Electronic Supplementary Information

Cationic polymerization of butadiene using alkyl aluminum compounds as co-initiators: an efficient approach toward solid polybutadienes

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Experimental

Polymerization procedures

Polymerization was performed in glass ampules (6 mL) equipped with magnetic stirrer under an argon atmosphere. In a typical polymerization, the ampule was charged by 2.3 mL of solution of butadiene (0.27 g, 5 mmol), isopropylchloride (0.25 g, 3.13 mmol) and CH_2Cl_2 and was thermostated at 20 ºC under agitation for 10 min. Then, the polymerization was initiated by the addition of 0.2 mL of solution of Et_2AlCl (1.5 mg, 0.0125 mmol). After predetermined time, the reaction was terminated by 0.1 mixture of propylene oxide with methanol. Then, the solution of N-isopropyl-N'-phenyl-1,4-phenylenediamine (4010 NA, 0.54 mg) in CH_2Cl_2 was added as an antioxidant into the ampoule. The polymer was isolated by evaporation of solvent and unreacted monomer from ampoules and dried in vacuum at 50 ºC up to constant weight. Monomer conversions were determined gravimetrically.

Characterization

The content of insoluble fraction (IF) in the polymer was determined by additional Soxhlet extraction in toluene for 24 h. The number-average (M_n) and weight-average (M_w) molecular weights as well as polydispersity (Đ) were measured by GPC using a Waters-Alliance GPCV-2000 chromatograph equipped with two detectors (refractometric and viscometric) and a set of Styrogel columns with the pore sizes of 500 (HR-2), 10^3 (HR-3), 10^4 (HR-4), and 10^5 (HR-5) Å thermostated at 30 °C. Toluene was used as the eluent and the elution rate was 1 mL min^{-1}. Before analyses, all polybutadiene samples were purified by column chromatography using Silica gel 60 from Fluka and chloroform as eluent. After purification, yield of polymer was 98–99% with respect to original (unpurified) polymer.

Results and discussion

Table S1 Cationic polymerization of butadiene with ^{i}PrCl/Et_2AlCl initiating system at different ^{i}PrCl to Et_2AlCl ratios at 20ºC [a]

^{i}PrCl / Et_2AlCl	Time (min)	Conv. (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	Đ	H_c [b] (mol%)	T_s [c] (ºC)
100	2	11.2	*ND* [d]	*ND*	*ND*	*ND*	*ND*
	5	53.5	4.7	43.6	9.3	*ND*	*ND*
	10	54.6	5.2	52.3	10.1	*ND*	*ND*
	30	60.2	5.1	132.5	26.0	*ND*	*ND*
	60	65.8	5.9	233.8	39.6	41	180
500	5	50.0	3.0	16.4	5.5	*ND*	*ND*
	30	57.9	4.0	31.9	8.0	44	155
	60	63.2	4.8	82.7	17.2	42	169
	240	68.4	4.9	202.6	41.3	39	173

[a] Polymerization conditions: $[C_4H_6]$ = 2.0 M, $[Et_2AlCl]$ = $5.0 \cdot 10^{-3}$ M, CH_2Cl_2. [b] Unsaturation (H_c) determined by ^{13}C NMR spectroscopy. [c] Softening point determined by ring-and-ball method.
[d] *ND*: not determined.

Table S2 Effect of the order of mixing of the components of catalytic system on the cationic polymerization of butadiene (BD) with ${}^{i}PrCl/Et_2AlCl$ initiating system at 20ºC [a]

Time (min)	Conversion (%)	
	BD + ${}^{i}PrCl$ + Et_2AlCl	BD + Et_2AlCl + ${}^{i}PrCl$
5.0	52.6	40.2
30.0	61.2	53.4
240.0	65.4	62.9
1440.0	74.1	72.0

Polymerization conditions: $[C_4H_6]$=2.0, $[Et_2AlCl]$=$5\cdot10^{-3}$M, ${}^{i}PrCl/Et_2AlCl$=250, CH_2Cl_2.

Table S3 Effect of temperature on the cationic polymerization of butadiene with ${}^{i}PrCl/AlEt_2Cl$ initiating system [a]

T (ºC)	Time (min)	Conv. (%)	$M_n\times10^{-3}$ (g mol^{-1})	$M_w\times10^{-3}$ (g mol^{-1})	Đ
- 30	30	1.8	*ND*[b]	*ND*	*ND*
	60	2.1	*ND*	*ND*	*ND*
	90	3.5	*ND*	*ND*	*ND*
	120	14.3	5.2	15.1	2.9
	240	37.5	5.9	68.9	11.7
	1440	48.9	8.2	400.7	48.9
- 78	120	0.8	*ND*	*ND*	*ND*
	240	1.0	*ND*	*ND*	*ND*
	1440	2.1	*ND*	*ND*	*ND*

Polymerization conditions: $[C_4H_6]$=2.0 M, $[Et_2AlCl]$=$5.0\cdot10^{-3}$ M, $[{}^{i}PrCl]/[Et_2AlCl]$=250, CH_2Cl_2. [b] *ND*: not determined.

