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Chemistry

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Abstract

Full Text

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Polymerization of Vinyl Chloride Initiated by the Reaction of Carbon Tetrachloride with Organometallic Titanium Compounds

Recently, a system consisting of triethylaluminum, CCl_4 , and TiCl_3 was successfully used as an initiator for the polymerization of vinyl chloride (¹). It may be assumed that polymerization of the monomer occurred as a result of the action of free radicals formed in the course of the reaction of triethylaluminum with CCl_4 . However, a substantial role was played by the influence of the titanium halide, which, as is known, readily exchanges a halogen atom for an alkyl group of an organoaluminum compound.

In this connection it seemed of interest to examine the action of individual organotitanium compounds (TiOC), whose reactions with halogen derivatives had been studied by us earlier (^{2, 3}). It was shown that compounds of tetravalent titanium, $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$, $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$, react with CCl_4 at 80° with the formation of chlorobenzene, methyl chloride, and hexachloroethane—products of typical homolytic interaction. Compounds of divalent titanium, $(\text{C}_5\text{H}_5)_2\text{Ti}$, $(\text{C}_6\text{H}_5)_2\text{Ti}$, are more reactive toward CCl_4 . In the first case the reaction proceeds at room temperature with the addition of two chlorine atoms to the $(\text{C}_5\text{H}_5)_2\text{Ti}$ group, which remains unchanged under the reaction conditions, and with the formation of stable $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. Diphenyltitanium under the action of CCl_4 , even under mild conditions (20°), completely cleaves the phenyl—titanium bonds; the final product of homolytic chlorination is TiCl_4 (⁴).

The results of our experiments on the polymerization of vinyl chloride are summarized in Table 1. All the TiOC studied did not cause polymerization of vinyl chloride. The systems $\text{TiOC} + \text{CCl}_4$ initiated polymerization with varying degrees of conversion, depending on the nature of the TiOC .

The most effective system, $(\text{C}_6\text{H}_5)_4\text{Ti} + \text{CCl}_4$ (the degree of conversion reached 55.0–60.0%), was studied in greater detail under conditions analogous to its initiating action. For this purpose, cooled CCl_4 was added in small portions to a solution of tetraphenyltitanium in ether at -80° . Vigorous interaction was observed, together with the appearance of a rapidly disappearing violet coloration. The reaction mixture was kept at -80° for two days, after which the temperature was slowly raised to room temperature. During the reaction the appearance

of the black coloration characteristic of diphenyltitanium was not observed. At room temperature the solution acquired a deep dark-red color. Chlorobenzene, diphenyl, hexachloroethane, benzene, and TiCl_4 were detected in the reaction products. Compounds of divalent and trivalent titanium were not detected in the final products. Quantitative analysis of the reaction products was hindered by strong resinification. The presence of chlorobenzene and hexachloroethane in the products of the reaction of $(\text{C}_6\text{H}_5)_4\text{Ti}$ with CCl_4 confirms the homolytic mechanism of the reaction.

In addition to tetraphenyltitanium, mixed π -cyclopentadienyl- σ -alkyl(aryl) derivatives were used for the polymerization of vinyl chloride: $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$; $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$; $\text{C}_5\text{H}_5\text{Ti}(\text{C}_6\text{H}_5)_3$. With the introduction into

Table 1

Polymerization of vinyl chloride in the presence of organotitanium compounds

(average values are given for $C_{\text{C}_2\text{H}_3\text{Cl}}^0 = 0.3$ mole, $C_{\text{CCl}_4}^0 = 0.02$ mole, $C_{\text{MeX}_n}^0 = 0.001$ mole, where Me = Ti, V, Fe)

No. of experiments	Initiating system	Reaction conditions, temp., °C	Reaction conditions, duration, h	PVC yield, %	η	PVC content, %
1	$(\text{C}_6\text{H}_5)_4\text{Ti}$ *	20	36	traces	—	—
2	$(\text{C}_6\text{H}_5)_4\text{Ti} + \text{CCl}_4$	20	36	55.0—60.0	0.40	55.5
3	$(\text{C}_6\text{H}_5)_4\text{Ti} + \text{C}_4\text{Cl}_6$	20	36	black suspension	—	—
4	$(\text{C}_6\text{H}_5)_4\text{Ti} + \gamma\text{-C}_5\text{Cl}_8$	20	36	black suspension	—	—
5	$(\text{C}_6\text{H}_5)_4\text{Ti} + \gamma\text{-C}_5\text{Cl}_6$	20	36	black suspension	—	—
6	$(\text{C}_6\text{H}_5)_4\text{Ti} + \text{TiCl}_4$	20	36	4.0—4.5	0.06	48.4
7	$(\text{C}_6\text{H}_5)_4\text{Ti} + \text{VCl}_3$	20	36	traces	—	—
8	$(\text{C}_6\text{H}_5)_4\text{Ti} + \text{FeCl}_3$	20	36	1.9—2.1	0.06	54.2
9	$\text{C}_5\text{H}_5\text{Ti}(\text{C}_6\text{H}_5)_3$ *	20	36	traces	—	—

