# *Stereoregular Polymers. VI. Copolymerization with the Ziegler Catalysts*[*]

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Binary copolymerizations of $\alpha$-olefins, which are known individually to form isotactic polymers with the Ziegler catalyst, were investigated to see if stereospecific copolymerization could be seen to yield crystalline copolymers.

Although there are a number of reports by Natta and his collaborators on copolymerization of propylene and ethylene with complex catalysts of the Ziegler type[1], one of the comonomers was always ethylene and this has substantially no concern with the assymmetricity on the polymer. Besides, ethylene has markedly higher activity towards the anionic polymerization as compared to propylene, and their efforts were apparently directed towards the study of amorphous copolymers.

In the present work, the situation was distinctly different from that in the case of Natta. Particular attention was directed to the formation of crystalline copolymers, because it was believed that crystalline copolymers could be produced if the isotactic orientation had been held during copolymerization**.

The monomers chosen here are styrene, allyl- and 3-butenyl-trimethylsilane, which are known by the present authors to yield the corresponding isotactic polymers by themselves and to have the similar reactivity towards the Ziegler catalyst[3,4].

The following abreviations will be used in

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[*] Presented at the 8th. Annual Meeting of Society of Polymer Science (Japan), May 30, 1959.

[1] G. Natta et al., *Chim. e ind.*, **39**, 733, 743, 825 (1957); **40**, 717, 896 (1958).

** In the course of our study, Reding has reported in a brief note the cocrystalline copolymers of 3-methyl-1-butene and 4-methyl-1-pentene, which were found to be surprisingly highly crystalline over the entire range of compositions.[2]

[2] F. P. Reding and E. R. Walter, *J. Polymer Sci.*, **37**, 555 (1959).

[3] S. Murahashi, S. Nozakura and M. Sumi, This Bulletin, **32**, 670 (1959).

[4] G. Natta, G. Mazzanti, P. Longi and F. Bernardini, *J. Polymer Sci.*, **31**, 181 (1958).

TABLE I. COPOLYMERIZATION OF STYRENE AND ALKENYLTRIMETHYLSILANES WITH $AlEt_3$-$TiCl_4$ CATALYST AT 70°C

| Combination of monomers | Monomer, mole | | Catalyst, millimole | | | $n$-Heptane ml. | Time hr. | Polymer yield, % | Composition, mole % of silane* | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Silane | St | $AlEt_3$ | $TiCl_4$ | Al/Ti ratio | | | | Monomer | Polymer |
| St-VSi | 0.0298 | 0.0290 | 4.30 | 1.79 | 2.40 | 20 | 7 | 16.0 | 50.48 | 1.94 |
| St-ASi | 0.0176 | 0.0724 | 5.61 | 2.26 | 2.48 | 20 | 3.5 | 13.2 | 19.56 | 6.19 |
| | 0.0166 | 0.0173 | 3.77 | 1.42 | 2.65 | 15 | 6 | 23.3 | 48.97 | 18.87 |
| | 0.0615 | 0.0165 | 5.87 | 2.21 | 2.66 | 20 | 2 | 10.1 | 78.85 | 66.62 |
| St-BSi | 0.0146 | 0.0624 | 5.70 | 2.21 | 2.58 | 20 | 3 | 15.3 | 18.96 | 10.64 |
| | 0.0378 | 0.0379 | 5.87 | 2.32 | 2.53 | 20 | 3 | 20.5 | 49.93 | 42.71 |
| | 0.0650 | 0.0170 | 6.87 | 2.63 | 2.60 | 20 | 4 | 27.4 | 79.27 | 70.21 |

* Copolymer composition was determined by the gravimetric analysis of silicon.