Table S4 Effect of fractional addition of ^{i}PrCl or Et_2AlCl on Et_2AlCl –co-initiated cationic polymerization of butadiene at 20°C [a]

Additive	Concentration of additive (M)	Time[b] (min)	Time[c] (min)	$[EtAlCl_2]_{total}$ (M)	$[^{i}PrCl]_{total}$ (M)	Conversion (%)
–	–	0	2	$5.0\cdot10^{-3}$	1.25	28.7
			5			52.6
			10			55.1
			15			57.9
			30			61.2
			60			62.7
			90			63.1
			120			63.9
^{i}PrCl	0.5	30	35	$5.0\cdot10^{-3}$	1.75	62.7
			45			63.0
			60			63.1
	0.5	60	65	$5.0\cdot10^{-3}$	2.25	64.6
			75			65.0
			90			65.5
	0.5	90	95	$5.0\cdot10^{-3}$	2.75	66.0
			105			66.2
			120			66.3
Et_2AlCl	$2.5\cdot10^{-3}$	30	32	$7.5\cdot10^{-3}$	1.25	73.8
			35			76.4
			45			79.3
			60			80.1
	$2.5\cdot10^{-3}$	60	62	$1.0\cdot10^{-2}$	1.25	86.1
			65			87.7
			75			89.3
			90			90.2
	$2.5\cdot10^{-3}$	90	92	$1.25\cdot10^{-2}$	1.25	94.1
			95			95.0
			105			96.9
			120			97.8
–	–	0	5	$1.25\cdot10^{-2}$	1.25	64.4
			30			73.9
			60			81.1
			90			83.0
			120			85.8

[a] Polymerization conditions: $[C_4H_6]$=2.0 моль/л; $[^{i}PrCl]_1=[^{i}PrCl]_2=[^{i}PrCl]_3=0.5$ M; $[Et_2AlCl]_1=[Et_2AlCl]_2=[Et_2AlCl]_3=2.5\cdot10^{-3}$ M, CH_2Cl_2. [b] Time of introduction of additive into reaction mixture since the beginning of reaction. [c] Total reaction time.

Table S5 Cationic polymerization of butadiene using ^{i}PrCl/EtAlCl$_2$ and ^{i}PrCl/Et$_3$Al initiating system at 20 ºC [a]

LA	^{i}PrCl / LA	Time (min)	Conv. (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	Đ
EtAlCl$_2$	0	1	5.5	*ND* [b]	*ND*	*ND*
	100	2	53.4	3.8	32.8	8.6
		5	59.2	4.2	42.5	10.1
		30	68.9	4.9	241.8	49.3
		60	70.4	*ND*	*ND*	*ND*
	500	1	51.8	2.9	20.7	7.1
		60	71.8	5.0	236.3	47.3
Et$_3$Al	0	30	0.2	*ND*	*ND*	*ND*
	500	60	3.2	*ND*	*ND*	*ND*

[a] Polymerization conditions: [C_4H_6]=2.0 M, [EtAlCl$_2$] = [Et$_3$Al] = $5.0 \cdot 10^{-3}$ M, CH$_2$Cl$_2$. LA: Lewis acid. [b] *ND*: not determined.

Table S6 Cationic polymerization of butadiene with 2-chlorobutane (CB)/Et$_2$AlCl initiating system at 20ºC [a]

CB / Et$_2$AlCl	Time (min)	Conv. (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	Đ
100	2	38.8	3.1	14.7	4.7
	5	46.7	3.3	19.4	5.9
	30	56.7	4.1	41.2	10.0
	240	68.3	4.9	109.1	22.3
	1440	71.9	5.7	222.0	38.9
500	5	45.7	2.6	11.9	4.6
	30	53.2	3.1	18.8	6.1
	60	58.5	3.2	23.9	7.5
	240	65.7	3.6	40.2	11.2
	1440	70.1	3.8	52.0	13.7

[a] Polymerization conditions: [C_4H_6]=2.0 M, [Et$_2$AlCl] = $5.0 \cdot 10^{-3}$ M, CH$_2$Cl$_2$.

Table S7 Effect of reaction temperature on the cationic polymerization of butadiene with 2-chlorobutane (CB)/Et_2AlCl initiating system [a]

T (°C)	Time (min)	Conv. (%)	$M_n\times10^{-3}$ (g mol^{-1})	$M_w\times10^{-3}$ (g mol^{-1})	Đ	IF[b] (%)	H_c (mol%)
- 30	30	1.1	*ND*[c]	*ND*	*ND*	*ND*	*ND*
	60	4.0	*ND*	*ND*	*ND*	*ND*	*ND*
	65	7.9	*ND*	*ND*	*ND*	*ND*	*ND*
	75	16.4	5.3	13.2	2.5	0	*ND*
	120	58.5	6.1	128.8	21.1	0	53
	240	65.3	6.6	546.0	82.7	0	48
	1440	78.4	*ND*	*ND*	*ND*	52.1	*ND*
- 78	120	0.5	*ND*	*ND*	*ND*	*ND*	*ND*
	240	1.8	*ND*	*ND*	*ND*	*ND*	*ND*
	1440	3.6	*ND*	*ND*	*ND*	*ND*	*ND*

[a] Polymerization conditions: $[C_4H_6]$ = 2.0 M, $[Et_2AlCl]$ = 5.0·10^{-3} M, CB/Et_2AlCl=250, CH_2Cl_2.
[b] IF: insoluble fraction. [c] *ND*: not determined.

