Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary information

A new insight into the polymerization mechanism of 1,3-dienes cationic polymerization. IV. Mechanism of unsaturation loss in the polymerization of isoprene

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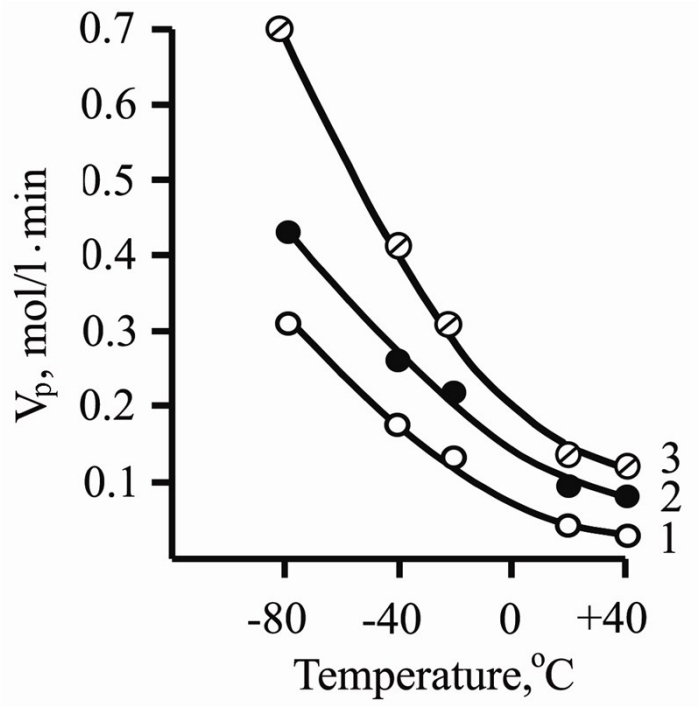

Fig. S1 Dependence of the reaction rate (V_p – the rate for first 5 min of the process) on temperature for the isoprene polymerization with ^{t}BuCl/$TiCl_4$ initiating system in CH_2Cl_2 at different ^{t}BuCl/$TiCl_4$ molar ratios: [C_5H_8]=4.0 M; [$TiCl_4$]=1.5·10^{-2} M. Ratio of ^{t}BuCl to $TiCl_4$: 20 (1), 100 (2) and 300 (3).

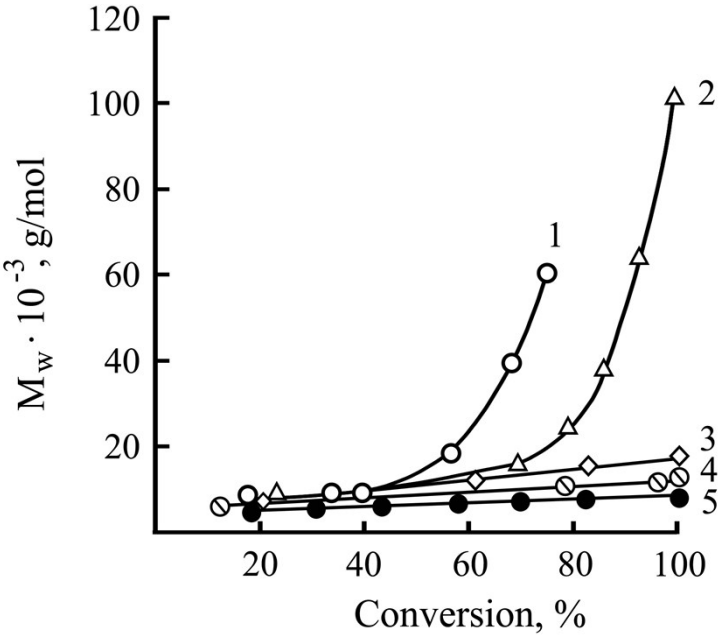

Fig. S2 The weight average molecular weight vs. conversion plots for the isoprene polymerization with ^{t}BuCl/$TiCl_4$ initiating system in CH_2Cl_2 at 20 ºC at different ^{t}BuCl/$TiCl_4$ molar ratios: [C_5H_8]=4.0 M; [$TiCl_4$]=1.5·10^{-2} M. . Ratio of ^{t}BuCl to $TiCl_4$: 5.0 (1), 20.0 (2), 50.0 (3), 100.0 (4) and 300.0 (5).

