STEREODIRECTEDNESS OF THE RADICAL TELOMERIZATION OF PROPYLENE WITH CCl_4 IN THE PRESENCE OF CERTAIN COMPOUNDS OF THE TRANSITION METALS

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The influence of salts and complexes of the transition metals on the stereodirectedness of homolytic processes has been little investigated, and then chiefly for reactions of polymerization. It has been established, in particular, that the initiation of radical polymerization by Ni, Fe, Co, Cr, Mn, W, and Mo carbonyls somewhat increases (evidently on account of complexation of the monomer with the metal) the probability of formation of isotactic sequences for polymethyl methacrylate [1] and syndiotactic sequences for polyvinyl chloride [2] and does not change the syndio-direction of growth of the polyacrylonitrile radical [3]. An appreciable increase in the isotacticity was observed in the polymerization of styrene with nickel peroxide NiH_6O_{11} [4], attributed by the authors to the formation of a metal – monomer π-complex. The addition of salts of the transition metals [$FeCl_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, etc.] has no significant influence on the microstructure of the products of radical polymerization of vinyl monomers [5]. In [6] a negligible change in the stereoregularity of polyvinyl chloride is indicated for the systems of salt of transition metal – organoaluminum compound. The possibility of a quantitative evaluation [7] of the yield of racemic iso-(i), syndio-(s), and hetero-(h) modifications of 1,1',1'',7-tetrachloro-3,5-dimethyloctane (T_3) and initiation of the radical telomerization of propylene with CCl_4 by compounds of the transition metals [8, 9] permitted a consideration of the influence of the latter on the stereodirectedness of telomerization, like that studied earlier with peroxide initiators [10].

In this work we determined the relative content of diastereomeric forms T_3 in the presence of the following compounds: $Fe(CO)_5$, iron triacetylacetonate $Fe(AA)_3$, π-allylirontricarbonyl chloride $\pi\text{-}C_3H_5Fe\cdot(CO)_3Cl$, $FeCl_3$, $Co_2(CO)_8$, and the catalytic system $\alpha\text{-}TiCl_3 - Al(C_2H_5)_3$ at temperatures from 90 to 200°.

EXPERIMENTAL

The experiments were conducted in glass ampoules or stainless steel autoclaves with thorough preliminary drying of the telogen and monomer over CaA molecular sieves. Anhydrous $FeCl_3$, $Fe(AA)_3$, $Al\cdot(C_2H_5)_3$, $Co_2(CO)_8$, $\pi\text{-}C_3H_5Fe(CO)_3Cl$ and $TiCl_3$ (α-modification), were used without additional treatment; $Fe\cdot(CO)_5$ was redistilled before the experiment in a stream of nitrogen under vacuum. In the experiments the following order of loading of the reagents was observed: initiator, telogen, monomer. $FeCl_3$ was introduced into the ampoule in a stream of dry purified nitrogen; the remaining initiators were loaded into the solution of the telogen immediately after the preparation of the latter. When the catalytic system $\alpha\text{-}TiCl_3 - Al(C_2H_5)_3$ (Ti – Al) was used, $TiCl_3$ powder was introduced into an ampoule cooled to –78° (in an atmosphere of dry nitrogen), then $Al(C_2H_5)_3$ and the required volume of CCl_4 and C_3H_6 were added (determined according to a calibrated gauge). The ampoules were sealed and heated to the temperature of the experiment. The method of gas – liquid chromatographic analysis and calculation of the particular transfer constants C_n did not differ from those described earlier [7, 10]. The data obtained are cited in Tables 1 and 2.