Table S8 Effect of Lewis acid (LA) nature on the cationic polymerization of butadiene and properties of obtained polybutadienes[a]

Lewis acid	$\frac{{}^{i}PrCl}{LA}$	Time (min)	Conv. (%)	H_c (mol%)	Content of units (mol%)	
					trans-1,4	1,2-
$AlEt_2Cl$	50	30	58.6	42	82	18
	250	3	45.4	45	81	19
		5	52.6	45	80	20
		30	61.2	43	80	20
		60	62.7	41	81	19
	500	30	57.9	44	80	20
		60	63.2	42	82	18
$AlEt_3$	500	140[b]	62.5	42	81	19
$AlEtCl_2$	500	60	71.8	41	82	18

[a] Polymerization conditions: $[C_4H_6]$ = 2.0 M, $[Et_2AlCl]$= $[EtAlCl_2]$= $[Et_3Al]$ = 5.0·10^{-3} M, 20°C, CH_2Cl_2. [b] Induction period: 80 min.

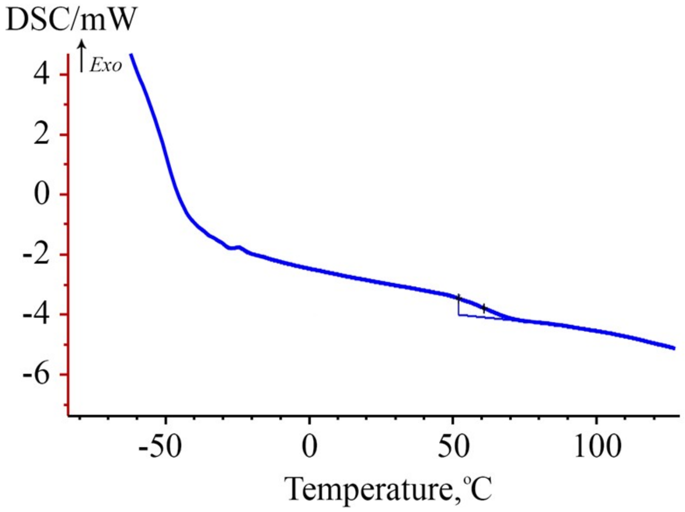

Fig.S1 DSC curve of polybutadiene synthesized using ${}^{i}PrCl/AlEt_2Cl$.

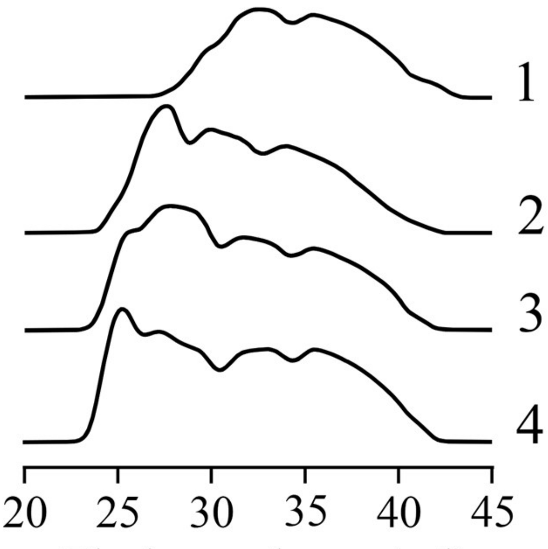

Fig. S2 SEC traces of polybutadienes synthesized with ${}^{i}PrCl/AlEtCl_2$ initiating system (${}^{i}PrCl/Et_2AlCl$=500) at different monomer conversions. Conversion (%): 51.8 (1), 58.9 (2), 70.7 (3), 71.8 (4). See Table 3 for experimental conditions.

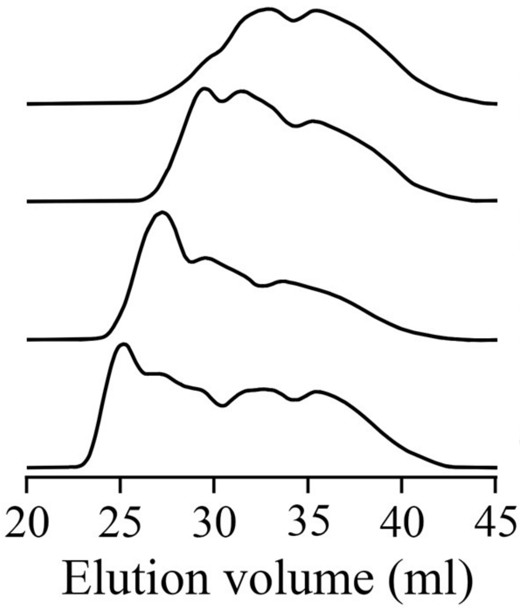

Fig. S3 SEC traces of polybutadienes synthesized with ^{i}PrCl/AlEt$_3$ initiating system (^{i}PrCl/Et$_2$AlCl=500) at different monomer conversions. Conversion (%): 55.0 (1), 60.8 (2), 61.9 (3), 70.7 (4). See Table S3 for experimental conditions.

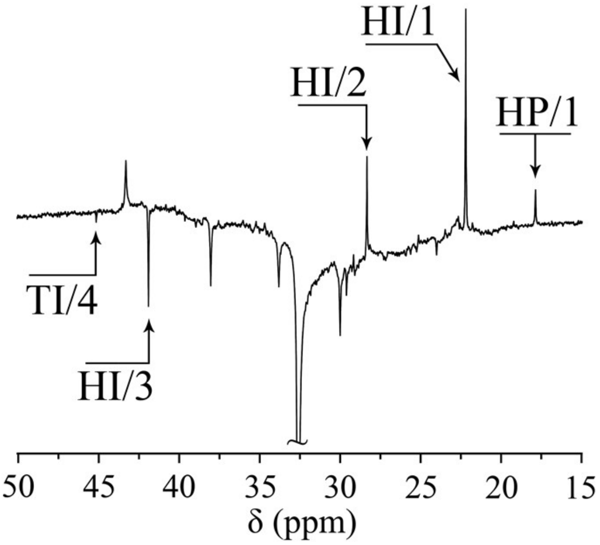

Fig. S4 ^{13}C DEPT-135° spectrum of polybutadiene synthesized with ^{i}PrCl/Et$_2$AlCl initiating system. The polymerization conditions presented in Fig. 4.