TABLE II. COPOLYMERIZATION OF ASi AND BSi WITH $AlEt_3$-$TiCl_4$ CATALYST AT 70°C

| Monomer, mole | | Catalyst, millimole | | | $n$-Heptane ml. | Time hr. | Polymer yield, % | Composition, mole % of silane | |
|---|---|---|---|---|---|---|---|---|---|
| ASi | BSi | $AlEt_3$ | $TiCl_4$ | Al/Ti ratio | | | | Monomer | Polymer |
| 0.0306 | 0.0289 | 5.35 | 2.21 | 2.42 | 20 | 3.5 | 22.1 | 51.43 | 8.74 |
| 0.0735 | 0.0192 | 6.58* | 2.63 | 2.50 | 25 | 3.5 | 9.9 | 79.29 | 48.72 |

* A solution of $AlEt_3$(3.86 millimole) was added to a boiling $n$-heptane solution of $TiCl_4$ (2.63 millimole) and after cooling it the precipitated mass was washed with $n$-heptane, and then $AlEt_3$(2.72 millimole) was added.

this paper for convenience:

| | |
|---|---|
| Vinyltrimethylsilane | VSi |
| Allyltrimethylsilane | ASi |
| 3-Butenyltrimethylsilane | BSi |
| Styrene | St |

## Results and Discussion

**Polymerization.** — Binary copolymerizations were carried out using these monomers with $AlEt_3$-$TiCl_4$ catalyst at 70°C. The results were summarized in Tables I and II.

VSi, the first member of alkenyltrimethylsilane, was found to enter into copolymerization with great difficulty as anticipated from the case of its homopolymerization with the same catalyst, and hence a further study was omitted from our program.

As is shown in Tables I and II, the compositions of the crude polymers varied with monomer compositions and copolymerization appeared at first to have been realized. The apparent monomer reactivities towards the Ziegler catalyst was found to be in the order of St > BSi > ASi ≫ VSi.

**Fractionation of the Crude Polymers.** — As these copolymers showed some degree of crystallinity on X-ray diffraction patterns, fractionations were carried out with a series of solvents selected from the knowledge of the solubility characteristics of the individual crystalline homopolymers. (Table III).

TABLE III. SOLUBILITY CHARACTERISTICS OF ISOTACTIC POLYMERS OF St, ASi AND BSi

| | $n$-Heptane | Toluene | Decalin |
|---|---|---|---|
| Poly(BSi) | Sol. in hot | Sol. | Sol. |
| Poly(St) | Insol. | Sol. in hot | Sol. |
| Poly(ASi) | Insol. | Insol. | Sol. in hot |

Thus, a St-BSi copolymer was fractionally extracted with a series of solvents: acetone, ether, methylethylketone, $n$-heptane and toluene under reflux in this order. The results are shown in Table IV in which was included, for reference, the results of model fractional extractions of an artificial mixture of two homopolymers, showing practically a complete separation of the crystalline parts into the original components. The acetone-, ether- and methylethylketone-soluble fractions of the copolymer are all found to give almost amorphous X-ray diffraction patterns, while both the $n$-heptane- and the toluene-fraction are found to give crystalline patterns. Analytical data of the last two fractions show that the $n$-heptane-fraction is closely similar to isotactic poly(BSi) with a minor amount of St, while the toluene-fraction is similar to isotactic poly(St) with a minor amount of BSi. The amount of the minor ingredient (St) in the former fraction showed no appreciable change even after repeated purification, that is, extraction with methylethylketone followed by dissolution of the residue into hot $n$-heptane and reprecipitation by cooling the solution. Therefore, it

TABLE IV. FRACTIONATION OF St-BSi COPOLYMERS

| Polymers | Composition of the crude polymer | Acetone-extract |  |  |  | Ether extract |  | M. E. K extract |  | *n*-Heptane extract |  | Toluene extract |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Sol. in cold |  | Sol. in hot |  |  |  |  |  |  |  |  |  |
|  | mole % of silane | % | mole % of silane | % | mole % of silane | % | mole % of silane | % | mole % of silane | % | mole % of silane | % | mole % of silane |
| Copolymer | 10.64 | 23.1 | 7.35 | 5.5 | 35.03 | 3.3 | 49.59 | 1.8 | — | 3.3 | 76.72 | 53.7 | 2.76 |
| Copolymer | 42.25 | 19.9 | 18.68 | 10.1 | 49.23 | 18.6 | 67.62 | 3.1 | 14.48 | 19.6 | 89.57 | 22.4 | 3.81 |
| Copolymer | 70.21 | 5.4 | 40.73 | 8.9 | 67.22 | 13.2 | 76.46 | 0.8 | — | 53.0 | 90.61 | 4.6 | 13.53 |
| Mixture | 40.64 | 5.8 | 22.75 | 1.2 | — | 6.2 | 94.60 | 0.7 | — | 29.4 | 92.79 | 43.7 | 0.19 |
| X-ray evidence |  | amorph. |  | amorph. |  | amorph. |  | amorph. |  | cryst. |  | cryst. |  |

