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Reprinted from

VOLUME XXXI, ISSUE NO. 122

AUGUST, 1958

Journal of POLYMER SCIENCE

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The author wishes to express his thanks to the Goodyear Tire and Rubber Company and H. J. Osterhof for permission to publish this work, and to P. J. Jones, D. J. Zimmerman, G. S. Trick, E. F. Devlin, and C. E. Gordon for determining the physical properties of the polymers.

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JOGINDER LAL

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Received May 14, 1958

Isotactic Polymers of Silicon-Containing Vinyl Monomers

The polymerization of silicon-containing vinyl monomers by means of the old conventional processes yields only low molecular weight polymers. In fact, such monomers with radical initiators, even if very high pressures in the range of 5,000 atm. are employed, yield only low polymers, *e.g.*, tetramers or hexamers.¹ Similarly, with cationic catalysts only liquid oily polymers were obtained from allyltrimethylsilane.²

We have now prepared high molecular weight polymers from monomers containing one vinylic unsaturation and one silicon atom for the first time, by using heterogeneous catalysts which act according to a mechanism of coordinated anionic catalysis. Such polymers contain linear, head-to-tail macromolecules having regular structure, which are crystallizable.

Monoallylsilane has been polymerized at 60–70°C. in the presence of catalysts prepared from violet titanium trichloride and triethyl aluminum. The polymer thus obtained is highly crystalline, melts completely at 127–128°C. near the melting point of polybutene-1³ and, when freshly prepared, is completely soluble in boiling *n*-heptane. This polymer, owing to the presence of Si—H bonds, can be easily crosslinked by the action of oxygen at 70–80°C. or by the action of water or alcohols in suitable conditions.

By polymerization of allyltrimethylsilane in heptane solution at a temperature of 70–80°C. in the presence of catalysts prepared by reaction of triethyl aluminum with titanium tetrachloride (moles Al(C₂H₅)₃/moles TiCl₄ = about 2), crude polymers having high molecular weight were obtained with good conversion yields.

The crude polymers, obtained from allyltrimethylsilane, have a silicon content of 24.35% (calculated for (C₈H₁₄Si)_n, Si 24.56%) and an intrinsic viscosity in tetraline at 135°C. of about 0.5.

They were fractionated by extraction with solvents, employed at their boiling point, in the following sequence: acetone, ether, *n*-heptane, xylene. In Table I the results of fractionation are reported, as well as some physical properties of the several resulting fractions. Fractions III and IV prove to be crystalline under x-rays and possess higher specific gravity and lower solubility than the corresponding fractions I and II, which are amorphous.

As we have previously found for the crystalline fractions and for the amorphous, non-crystallizable fractions of poly- α -olefins, the solubility of the different fractions depends mainly on their steric structure.⁴

TABLE I
 Fractionation and Physical Properties of Polyallyltrimethylsilane prepared at 80°C. in the Presence of Catalysts Obtained from $\text{Al}(\text{C}_2\text{H}_5)_3$ and TiCl_4

I Refer- ence no.	II Ether extractable fraction		III Heptane extractable fraction		IV Xylene extractable fraction			V Residue (highly crystalline by x-rays)			
	% ^a	η^b	% ^a	η^b	% ^a	η^b	m.p., °C. ^c	d^{30}	% ^a	η^b	m.p. °C. ^c
1	9.4	0.47	1.9	0.25	2.8	0.28	125	0.870	72.8	0.53	360
2	15.0	0.06	3.6	0.21	4.8	0.34	123	0.866	66.0	0.49	351

^a Weight percentage of polymer, extractable with boiling solvents.

^b Intrinsic viscosity in tetraline at 135°C.

^c Melting temperature, determined by polarizing microscope, by heating at a rate of 1°C./min.

The highly crystalline fractions possess a very high melting point (350–360°C.) and can be extruded, in the melted state, in filaments and then stretched.

The x-ray fiber spectra indicate a helical structure with a ternary symmetry, and an identity period of 6.5 Å. of the chain, attributable to an isotactic structure.

The fractions possessing higher solubility show lower crystallinity, lower specific gravity, and lower melting points than those of the highly crystalline isotactic polymers. The very low melting point of some fractions may depend not only on the lower molecular weight, but also on the presence of steric irregularities along the chains (stereoblock polymers).