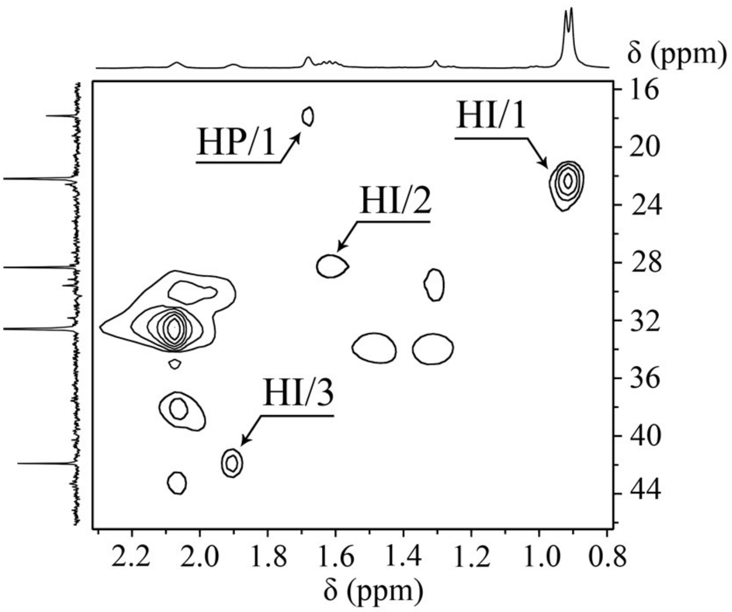

Fig. S5 Aliphatic part of ^{1}H, ^{13}C HSQC NMR spectrum of polybutadiene synthesized with $^{i}PrCl/Et_2AlCl$ initiating system. The polymerization conditions presented in Fig. 4.

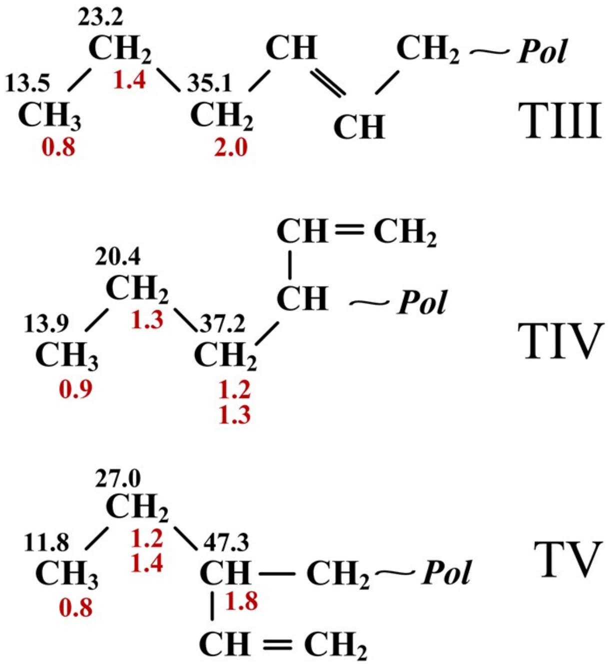

Fig. S6 The tentative structures of terminal units possessing ethyl group connected with *trans*-1,4- (TIII), 1,2- (TIV) and 2,1- (TV), which are formed after chain-transfer to $Et_{3-n}AlCl_n$ (n=0, 1, 2). Numbers indicate the calculated chemical shifts for carbon (above C) and hydrogen (below H) atoms.

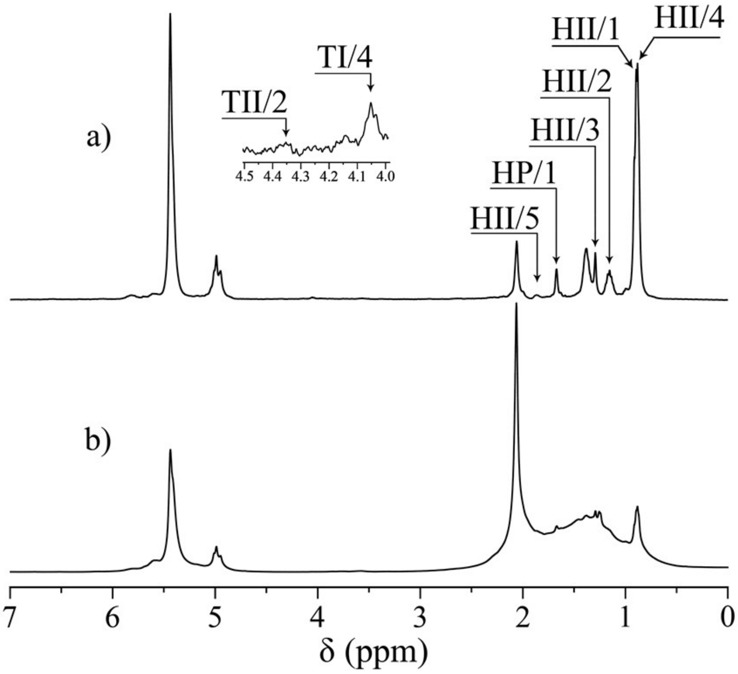

Fig. S7 ^1H NMR spectrum of polybutadiene recorded with (a) and without (b) T_2 filter synthesized with CB/Et_2AlCl initiating system. Polymerization conditions: $[C_4H_6] = 2.0$ M, $[Et_2AlCl] = 5.0 \cdot 10^{-3}$ M, CB/$AlEt_2Cl$ = 250, CH_2Cl_2. Temperature: –30 ºC, time: 2 h, conversion 58.5 %.