TABLE V. FRACTIONATION OF St-ASi COPOLYMERS

| Polymers | Composition of the crude polymer | Acetone extract |  | Ether extract |  | *n*-Heptane extract |  | M. E. K. extract |  | Toluene extract |  | Toluene residue |  | Decalin extract |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | mole % of ASi | % | mole % of ASi | % | mole % of ASi | % | mole % of ASi | % | mole % of ASi | % | mole % of ASi | % | mole % of ASi | % | mole % of ASi |
| Copolymer | 6.19 | 9.0 | 19.84 | 1.3 | — | 1.4 | — | 2.5 | — | 78.1 | 1.52 | 1.2 | — |  |  |
| Copolymer | 18.89 | 13.3 | 33.76 | 4.8 | 51.57 | 1.2 | 53.91 | 0.9 | 18.02 | 63.4 | 2.48 | 10.6 | 77.44 |  |  |
| Copolymer | 66.62 | 16.1 | — | 11.5 | — | 4.2 | — | 0.9 | — | 17.9 | 9.19 |  |  | 0.79 | 85.07 |
| Micture | 19.39 | 6.4 | 52.14 | 2.4 | — | 1.0 | — | 0.5 | — | 68.8 | 0.22 | 11.8 | 95.50 |  |  |
| X-ray evidence |  | amorph. |  | amorph. |  | amorph. |  | amorph. |  | cryst. |  | cryst. |  |  |  |

TABLE VI. FRACTIONATION OF ASi-BSi COPOLYMERS

| Polymers | Crude polymers Si, %* | Acetone extract % | Ether extract % | *n*-Heptane extract |  | Decalin extract |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | % | Si, %* | % | Si, %* |
| Copolymer | 22.13 | 20.3 | 45.7 | 18.6 | — | 6.6 | — |
| Copolymer | 23.13 | 15.9 | 29.3 | 14.7 | 21.0 | 31.0 | 24.0 |
| X-ray evidence |  | amorph. | amorph. | cryst. |  | cryst. |  |

* The theoretical Si content of BSi and ASi are 21.90 and 24.59%, respectively. The analysis of the fractions was carried out on a microscale.

was concluded that the *n*-heptane-fraction might not be a mixture but a genuine copolymer. It was also found that the same was held to be the case by the latter fraction.

An additional evidence for the copolymeric character of the two crystalline fractions is the change of their compositions with the fed monomer compositions. By increasing the silane content in monomer composition, the silane content of both the *n*-heptane- and the toluene-fraction increased.

Thus, it was confirmed that the crystalline portion of the St–BSi polymer consisted of two kinds of crystalline copolymers of quite different compositions, that is, both a crystalline copolymer with a predominant portion of one component and another crystalline copolymer of another predominant component were produced side by side.

Similar results hold in the copolymerization with the combinations of St–ASi and ASi–BSi (Tables V and VI), though in the latter case the pair selected was of very similar monomers.

From these results, one might postulate that the catalyst surface might possess two kinds of isotactically active sites for each monomer. One kind of the sites is more favorable to polymerize one monomer than other monomers and this is true of other site. More generally, one might say that the catalytic surface possesses several different kinds of active sites suitable for some kinds of monomers. Copolymerization would have taken place on such sites, leading to the crystalline copolymers of different compositions.

An alternative interpretation might also be possible where the nature of an active site may not have been set specifically beforehand at the time when the catalyst is formed, and may become specific after the first attack of a monomer molecule on the catalyst site.