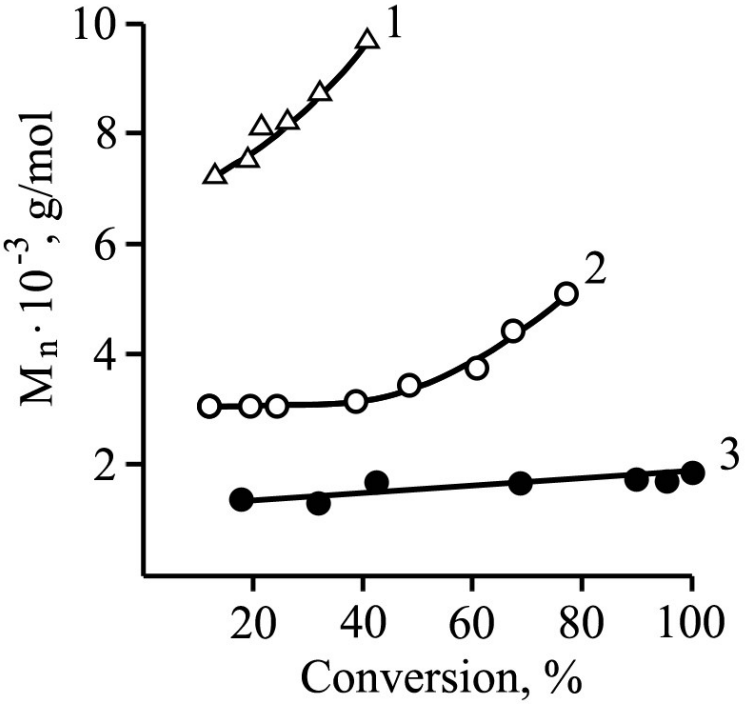

Fig. S3 M_n vs. conversion plots for the isoprene polymerization with $^tBuCl/TiCl_4$ initiating system in CH_2Cl_2 at different temperatures: $[C_5H_8]$=4.0 M; $[TiCl_4]=1.5\cdot10^{-2}$ M; $^tBuCl/TiCl_4$=300. Temperature: -78°C (1), -20°C (2) и 20°C (3).

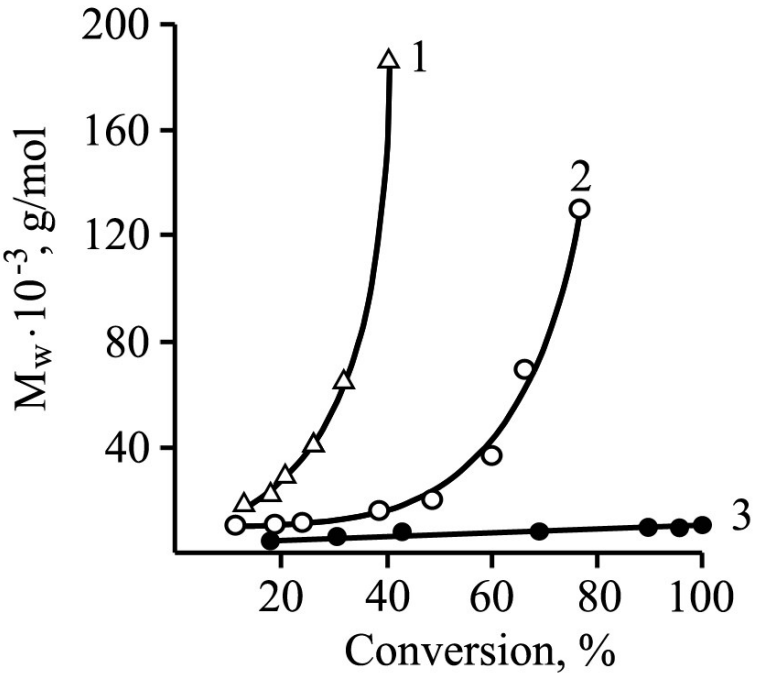

Fig. S4 M_w vs. conversion plots for the isoprene polymerization with $^tBuCl/TiCl_4$ initiating system in CH_2Cl_2 at different temperatures: $[C_5H_8]$=4.0 M; $[TiCl_4]=1.5\cdot10^{-2}$ M; $^tBuCl/TiCl_4$=300. Temperature: -78°C (1), -20°C (2) и 20°C.