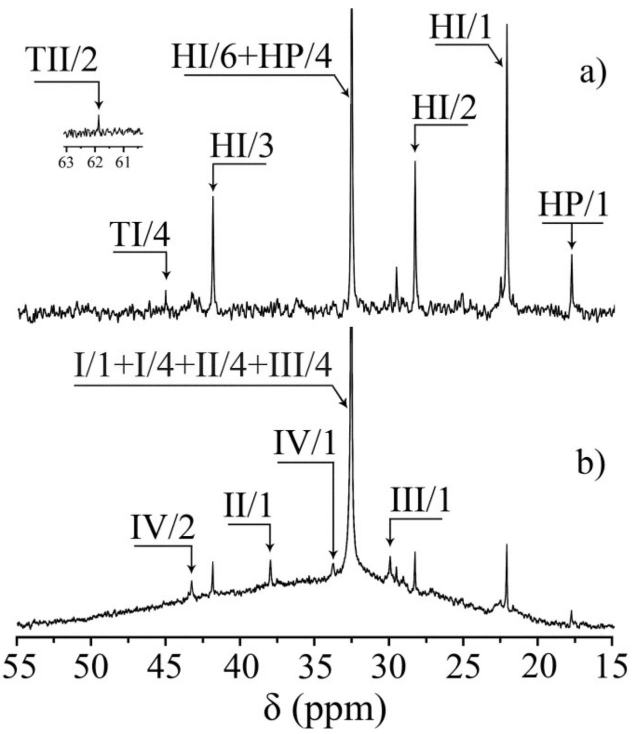

Fig. S8 Aliphatic regions of ^{13}C NMR spectra of polybutadiene recorded with (**a**) and without T_2 filter (**b**), respectively. Polymerization conditions: $[C_4H_6] = 2.0$ M, $[Et_2AlCl] = 5.0 \cdot 10^{-3}$ M, $^{i}PrCl/Et_2AlCl = 250$, 20ºC, CH_2Cl_2, time: 60 min, conversion 62.7%. $M_n=5.2 \cdot 10^3$ g mol^{-1}, $M_w=76.4 \cdot 10^3$ g mol^{-1}, Đ=14.7

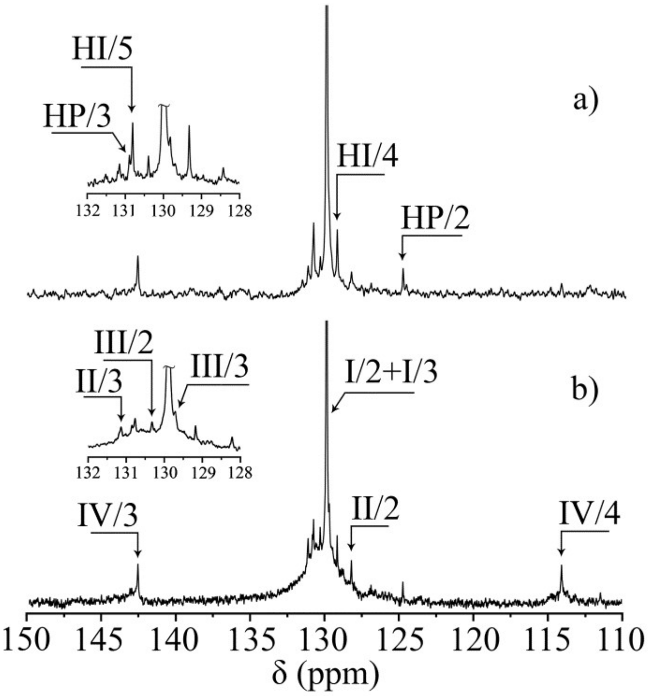

Fig. S9 Olefinic regions of ^{13}C NMR spectra of polybutadiene recorded with (**a**) and without T_2 filter (**b**), respectively. See Fig. S8 for polymerization conditions.