It may not be easy to distinguish which of the two alternative mechanisms is more favorable in our case, but the following experimental results seems to show that the former mechanism might be more favorable. It was demonstrated in one experiment where a small amount of one monomer (about 1millimole) was added preliminarily to the catalyst at 70°C, and after 20 minutes of polymerization a mixture of two monomers St and ASi (20 millimole : 20 millimole) was then added. Two runs that were carried out by the preliminary addition of St in one case and ASi in another case resulted in practically the same distribution of fractions in the extraction experiment.

**X-Ray Examination of the Crystalline Fractions.**—In the case of the copolymerization of St and BSi, for instance, the *n*-heptane- and the toluene-fraction showed some degree of

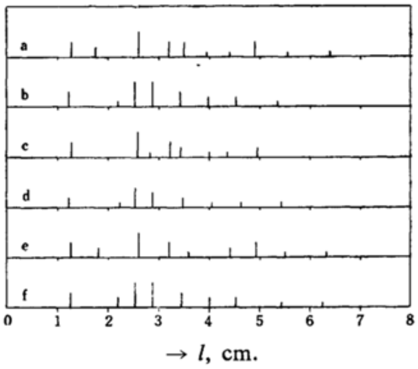

Fig. 1. X-Ray spectra of ASi-St copolymers. ($R$=4.45 cm.)
- a) Copolymer : silane, 77.4 mole %.
- b) Copolymer : silane, 9.1 mole %.
- c) Artificial mixture : silane, 77 mole %.
- d) Artificial mixture : silane, 9.2 mole %.
- e) Isotactic poly(allylsilane).
- f) Isotactic polystyrene.

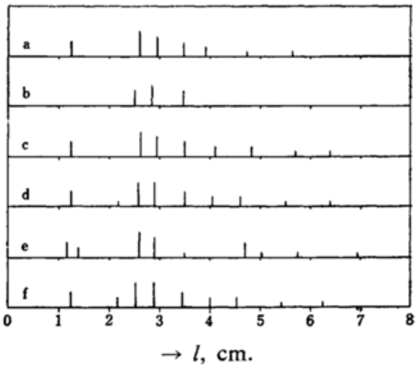

Fig. 2. X-Ray spectra of BSi-St copolymers. ($R$=4.45 cm.)
- a) Copolymer : silane, 89.6 mole %.
- b) Copolymer : silane, 13.5 mole %.
- c) Artificial mixture : silane, 73 mole %.
- d) Artificial mixture : silane. 23 mole %.
- e) Isotactic poly(3-butenylsilane).
- f) Isotactic polystyrene.

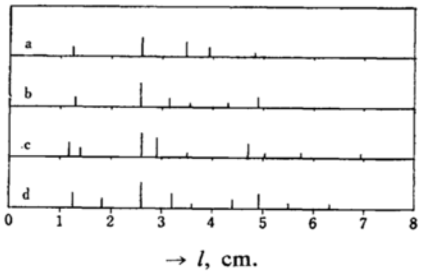

Fig. 3. X-Ray spectra of ASi-BSi copolymers. ($R$=4.45 cm.)
- a) Copolymer : the *n*-heptane-fraction.
- b) Copolymer : the decalin-fraction.
- c) Isotactic poly(3-butenylsilane).
- d) Isotactic poly(allylsilane).

crystalline patterns on X-ray diagrams. X-Ray powder patterns of these two fractions were compared with those of two homopolymers and of the artificial mixtures of similar compositions. The same comparison was also made in other cases. X-Ray spectra of St–ASi copolymers, St–BSi copolymers, and ASi–BSi copolymers were shown in Figs. 1, 2 and 3, respectively***.

From the close inspection of these results, it was found that in some cases the patterns closely resemble those of artificial mixtures of the similar compositions (Figs. 1a and 1b), some had a new kind of additional reflections over those of artificial mixtures or a superposition of homopolymers (Figs. 2a and 3a), and others showed only very diffuse reflections of one homopolymer (Figs. 2b and 3b). These facts might suggest the possible existence of constitutional varieties in copolymers with the change of monomer species, that is, one copolymer might have a structure of block copolymer and another might have a structure of random copolymer. For instance, the decalin-fraction (Fig. 1a) of St–ASi copolymer has a rather high crystallinity which is comparable to that of poly(ASi) and shows a diffraction pattern that is closely similar to an artificial mixture of the same composition, suggesting a block structure. If it were a random copolymer, incorporation of about 20% of St units, as is the case, would almost destroy the crystallinity of the copolymer.