It should be noted that we verified the possibility of initiating telomerization with a system Ti – Al (or each of the components individually) in a broad range of temperatures. However, for temperatures

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TABLE 1. Telomerization of Propylene with CCl_4 in the Presence of Compounds of the Transition Metals*

Experiment No.	$[M]_i$, M	$[S]_i$, M	$[Init]_i$, M · 10^2	T, °C	τ, min	K_M, %	K_S, %	$R_t \cdot 10^3$, moles/liter · min	$[Init]_i \cdot 10^3 / [M]_i$	$\frac{[M]}{[S]}$ average	Telomer homologs, mole %			Modification of T_3, rel. %			C_1††	C_2††
											T_1	T_2	T_3	n-T_3	s-T_3	i-T_3		
$Fe(CO)_5$																		
1	9,43	1,11	8,94	145	45	14,7	68,0	16,8	9,48	13,9	27,8	59,1	13,1	39,0	51,0	10,0	5,35	62,8
2	9,18	0,962	32,3	145	45	6,7	33,7	7,21	35,2	11,5	27,6	56,6	15,8	45,3	47,0	7,7	4,38	41,2
3	9,46	0,538	48,5	145	45	3,2	25,0	2,99	51,3	20,1	14,0	50,4	35,6	37,0	49,5	13,5	3,28	28,4
$Fe(AA)_3$																		
4	10,3	0,598	1,81	145	30	0,9	9,3	1,86	1,76	18,0	43,8	41,8	14,4	35,3	51,3	13,4	14,0	52,2
5	10,3	0,603	12,4	145	30	1,5	14,3	2,87	12,0	18,3	34,9	51,0	14,1	35,9	52,0	12,1	9,82	66,4
6	10,4	0,534	13,9	145	30	1,6	18,8	3,35	13,4	21,4	51,3	37,8	10,9	34,8	52,0	13,2	22,5	74,1
$Co_2(CO)_8$																		
7	9,45	1,17	7,61	145	45	4,3	23,2	6,03	8,06	9,1	53,4	42,6	4,0	46,9	40,8	12,3	10,4	97,0
8	9,44	1,21	18,3	145	15	0,3	1,3	1,05	19,4	7,8	31,6	60,3	8,1	40,3	48,7	11,0	3,61	58,2
9	9,56	1,14	4,72	200	10	5,3	26,6	30,3	4,93	9,7	42,6	48,0	9,4	41,8	45,1	12,1	7,20	49,5
10	9,77	0,977	6,94	200	10	3,7	22,8	22,3	7,10	10,7	38,2	51,1	10,7	37,9	50,4	11,7	6,62	51,1
11	9,53	1,14	8,02	200	10	0,7	3,6	4,1	8,42	8,5	43,4	47,8	8,8	36,0	51,3	12,7	6,52	46,2
π-$C_3H_5Fe(CO)_3Cl$																		
12	10,5	0,566	0,451	105	60	0,1	1,3	0,09	0,43	19,0	35,8	43,4	20,8	37,9	53,6	8,5	10,6	39,6
13	10,5	0,484	3,35	105	60	0,3	4,4	0,36	3,20	22,1	59,3	32,2	8,5	42,3	50,5	7,2	32,2	83,7
14	10,4	0,531	7,38	105	60	0,7	6,8	0,60	7,10	20,3	26,1	54,5	19,4	49,4	43,6	7,0	7,17	57,0
15	10.1	0,758	15,5	105	70	2,0	14,3	1,55	15,4	14,6	33,0	51,8	15.2	43,5	45,8	10,7	7,18	49,8
16	9,26	1,35	4,80	105	60	1,1	5,8	1,30	5,19	7,0	71,4	26,0	2,6	42,2	43,8	15,0	17,5	70,2
17	8,96	1,57	5,64	105	60	1,1	4,9	1,28	6,30	5,8	73,7	24,4	1,9	43,3	34,0	22,7	16,4	75,0
18	9,31	1,32	10,1	105	60	1,7	8,2	1,80	10,8	7,3	61,7	34,6	3,7	51,2	28,8	20,0	11,7	68,2
$FeCl_3$																		
19	10,4	0,535	6,51	145	60	0,5	6,6	0,59	6,27	20,0	64,5	25,2	10,3	35,6	52,2	12,2	36,3	49,0
20	10,2	0,683	15,4	145	60	1,1	10,2	1,16	15,1	15,7	55,7	32,7	11,6	36,3	54,6	9,1	19,7	44,2
21	10,2	0,657	31,0	145	45	0,8	10,0	1,46	30,3	16,4	75,0	18,0	7,0	37,7	50,4	11,9	49,2	42,2
22	10,3	0,588	6,48	200	30	2,1	22,8	4,47	6,28	19,8	50,9	33,9	15,2	35,3	52,3	12,4	20,5	44,2
23	9,82	0,863	20,1	200	30	3,3	28,5	8,21	20,5	13,6	72,5	21,8	5,7	36,1	53,0	10,9	35,8	52,0
24	10,3	0,587	27,9	200	30	3,2	30,0	5,87	27,1	21,0	39,0	35,6	25,4	33,8	54,1	12,1	13,4	29,5
α-$TiCl_3$ — $Al(C_2H_5)_3$**																		
25†	9,29	1,33	1,17	50	300	<0,1	<0,1	—	—	7,0	—	—	—	—	—	—	—	—
26‡	9,29	1,33	5,83	50	300	—	—	—	—	7,0	—	—	—	—	—	—	—	—
27	10,1	0.723	3,18	90	1080	0,1	1,8	0,01	—	14,2	43,1	51,3	5,6	37,0	54,0	9,0	10,8	130
28	10,0	0,772	3,39	90	1080	0,1	2,0	0,01	—	13,2	61,3	35,8	2,9	38,0	54,0	8,0	20,9	163
29	10.3	0.642	—	90	900	—	—	—	—	16,0	—	—	—	—	—	—	—	—
30	10,3	0,632	3,30	90	900	0,4	3,0	0,02	—	16,7	24,8	54,0	21,2	39,8	53,6	6,6	5,5	42,6