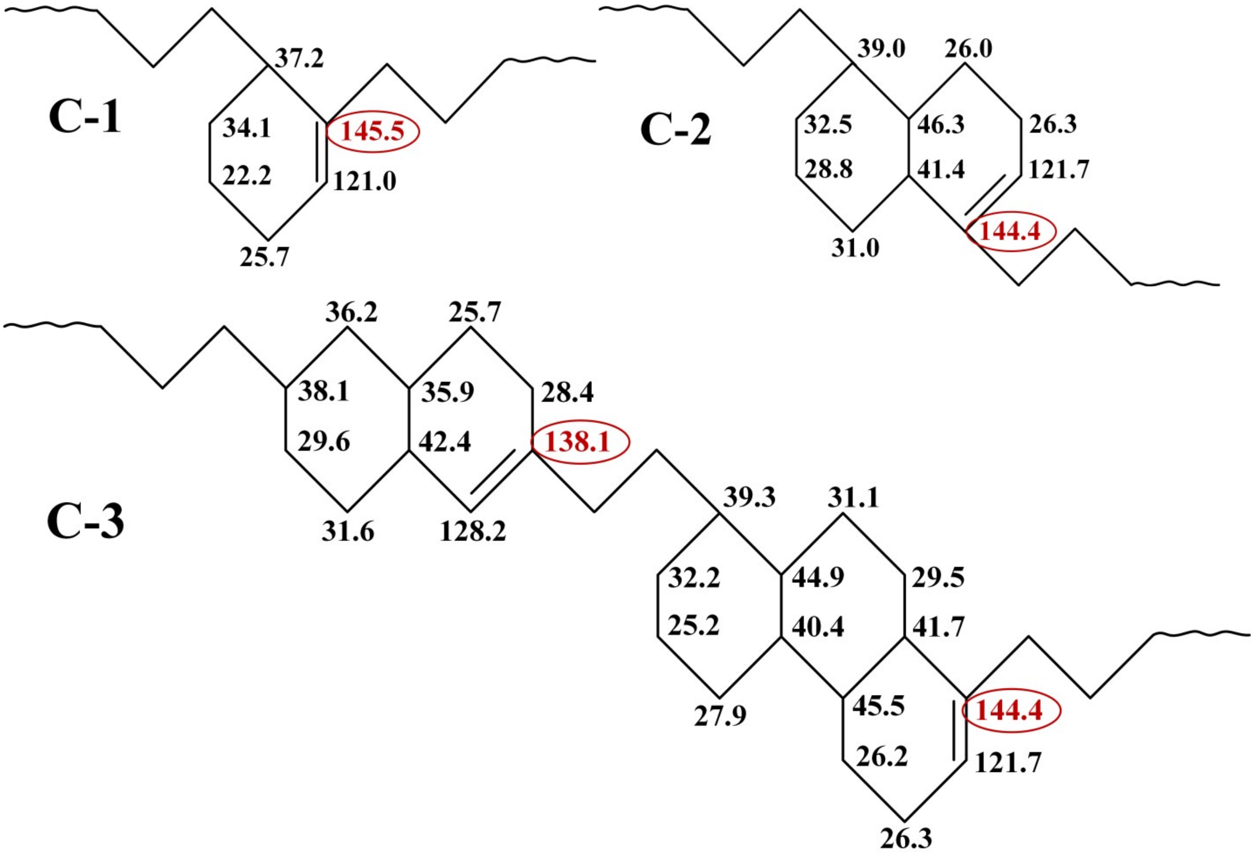

Fig. S10 Calculated values of chemical shifts of carbon atoms in six-membered cyclic structures proposed in [41, 42].

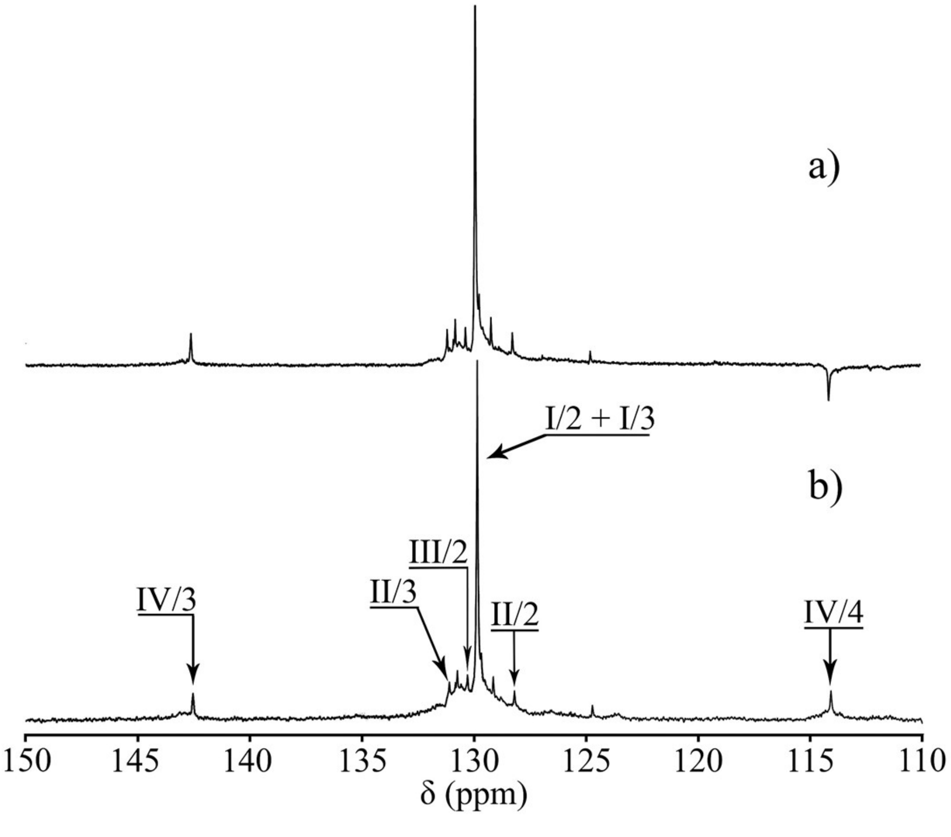

Fig. S11 Olefinic regions of DEPT-135° ^{13}C NMR (a) and ^{13}C NMR-spectra (b) of polybutadiene, respectively. Polymerization condition see in Fig. 4.

