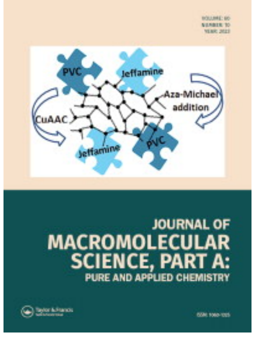

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Diethylaluminum chloride-co-initiated cationic polymerization of isoprene: dramatic effect of the nature of alkyl halide on the properties of synthesized polymers

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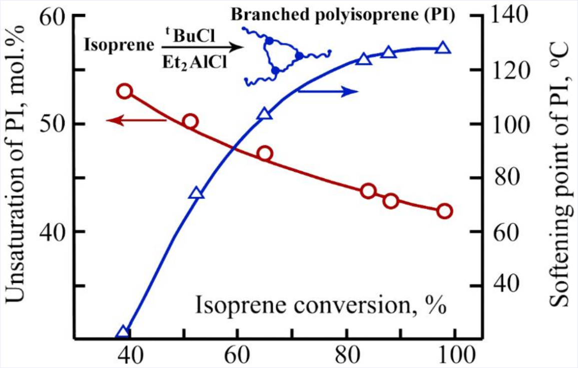
ABSTRACT

The cationic polymerization of isoprene using alkyl halide/Et_2AlCl initiating system (alkyl halide: *tert*-butyl chloride, *tert*-butyl bromide, 2-chloro-2-methylbutane and isopropyl chloride) at different temperatures has been studied. It was shown for the first time that using of tertiary alkyl halide in conjunction with Et_2AlCl allowed to synthesize fully soluble solid thermoplastic polymers with reduced unsaturation (41–48 mol%) as well as relatively high glass transition temperature (52–60°C) and softening point (102–128°C). The substitution of tertiary alkyl halides on the secondary one (isopropyl chloride) results in the obtaining of cross-linked polymers due to the low activity of isopropyl chloride in chain transfer to alkyl halide. It was found that alkyl halide nature, the ratio of alkyl halide to Et_2AlCl, duration and temperature of the polymerization of isoprene have dramatic effect on the unsaturation of synthesized polymers as well as their molecular weight, polydispersity, physical and chemical properties.

GRAPHICAL ABSTRACT



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Alkyl halides; cationic polymerization; diethylaluminum chloride; isoprene; solid thermoplastic polymers

1. Introduction

Cationic polymerization is an industrially important technique to synthesize oligomers, (co)polymers or functional polymers from different vinyl monomers.[1–3] Among them, the cationic (co)polymerization of isobutylene represents significant interest due to its use for the production of elastomers, precursors for oil additives and plasticizers.[1–6] A large number of publications on the cationic polymerization are devoted to the investigation of kinetics and mechanism of cationic polymerization of isobutylene as well as preparation of end-functional polyisobutylene, block copolymers, star-shaped (co)polymers and other macromolecular architectures.[1,3–6] Considerably less attention is paid to the cationic polymerization of conjugated 1,3-dienes such as 1,3-pentadiene or isoprene. This is consistent with the side reactions with the participation of double bond of polymer leading to the formation of insoluble cross-linked polymers.[3,7,8]

It is well known that poly(1,3-diene)s with reduced unsaturation are typically formed in the course of cationic polymerization of 1,3-dienes.[7–11]

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Two different views exist in the literature on the reasons of the formation of polymers with reduced unsaturation during the cationic polymerization of 1,3-dienes. One of the explanations is the assumption about the side reaction of intramolecular cyclization with the generation of six-membered cyclic structures.[11–15] Another explanation based on the series of work convincingly showing that reason for the loss of unsaturation of polydienes is the chain transfer to double bond of “own” or “alien” polymer chain with the formation of branched, partially cross-linked or fully cross-linked (insoluble) macromolecules.[9,10,16–18]