Table S1 Microstructure of the unsaturated part of polyisoprene chain synthesized in CH_2Cl_2 at different temperatures and monomer conversions [a]

T (°C)	Yield (%)	Content of structural units (mol%)							
		trans-1,4				1,2-	3,4-		
		Total	head-to-tail	tail-to-tail	head-to-head		total	chain	EG[b]
-78	13.3	93.0	55.0	20.0	18.0	3.5	3.5	3.0	0.5
	21.2	94.0	55.0	20.5	18.5	3.0	3.0	2.5	0.5
	26.5	93.0	55.0	20.0	18.0	3.5	3.5	3.0	0.5
	32.3	94.0	55.0	20.5	18.5	3.0	3.0	2.5	0.5
-20	11.7	95.0	63.0	17.0	15.0	2.0	3.0	2.0	1.0
	19.6	95.0	62.0	18.0	15.0	2.0	3.0	2.0	1.0
	24.3	95.0	61.0	18.0	16.0	2.0	3.0	2.0	1.0
	38.6	95.0	59.0	19.0	17.0	2.0	3.0	2.0	1.0
	77.0	95.0	59.0	19.0	17.0	2.0	3.0	2.0	1.0
+20	42.8	95.0	61	18	16	1.5	3.5	1.5	2.0

[a] Polymerization conditions: ^{t}BuCl/$TiCl_4$=300, [C_5H_8]=4.0 M, [$TiCl_4$]=$1.5\cdot10^{-2}$ M. [b]EG: end group

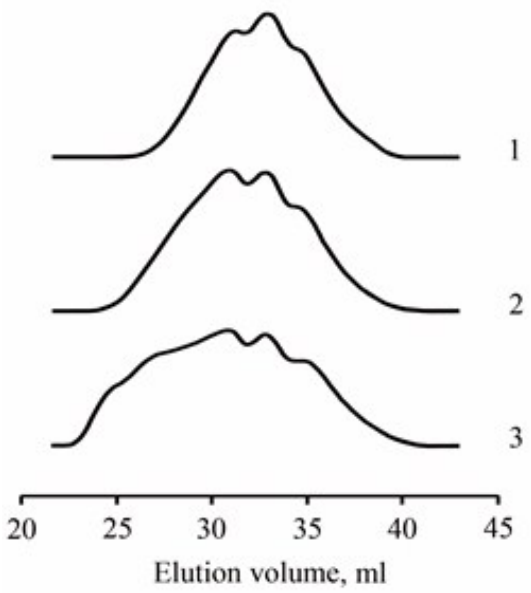

Fig. S5. GPC traces of polyisoprene before (**1**) and after treatment by ^{t}BuCl/$TiCl_4$ initiating system during 15 min (**2**) and 120 min (**3**). The conditions of treatment a described in Experimental part.

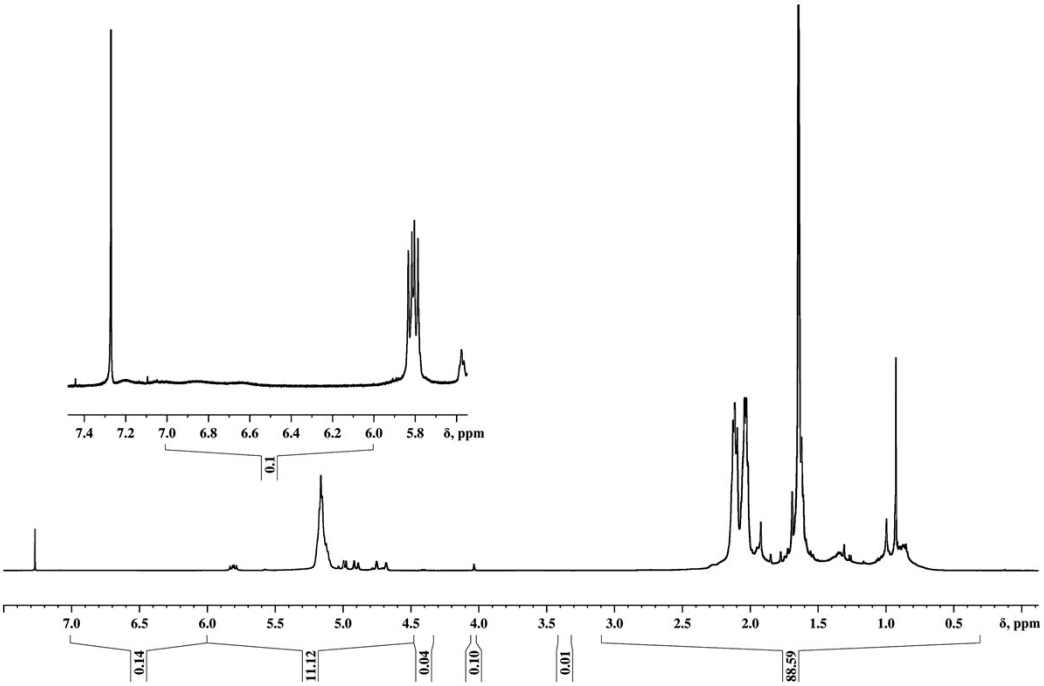

Fig. S6 ^{1}H NMR spectrum of polyisoprene synthesized using ^{t}BuCl/$TiCl_4$ initiating system at -78ºC (conv.=13.3%): ^{t}BuCl/$TiCl_4$=300; [C_5H_8]=4.0 M; [$TiCl_4$]=1.5·10^{-2} M.