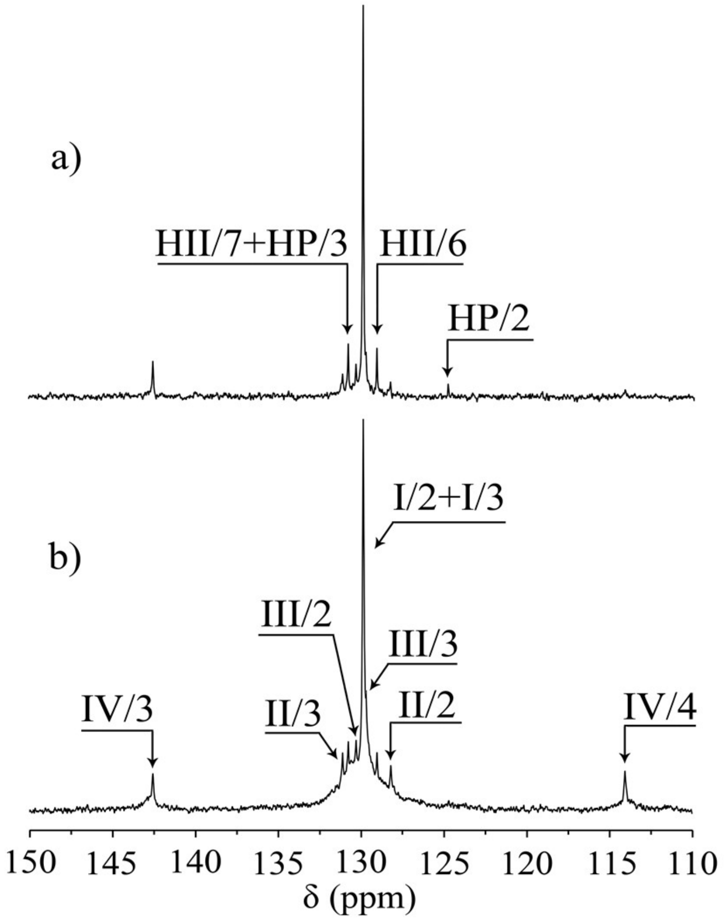

Fig. S12 Olefinic parts of ^{13}C NMR spectra of polybutadiene recorded with (a) and without (b) T_2 filter: $[C_4H_6] = 2.0$ M, $[Et_2AlCl] = 5.0 \cdot 10^{-3}$ M, CB/Et_2AlCl = 250, CH_2Cl_2. Temperature: –30 ºC, time: 2h, conversion 58.5 %.

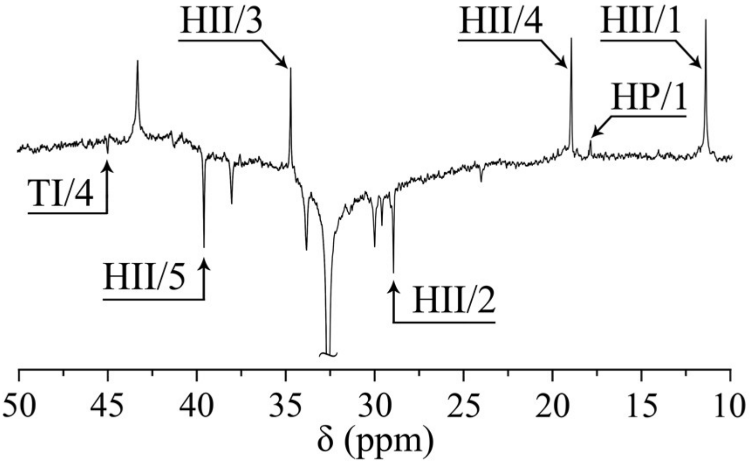

Fig. S13 Aliphatic part of ^{13}C DEPT-135º NMR spectrum of polybutadiene synthesized with CB/Et_2AlCl initiating system. Polymerization conditions see in Fig. S4.

