4% was calculated. Although the weight % of both monomers was initially the same, most of the siloxane was recovered by extraction with ether.

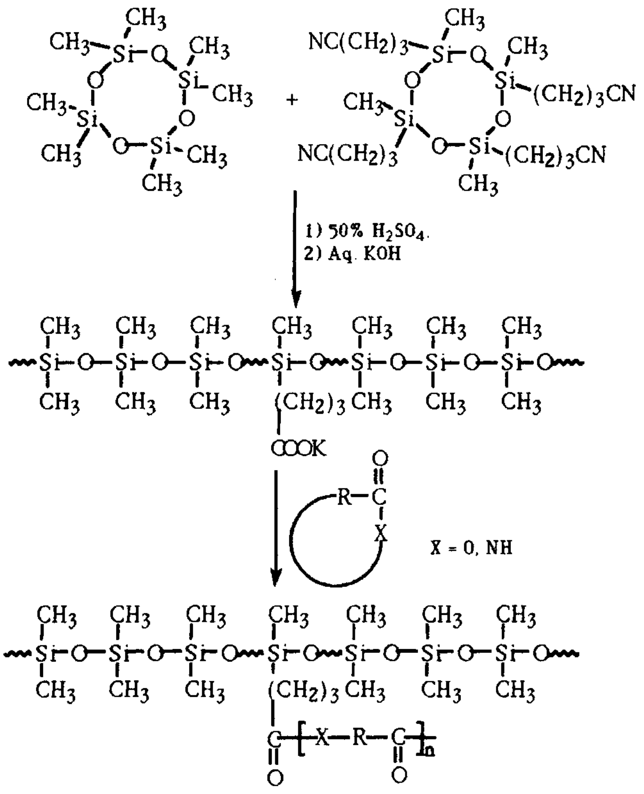

FIGURE 1 Synthesis of graft copolymers with lactones and lactams.

TABLE I Reaction conditions for the formation of graft-copolymers

Reagent	*Conditions*	*Film formation*
Pivalolactone	18-crown-6, THF, 20°C	+ +
g-valerolactone	18-crown-6, THF, 80°C	–
e-caprolactam	1-250°C, Sealed tube, Vac. 2-180°C, Atm. P.	+ +

Carbon NMR did not show signal for the CH_3—Si group due to the low siloxane content in the copolymer, while the signal for the C=O of the lactam segment (178.4 ppm), was noticeably intense. IR of copolymer films showed the characteristic signals of polyamides such as N—H stretching

(3250–3050 cm^{-1}), amide bands 1 and 2 (1625, 1530) and the Si—O stretching (1070).

Surface analysis of the films by XPS shows a 61.1/18.3 C/Si ratio which indicates a surface rich in siloxane when compared to 50/25 for PDMS and 74.6/0.6 for the same copolymer where both siloxane and lactam shared the surface. Siloxane rich surface should be hydrophobic, as confirmed by the water contact angle = 90.5° measured on the copolymer films. Phase segregation of the siloxane and the lactam components was also observed by optical microscopy using 90° polarized light. The crystalline phase, shows birefringence and appears as a white solid while the amorphous phase constitutes the black background in the picture.

Thermogravimetric analysis of copolymer films showed stability of the material up to 380°C.

In an attempt to increase the incorporation of siloxane in the product, the reaction mixture was dissolved in toluene and left refluxing at 120°C for several hours under argon atmosphere. Then the temperature was gradually increased to a maximum of 250°C to distill the solvent. The product, purified and characterized as before, contained 18% of the siloxane segment but did not produce free standing films. This is due to the lower molecular weight of the poly (caprolactam) segment calculated as 12500 by ^1H NMR as opposed to Mn of 78,000 for the poly(caprolactam) segment of the initial copolymer containing 2–4% siloxane.

In contrast with the copolymer containing 2–4% siloxane, ^{13}C NMR of the copolymer containing 18% siloxane, showed a signal for CH_3—Si groups while the signal for the C=O was very small.

CONCLUSIONS

Both pivalolactone and ε-caprolactam graft copolymers with siloxanes show good phase segregation, fulfilling one of the requirements of thermoplastic elastomers. However, while poly(siloxane-*g*-pivalolactone) copolymers with various compositions of the two segments all show phase segregation, only poly(siloxane-*g*-ε-caprolactam) copolymers with low siloxane content show this property, thus precluding their use as thermoplastic elastomers.

On the other hand, migration of the siloxane to the surface makes poly (siloxane-*g*-ε-caprolactam) a surface modified nylon. Furthermore, successful oxygen permeation tests performed on these copolymers might lead to useful applications.

TABLE II XPS data of a poly(siloxane-*g*-ε-caprolactam) film

Elemen.	*Posit. (eV)*	*wid.(eV)*	*cuant. Factor*	*Atom. Mass*	*C. Atom %*	*C. in mass*
C1S	285.05	2.04	1.00	12.01	61.12	46.67
O1S	532.20	1.89	1.71	16.00	18.06	18.37
NiS	399.95	1.86	1.42	14.01	2.48	2.21
Si2P	102.65	1.89	1.17	28.09	18.34	32.75

EXPERIMENTAL SECTION

NMR spectra were obtained on a Varian XL-200 series spectrometer; for copolymers containing siloxanes the methyl signal of the methyl siloxane was used as reference. GPC was performed on a Waters LC equipped with RI and UV detectors, IR spectra on a Perkin Elmer 281, VPO on a Wescan 233 osmometer, TGA on a V5.1A DuPont 2000, XPS in a Kratos XSSAM 800 and water contact angle on a NRL C.A. goniometer.

The synthesized copolymers were characterized as follows: Poly(dimethyl-co-methylcarboxypropyl-siloxane) : IR (cm^{-1}) 1700 (CO), 1050 (Si—O—Si), 780 (Si—C). ^{1}H NMR (δ, ppm): 0.0 s, (CH_3—Si); 0.6 m, (CH_2—Si); 1.24 m, (CH_2—CH_2—Si); 2.4 t, (CH_2—CO). VPO (toluene, 50°C) Mn 4600; GPC (THF, 1.0 ml/min) Mn 6500, PS standard. Poly (siloxane-*g*-pivalolactone): Characterized as before [1]. Films were obtained from 10–20% (w/v) dichlorometano/hexafluoroisopropanol solutions.

Poly (siloxane-*g*-δ-valerolactone) : IR (cm^{-1}) : 1720 (CO), 1255 (CO), 1050 (Si—O—Si), 800 (Si—C). ^{1}H NMR (δ, ppm) : 0.0 S, CH_3—Si, 1.6 CH_2—CH_2, 2.3 CH_3—CO, 4.0 CH_2—O. GPC (THF, 1.0ml/min) 15300, PS standard. Poly (siloxane-*g*-ε-caprolactam) : IR (cm^{-1}, film) : 3260, (N—H), 2920, 2860 (C—H), 1625 (CO), 1530 (N—H), 1060 (Si—O—Si), 780 (Si—C), 675 (N—H). ^{1}H NMR (δ, ppm) : 0.0s, CH_3—Si; 1.6 m, CH_2; 2.3 t, CH_2—CO; 3.2t, CH_2—N; 7.3s,.a., N—H. water contact angle : 90.5°. XPS data are shown in Table II.

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