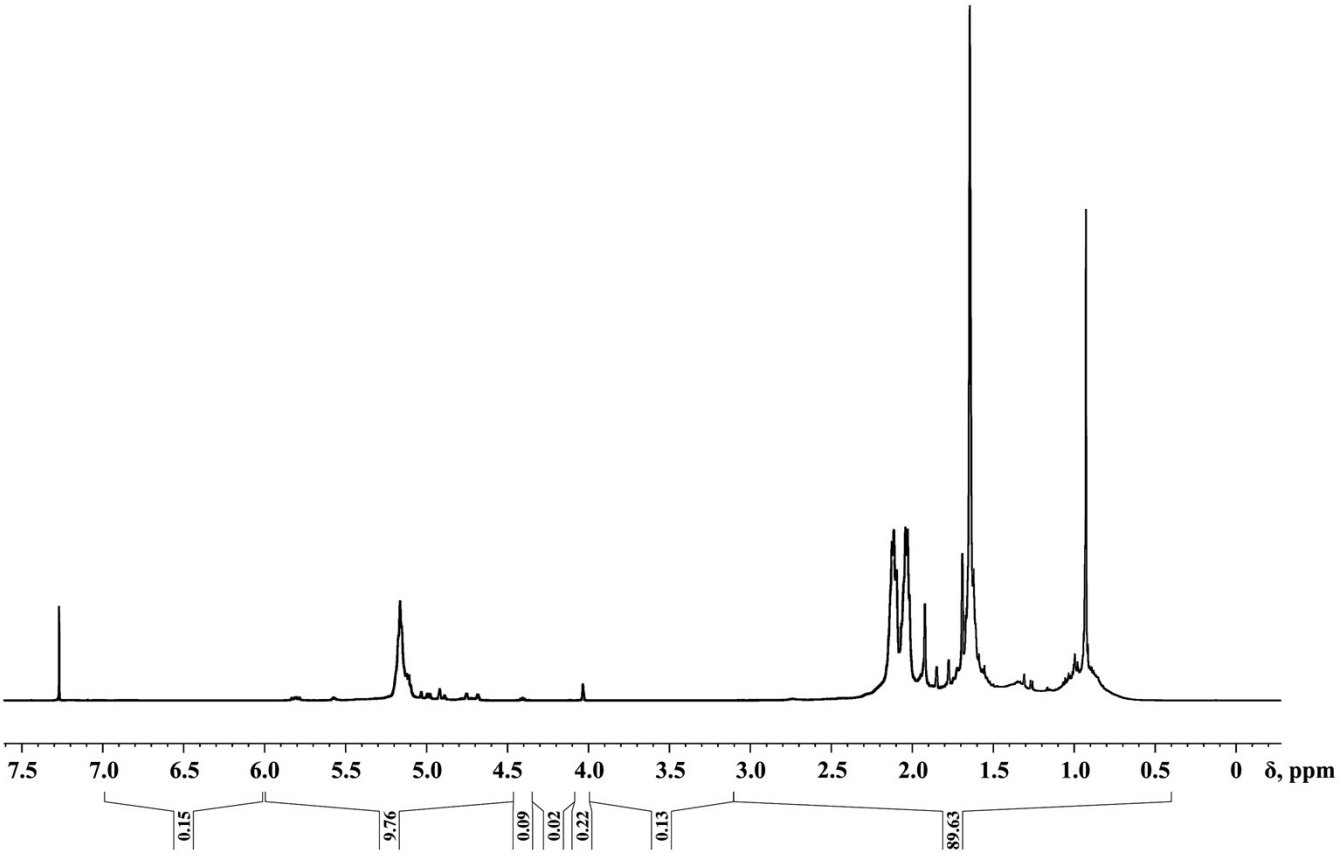

Fig. S7 ^{1}H NMR spectrum of polyisoprene synthesized using ^{t}BuCl/$TiCl_4$ initiating system at -20ºC (conv.=77.0%): ^{t}BuCl/$TiCl_4$=300; [C_5H_8]=4.0 M; [$TiCl_4$]=1.5·10^{-2} M.