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Received May 16, 1958

Nuclear Magnetic Resonance Absorption in Various Polytetrafluoroethylenes

We here report a remarkably large effect of crystallinity on the nuclear magnetic resonance absorption line width of polytetrafluoroethylene (PTFE). We were led to this study by a reported large discrepancy in measurements on this material.¹ The difference is to be seen in Figures 1 and 2 where we show curves of line width (ΔH) in gauss (defined as the distance between points of maximum slope on the derivative curve) versus temperature for, among others, the samples of Teflon (Du Pont PTFE) measured by Slichter¹ (Sl on Fig. 1) and for samples of Fluon (I.C.I. PTFE) measured by Smith² (Sm on Fig. 2). Slichter has suggested that Fluon may contain a mobile impurity which leads to an apparent line narrowing at a lower temperature than the true one in a manner not unknown in nuclear magnetic resonance.³

A study of the literature reveals that other measurements, whether on Teflon or Fluon, agree substantially with Smith's result. All the available results on Teflon^{1,4,5} are plotted in Figure 1 including two samples, one slow cooled (ST) and one quenched (QT), which we have measured ourselves and for which full details of heat treatment and crystallinity are available and are given in Table I. We have plotted only some points from Wilson and Pake⁴ where they give actual line widths since it is not stated how they derive T_2 from ΔH .

Figure 2 shows results on Fluon, including our own for two well-defined samples, one slow cooled (SF) and one quenched (QF), and Smith's results (Sm) already referred to.²

A comparison of Figure 1 and 2 show that the results for Teflon and Fluon are substantially the same with the exception of Sl and other smaller differences discussed below.

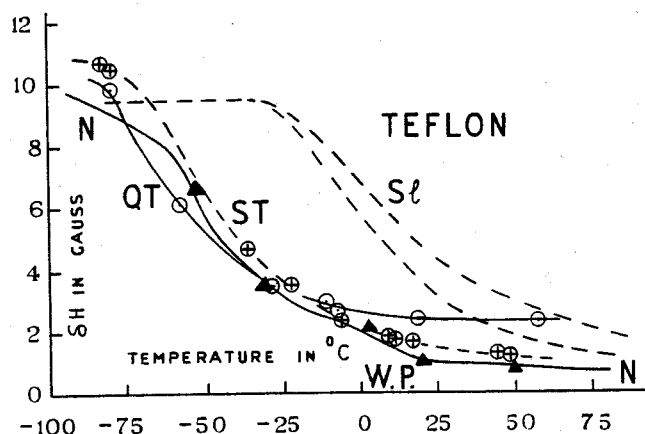


Fig. 1. Nuclear resonance absorption line width *versus* temperature for various samples of Du Pont PTFE. Sl from ref. 1. N from ref. 5. W. P. from ref. 4. QT from this paper, see Table I. ST from this paper, see Table I.

TABLE I

Sample	Manufacturer	Crystallinity by x-ray per cent	Heat treatment
QT (Fig. 1)	Du Pont	42	Sample melted and plunged in water at room temperature
ST (Fig. 1)	"	55	Melted and cooled from 360°C. to room temperature with time constant of 80 min.
QF (Fig. 2)	I.C.I.	58	As for QT
SF (Fig. 2)	"	76	As for ST
V (Fig. 3)	"	90	None
M (Fig. 3)	"	55	Held at 365°C. for 15 min. and cooled to room temperature with time constant about 15 min.

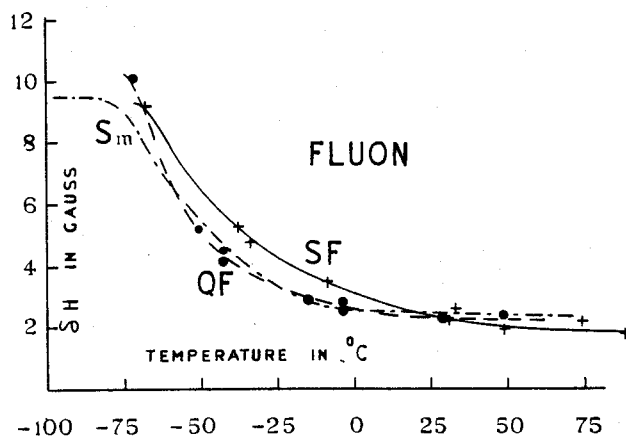


Fig. 2. Nuclear resonance absorption line width *versus* temperature for various samples of I.C.I. PTFE. Sm from ref. 2. QF from this paper, see Table I. SF from this paper, see Table I.

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