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*$[M]_i$, $[S]_i$, and $[Init]_i$ are the initial concentrations of the monomer, telogen, and transition metal compound; they were calculated considering V_f, assuming that the content of the reagents in the gas phase can be neglected; V_f is the volume of the liquid phase at the temperature of the experiment (from 70 to 95% of the free volume of the ampoule or autoclave); $Fe(AA)_3$ represents iron triacetylacetonate; π-$C_3H_5Fe(CO)_3Cl$ represents π-allylirontricarbonyl chloride; K_M and K_S are the conversions of C_3H_6 and CCl_4, calculated according to the chromatographic data; R_t is the initial rate of telomerization (determined according to the degree of conversion of the more rapidly consumed telogen); T_1-T_3 are the telomer homologs $CCl_3[CH_2CH(CH)_3]_nCl$ with n = 1-3; experiments 1-24 were conducted in stainless steel autoclaves (volume ~10 ml); the remainder in glass ampoules (2-15 ml) at a degree of filling no less than 60%.

†According to the data of gas–liquid chromatographic analysis, T_1 and T_2 are formed in small quantities.

‡Added 1.25 M toluene; only polymerization is observed, and no telomers are detected in the reaction mixture.

**In experiments 25-29, ~0.006 M α-$TiCl_3$ was introduced; the content of $[Al(C_2H_5)_3]_i$ is cited in the column $[Init]_i$ for these experiments.

††The average values of the particular transfer constants C_1 and C_2 in the telomerization of C_3H_6 with CCl_4, initiated by azobisisobutyrodinitrile [7] or benzoyl peroxide [10], are 2.28 and 43 at 105° [7], 3.65 and 33 at 145° [7], and 5.64 and 40.3 at 200° [10], respectively.

below 0, +20, and 50°, regardless of the Ti : Al ratio (from 1 : 1 to 1 : 7), the formation of high-molecular compounds is observed (only at 50° were T_1 and T_2 detected in the reaction with a yield of ~0.1%, experiment 25, see Table 1). The introduction of toluene led to intensive polymerization and complete suppression of telomerization (experiment 26). Appreciable amounts of the telomer homologs (experiments 27 and 28) were obtained only when the temperature is increased to 90° in the presence of a substantial excess of triethylaluminum (Ti : Al = 1 : 7-8) and a very long duration of the experiments. The distribution of the