## Experimental

**Materials.**—A commercial styrene was purified according to the usual method⁽5⁾.

Vinyl-, allyl, and 3-butenyl-trimethylsilane are prepared and purified just as described in the previous paper⁽3⁾.

$AlEt_3$ and $TiCl_4$ are the products of Mitsui Chem. Ind. Co. and Osaka Titanium Co., respectively and were used as about 30 and 21% solutions in *n*-heptane.

**Polymerization.**—Polymerization was carried out without agitation in an apparatus described in the previous paper⁽6⁾. The solution of $AlEt_3$ was added first to *n*-heptane in the apparatus under nitrogen, and mixed, and then the solution of $TiCl_4$ was dropped slowly along the wall of the vessel. After ten minutes, the mixed monomers were added and polymerization was carried out without agitation.

Polymerization was stopped by the addition of methanol (2 ml.) and concentrated hydrochloric acid (0.3 ml.), and the mixture was poured into a large amount of methanol. After being kept overnight, the polymer was collected, washed with methanol and dried.

**Fractionation of the Crude Copolymers.** — Hot extraction was carried out at the boiling temperature of the solvents, using a modified Soxhlet extraction apparatus. Complete extraction with one solvent generally took about seven to ten hours. After the completion of one extraction, the extraction cup with the residual polymer in it was dried, and was subjected to the next extraction. Each extract was concentrated to about 50 ml. and poured into a large amount of methanol, and the precipitate was collected, washed and dried.

Purification of the crystalline fraction, for example, the *n*-heptane fraction of St–BSi copolymer was carried out as follows: the fraction (Si, 20.08%) was extracted with methyl ethyl ketone, and dissolved in hot *n*-heptane. The hot solution, after being filtered through a glass filter, was poured into a large amount of methanol. The precipitated polymer was collected, washed and dried in vacuum at about 100°C (Si, 19.92%). The toluene fraction (Si, 1.80%) of the polymer was also purified by extraction with *n*-heptane followed by dissolution in toluene and reprecipitation with methanol, giving the silicon content of 1.40 and 1.48%, successively.

**Preparation of Artificial Mixture of Homopolymers.** — Generally, a mechanical mixture of two kinds of polymers was dissolved in a hot solvent common to them and poured quickly into a large amount of methanol and then the precipitate was collected.

**Determination of Copolymer Composition.**—The composition of copolymers was determined by the gravimetric analysis of silicon. Analysis was carried out by wet digestion with fuming sulfuric acid in a platinum crucible. The ignited silica was ascertained by treating it with 60% hydrofluoric acid.

**X-Ray Study.** — All samples were annealed at 150∼160°C for 2 hr. The diffraction patterns were taken using nickel filtered Cu$K\alpha$ radiation. The film distance was 4.45 cm.

## Summary

Binary copolymerization of styrene, allyltrimethylsilane and 3-butenyltrimethylsilane was investigated using the Ziegler catalyst at 70°C. It was found to be possible to separate the crystalline part of copolymers by fractional extraction into two kinds of genuine crystalline copolymers, each of which has an extremely different composition from the other.

The nature of the active sites on the catalytic surface was discussed in order to elucidate the above fact.

The constitution of the individual crystalline fractions appeared to vary case by case, i. e., the structure of blockcopolymer might be assigned to some cases and random copolymers to some other cases.

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*** Since the exact copolymer composition was not obvious in the case of ASi-BSi copolymer because of the small difference of silicon content between ASi and BSi units, comparison with artificial mixtures was not indicated in the list.

5) E. R. Blout and H. Mark, "Monomers", Interscience Publisher (1944).

6) S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, This Bulletin, 32, 1094 (1959).