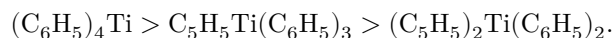
No. of experiments	Initiating system	Reaction conditions, temp., °C	Reaction conditions, duration, h	PVC yield, %	η	PVC content, %
10	$C_5H_5Ti(C_6H_5)_3 + CCl_4$	20	36	5.5–6.0	–	54.6
11	$C_5H_5Ti(C_6H_5)_3 + CCl_4$	60	36	37.0–39.0	–	–
12	$(C_5H_5)_2Ti(C_6H_5)_2$ **	20	36	does not polymerize	does not polymerize	does not polymerize
13	$(C_5H_5)_2Ti(C_6H_5)_2 + CCl_4$	20	36	3.6–3.8	0.98	52.5
14	$(C_5H_5)_2Ti(C_6H_5)_2 + CCl_4$	60	36	26.5–29.0	0.30	54.8
15	$(C_5H_5)_2Ti(CH_3)_2$ **	20	48	traces	–	–
16	$(C_5H_5)_2Ti(CH_3)_2 + CCl_4$	20	36	6.0–6.6	0.02	55.4
17	$(C_6H_5)_2Ti$ ***	20 (60)	48	does not polymerize	does not polymerize	does not polymerize
18	$(C_6H_5)_2Ti + CCl_4$	20	36	traces	–	–
19	$(C_6H_5)_2Ti + CCl_4$	60	36	7.0–7.3	0.31	54.8
20	$C_5H_5TiC_6H_5$ ***	20	36	does not polymerize	does not polymerize	does not polymerize
21	$C_5H_5TiC_6H_5 + CCl_4$	20	36	2.4–3.0	0.03	55.4
22	$(C_5H_5)_2Ti \cdot$ THF ***	20	36	does not polymerize	does not polymerize	does not polymerize
23	$(C_5H_5)_2Ti \cdot$ THF + CCl_4	20	36	traces	–	–
24	$(C_5H_5)_2Ti \cdot$ THF + CCl_4	60	36	3.1–3.3	0.06	56.1

* For the polymerization, 5 ml of a 0.25 M ether solution of TiOC at -80° was used.

** TiOC samples of 0.1 g were used.

*** 5 ml of a 0.25 M ether solution of TiOC at 20° was taken.

With the introduction of π -cyclopentadienyl groups into the TiOC molecule, the effectiveness of the compound as a catalyst for the polymerization of vinyl chloride decreased sharply:



The yield of polyvinyl chloride at 20° was 55.0–60.0%; 5.5–6.0%; and 3.6–3.8%, respectively; for the last two members of the series at 60° it was 37.0–39.0% and 26.5–29.0%.

Replacement of aryl radicals by alkyl radicals in compounds of the type $(\text{C}_5\text{H}_5)_2\text{TiR}_2$ increased the yield of polyvinyl chloride from 3.6–3.8% for the diphenyl derivative to 6.0–6.6% for the dimethyl derivative at 20° . Derivatives of divalent titanium, in comparison with the preceding ones, proved to be less active initiators; polymerization of vinyl chloride occurred only on heating to 60° . The yield of polyvinyl chloride in the case of diphenyltitanium was greater (7.0–7.7%) than in the case of biscyclopentadienyltitanium tetrahydrofuranate (3.1–3.3%). The exception is monocyclopentadienyltitanium (5), in the presence of which vinyl chloride polymerized at room temperature with a conversion of 2.4–3.0%.

Special experiments showed that the initial reaction products (titanium tetrachloride, monocyclopentadienyltitanium trichloride, phenyllithium) did not cause polymerization of vinyl chloride. In addition to CCl_4 , additives of other halogen derivatives were used (Table 1, experiments 3, 4, 5), as well as halides of transition metals (Table 1, experiments 6, 7, 8). However, the yields of polyvinyl chloride in all these cases were low.

With regard to the properties of the synthesized polyvinyl chloride, it should be noted that the samples obtained were finely dispersed powders of white (gray) color. With the exception of the polymer obtained in the system $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2 + \text{CCl}_4$, the polymerization products were characterized by a low molecular weight (limiting viscosity number at 20° in cyclohexanone ≈ 0.1 –0.4). The other properties (heat resistance, decomposition temperature) were at the level of polyvinyl chloride that is the product of ordinary free-radical polymerization.

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