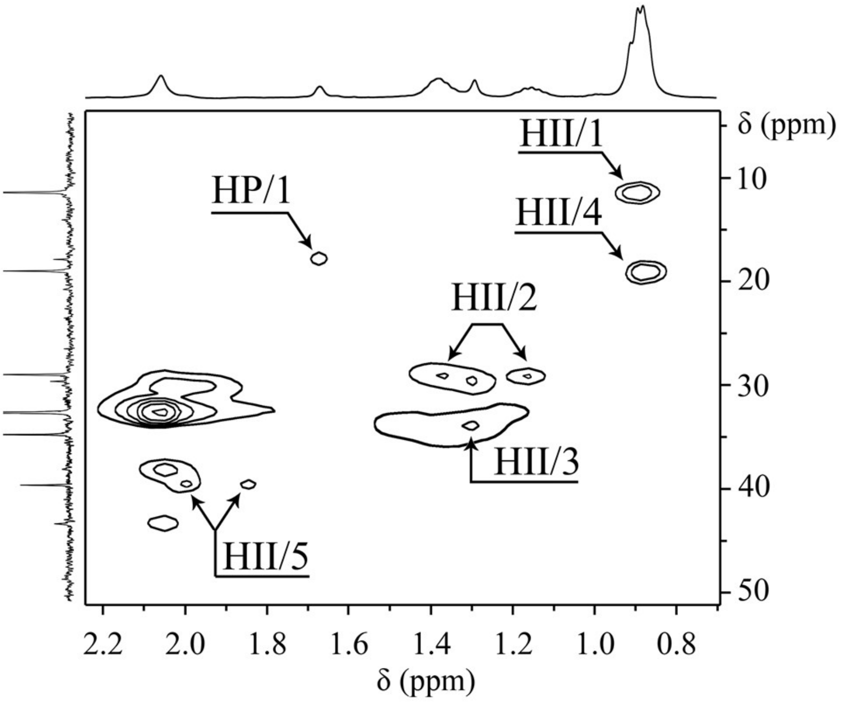

Fig. S14 Aliphatic part of ^{1}H, ^{13}C HSQC 2D ЯМР NMR spectrum of polybutadiene synthesized with CB/Et_2AlCl initiating system. Polymerization conditions see in Fig. S4.

Structure of polybutadiene synthesized with CB/Et_2AlCl initiating system

According to ^{1}H, ^{13}C HSQC 2D NMR spectrum (Fig. S8), the signals of carbon atoms HII/1 and HII/4 at 11.4 ppm and 18.9 ppm on the carbon scale of the spectrum are located at 0.90 ppm and 0.88 ppm on the proton scale, respectively. As it is seen from fragment of фрагмента ^{1}H, ^{13}C HMBC 2D NMR spectrum (Fig. 9a), the cross-peaks at 28.9 ppm, 34.7 ppm and 39.6 ppm are observed on a vertical line with signal at 0.88 ppm.

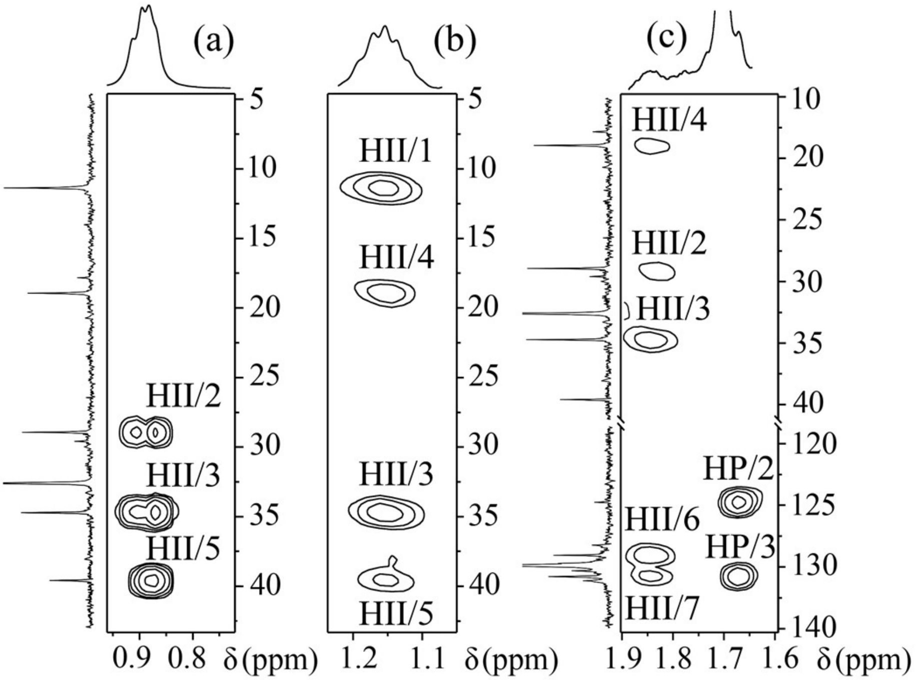

Fig. S15 Fragments of ^{1}H, ^{13}C HMBC 2D NMR spectra of polybutadienes in the regions between 0.80 – 0.90 ppm (a), 1.10 – 1.20 ppm (b) and 1.60 – 1.90 ppm (c) on a proton scale. Polymerization conditions see in Fig. 8.

According to Fig. S8, the signal of carbon atom HII/2 at 28.9 ppm is located in two regions of ^{1}H NMR spectrum at 1.15 ppm and 1.38 ppm, respectively. On the vertical line at 1.15 ppm in ^{1}H, ^{13}C HMBC 2D NMR spectrum of polybutadiene, the cross-peaks at 11.4 ppm, 18.9 ppm, 34.4 ppm and 39.6 ppm were observed (Fig. 9b). This unambiguously proved the belonging of carbon atoms HII/1, HII/2, HII/3, HII/4 and HII/5 to the same structure.

The identification of the position of olefinic carbon atoms in structure HII was performed with the help of ^{1}H, ^{13}C HSQC and ^{1}H, ^{13}C HMBC NMR spectroscopy. According to ^{1}H, ^{13}C HSQC 2D NMR spectroscopy, the signal of carbon atom

HII/5 is located in two regions of ^{1}H NMR spectrum at 1.85 ppm and 2.01 ppm, respectively (Fig. S8). On the vertical line of ^{1}H, ^{13}C HMBC 2D NMR spectrum at 1.85 ppm, the cross-peaks with the signals at 18.9 ppm, 28.9 ppm, 34.7 ppm, 129.0 ppm and 130.8 ppm were observed (Fig. 9c). Last two signals belong to olefinic carbon atoms HII/6 and HII/7 of head group of structure II. It should be noted that signal of carbon atom HII/7 at 130.8 ppm almost coincides with the signal of olefinic carbon atom HP/III of head group of structure HP, which is generated due to protonic initiation [18].