NOTES

Homopolymerization of p-*Trimethylsilylstyrene*

Recent communications in the literature have reported the synthesis[1,2] and the copolymerization[2] of *p*-trimethylsilylstyrene. However, little information concerning the homopolymerization of this silane monomer was given. During the course of a related project in these laboratories, an alternate synthesis of *p*-trimethylsilylstyrene was developed and further information on the homopolymerization of this compound obtained. It is felt that these results are of interest in view of the previous work.[1,2]

The procedure reported for the synthesis of *p*-trimethylsilylstyrene[1,2] involved the treatment of the Grignard reagent of *p*-ethylbromobenzene with silicon tetrachloride. Chlorination followed by dehydrohalogenation gave *p*-trichlorosilylstyrene. Treatment of this material with methylmagnesium bromide yielded *p*-trimethylsilylstyrene. In the present work the procedure reported by Leebrick and Ramsden[3] for the synthesis of *p*-vinylphenyltriphenyltin was adopted. This method involved the use of the Grignard reagent prepared from *p*-chlorostyrene.[5] The reaction sequence is outlined below.

$$p\text{-Cl—C}_6\text{H}_4\text{—CH=CH}_2 \xrightarrow[\text{THF}]{\text{Mg}} p\text{-ClMg—C}_6\text{H}_4\text{—CH=CH}_2 \xrightarrow{(\text{CH}_3)_3\text{SiCl}}$$

$$p\text{-(CH}_3)_3\text{Si—C}_6\text{H}_4\text{—CH=CH}_2$$

A crude yield of 41 mole-% was realized using this procedure.

The homopolymerization of *p*-trimethylsilylstyrene was carried out in bulk using acetyl peroxide as the initiator. The white polymer was soluble in aromatic solvents, such as benzene and toluene, but insoluble in isopropyl and methyl alcohol. It had a softening point in the range of 170–180°. Fibers drawn from the hot melt of this material were brittle.

The intrinsic viscosity of the polymer was determined using toluene as the solvent. The data for the viscosity determinations are summarized in Table I.

TABLE I
Viscosity of Poly-*p*-trimethylsilylstyrene in Toluene

Concentration, g./100 ml.	Time, sec.	η_{sp}/c
Solvent	55.6	—
0.050	56.5	0.320
0.100	57.5	0.341
0.300	62.6	0.416

A plot of η_{sp}/c vs. concentration gave a value of 0.305 for the intrinsic viscosity of the polymer. From this result it is reasonable to assume that high molecular weight polymers of this monomer may be obtained under suitable conditions.

Experimental

p-Trimethylsilylstyrene was prepared using the procedure described by Leebrick and Ramsden.[3] The intermediated Grignard reagent was obtained using magnesium (4.85 g., 0.2 mole) and *p*-chlorostyrene (13.8 g., 0.1 mole) in tetrahydrofuran (50 ml.) solvent. Treatment of the Grignard reagent with trimethylchlorosilane (10.8 g., 0.1 mole) dissolved in tetrahydrofuran (25 ml.) followed by hydrolysis and isolation of the desired product by ether extraction and fractionation gave *p*-trimethylsilylstyrene, 7.2 g. (41 mole-% based on *p*-chlorostyrene). The material had b.p. 72° (9.0 mm.) to 87° (11.0 mm.), n_D^{25} 1.5197–1.5219. Redistillation of an analytical sample through a semimicrocolumn[4] gave b.p. 91° (10 mm.), n_D^{25} 1.5212.

ANAL.: Calcd. for $C_{11}H_{16}Si$: C, 74.9; H, 9.1; Si, 15.9. Found: C, 74.5; H, 9.2; Si, 15.2.

The infrared spectrum of this material confirmed the structure for *p*-trimethylsilylstyrene.

Homopolymerization of p-*Trimethylsilylstyrene.* In a 2″ test tube, previously flushed with nitrogen, 0.5 g. of the above monomer was placed together with acetyl peroxide (0.05 ml., 25 wt.-% in dimethyl phthalate). The stoppered tube was placed in an oven at 90° for a period of 10 hours. A clear, hard, polymeric material formed during this period. The polymer was dissolved in benzene (5.0 ml.) and precipitated by pouring the benzene solution with stirring into isopropyl alcohol (75 ml.). The white precipitate which formed was removed by filtration under suction, washed with two 25-ml. portions of isopropyl alcohol, and then dried at 50° (2.0 mm.) for 4 hours. The polymer weighed 0.43 g. and had a softening point of 170–180° (sealed capillary tube).

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References

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4. Gould, C. W., Jr., G. Holzman, and C. Niemann, *Anal. Chem.*, **20,** 361 (1948).
5. *p*-Chlorostyrene may be purchased from Monomer-Polymer, Leominster, Massachusetts.

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*Nachweis der taktischen Struktur an einem nicht kristallisierbaren Polymeren**

Alle bisher bekannten Methoden zur Erkennung der taktischen Struktur von Vinylpolymeren beruhen letzten Endes auf der Untersuchung der Proben im kristallisierten Zustand. Neben der Röntgenbeugung gehört dazu die Untersuchung der IR-Spektren,[1,2] des Schmelzverhaltens, der Dichte sowie des dynamisch-mechanischen Verhaltens.[3]

Es erhebt sich jedoch grundsätzlich die Frage, ob es nicht Polymere gibt, die zwar eine taktische Struktur besitzen, jedoch nicht kristallisierbar sind, sei es aus räumlichen Gründen beim Einbau in das Kristallgitter, sei es, weil bisher geeignete Methoden zur Kristallisation fehlen, oder auch aus anderen Gründen. So konnte zum Beispiel von

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