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Synthesis

Synthesis of new polydimethylsiloxane-ε-caprolactam block copolymers

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Summary

Poly(dimethylsiloxane-ε-caprolactam) block copolymers were prepared from ε-caprolactam and anhydride-terminated polydimethylsiloxane oligomers under anionic conditions in the melt.

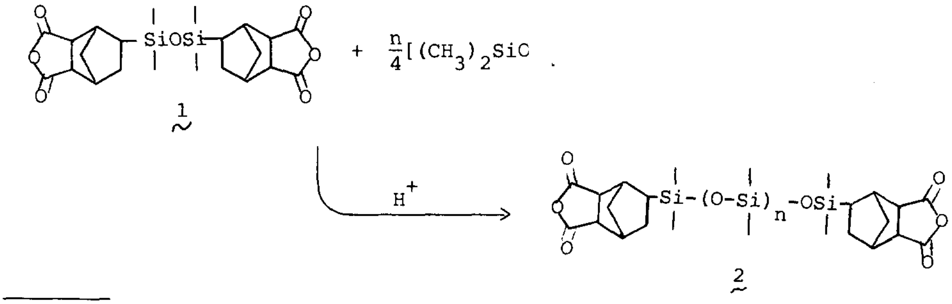
Results and Discussion

Two conflicting reports have appeared on the preparation of poly(dimethylsiloxane-ε-caprolactam) copolymers employing ε-caprolactam and initiator-terminated siloxane oligomers under anionic conditions. The earlier work of Owen and Thompson (1) was not supported by the recent investigations of Jerome et al (2) which indicated that polydimethylsiloxane functionality is readily degraded under anionic caprolactam polymerization conditions in hydrocarbon solvents. We report our preliminary results here on the melt preparation of poly(dimethylsiloxane-ε-caprolactam) block polymers which are stable to anionic caprolactam polymerization conditions.

Our approach utilizes 1,2-bis(5-norbornyl-2,3-dicarboxylic anhydride-1,1,2,2-tetramethyldisiloxane) (1), which was equilibrated with octamethylcyclotetrasiloxane (Scheme 1) under acidic conditions to provide an anhydride-terminated polydimethylsiloxane oligomer (2) (3) with an average repeat unit of 99 based on analysis by high field ^{29}Si NMR spectroscopy.

The oligomer obtained from disiloxane 1 was observed to initiate the polymerization of ε-caprolactam in the presence of a catalytic quantity of sodium caprolactimide to provide copolymer 3 (Scheme 2). The reaction was rapid in the melt at 130°C, providing a characteristically tough material in two minutes from oligomer charged at the 50 weight % level. The polymer was soluble in m-cresol; however, it was insoluble in formic acid, a

Scheme 1



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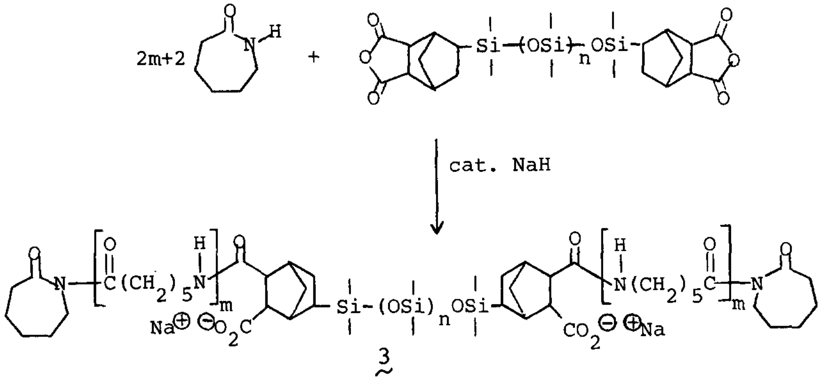
Scheme 2



solvent for Nylon-6. ^{29}Si NMR analysis of the crude polymer indicated the integrity of the silicone block remained intact and no cleavage products, such as silanolates or N-siloxylactams, were observed. Infrared spectroscopy of the crude polymer showed complete absence of norbornyl anhydride absorption at 1850 and 1765 cm^{-1} demonstrating complete reaction of the initiator species. The polymer was cryogenically ground to a powder and was extracted exhaustively with hot toluene for several days, providing 5 weight % of toluene soluble extract. Analysis of the extract by ^{1}H NMR and gas chromatography indicated it was comprised of ε-caprolactam almost exclusively, along with only trace amounts of methylsiloxane containing materials.

The nature of the linkage group connecting the hard and soft blocks of the copolymer has not been determined unambiguously; however, it is presumed to be either an imide or mixed amide sodium carboxylate. The lack of infrared absorption near or above 1695 cm $^{-1}$ in the carbonyl region suggests the latter type of linkage based on an analysis of model compounds (4).

In conclusion, a novel melt preparation of polydimethylsiloxane-polycaprolactam block copolymers has been demonstrated. The copolymerization was found to be highly efficient in lactam conversion and selective in that side reactions leading to siloxane chain degradation were not observed. These materials offer obvious advantages compared to similar materials prepared previously where caprolactam conversion was limited to 50% and silicone incorporation was less than 15% of the initial amount charged.

Further characterization of these materials is ongoing and will be the subject of a future report.

Experimental

To 180 mg (0.0075 mol) sodium hydride was added 10.0 g (0.88 mol) dry ε-caprolactam at 130°C under nitrogen. When hydrogen evolution ceased, 9.9 g (0.0013 mol) of oligomer 2 was added at once with efficient stirring. The reaction contents initially appeared heterogeneous, but became homogeneous within 40 seconds. After 2 minutes the charge cured to a tough solid mass. Differential Scanning Calorimetric Analysis (heating rate 40°C/min, under nitrogen): T_m = 212°C; Intrinsic Viscosity (25°C in m-cresol) = 0.9 dL/g; IR (film) 3280, 2920, 1630, 1535, 1250, 1110-1000 cm^{-1}; ^{29}Si NMR (m-cresol) δ 6.2 (2 Si, s), -21 (99 Si, m); fully decoupled

^{13}C NMR (m-cresol) 174.75, 28.58, 26.09, 24.93, 19.74, 19.38, 0.64.

References

1. M.J. Owen, J. Thompson, Br.Polym.J. 4, 297 (1972).
2. P.M. Lefebvre, R. Jerome, P. Teyssie, Makromol.Chem. 183, 2453, (1982).
3. H.-S. Ryang, U.S. Patent 4,381,396 (General Electric Company) (1983).
4. For example, carbonyl absorption of the bis N-butylimide of anhydride **1** is observed at 1695 and 1770 cm^{-1} in the infrared (neat film).

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