From a practical point of view, three different approaches are used for the synthesis of completely soluble poly(1,3-dienes) *via* the cationic mechanism. Historically, the first approach to suppress the formation of insoluble fraction (gel formation) during the cationic polymerization of 1,3-dienes was the introduction of certain olefins such as cyclopentene, 2-methyl-2-butene, 2-methyl-1-butene and others.[7,19–21] This approach is widely used in industry for the production of aliphatic hydrocarbon resins, liquid rubber SKOP (synthetic caoutchouc oligomer of piperylene) and other polymers. The disadvantages of this method are the necessity to use olefins of a given structure as well as the strict control of the ratio of 1,3-diene to olefin in the initial mixture.[7,19,20] This significantly complicates the technology of production of poly(1,3-dienes).

The second approach is based on the using of relatively weak Lewis acids such as $BF_3{\cdot}OEt_2$,[22] $B(C_6F_5)$,[15] $ZnCl_2$, $ZnBr_2$,[23] complexes of $AlCl_3$ with ethers or amines,[24,25] as well as different ionic liquids.[21,26] This allows to suppress the chain transfer to polymer to some extent. As a result, the fully soluble in organic solvents polydienes with high degree of unsaturation (in some cases up to 100 mol% from theoretical) were obtained. The disadvantages of this approach are the low reaction rates and low polymer yields. For example, it was shown that high monomer conversion during cationic polymerization of isoprene co-initiated by ionic liquids was achieved only after 28–150 h that is unacceptable for practical use.[26]

Finally, the third approach consists in using conventional Lewis acids ($TiCl_4$, $VOCl_3$, etc.) as co-initiators of the cationic polymerization of 1,3-dienes in conjunction with the high excess of initiator/chain transfer agent.[10,16,18,27,28] For example, in the cationic polymerization of isoprene with *tert*-butyl chloride (^{t}BuCl)/$TiCl_4$ initiating system, ^{t}BuCl acts simultaneously as an initiator and a chain transfer agent.[10] The presence of high excess of ^{t}BuCl as compared to Lewis acid results in predominant chain transfer to initiator that allows preparing fully soluble polymer. The main advantages of this approach are high reaction rate and monomer conversion as well as possibility to control molecular weight and unsaturation of poly(1,3-dienes) by changing the ratio of ^{t}BuCl to $TiCl_4$ and polymerization conditions. After the completion of polymerization, the unreacted ^{t}BuCl can be recycled and used again. In this approach, the obtaining of poly(1,3-dienes) with high degree of unsaturation is not the dominated task. On the contrary, as shown in our previous works,[18,28–30] the decrease of unsaturation of polymers to the level of 40–50 mol% allowed to synthesize solid thermoplastic poly(1,3-dienes). It should be noted that at higher degree of unsaturation the synthesized polymers are typically viscous liquids. Therefore, the isolation, transportation and dosage of such viscous liquids significantly complicate the technologies for the industrial production as well as the use of such polymers by consumers.

In this work, we report the synthesis of solid thermoplastic polyisoprene *via* Et_2AlCl-co-initiated cationic polymerization of isoprene in the presence of excess of different aliphatic alkyl halides as initiators/chain transfer agents.

2. Experimental

2.1. Materials

Isoprene purchased from JSC «Sintez-Kauchuk» (Sterlitamak) had the following composition (wt.%): isoprene: 97.5; 2-methyl-1-butene: 0.4; 2-methyl-2-butene: 1.2; 3-methyl-1-butene: 0.6; 2-pentene: 0.1; saturated hydrocarbons: 0.2. Before experiments, isoprene was washed with water, dried on NaX molecular sieves, and then distilled over CaH_2 under argon flow. CH_2Cl_2 (Biosolve, >99%), 2-chloropropane or isopropyl chloride (^{i}PrCl, Aldrich, >99%), 2-chloro-2-methylpropane or *tert*-butyl chloride (^{t}BuCl, Aldrich, >99.5%), 2-bromo-2-methylpropane or *tert*-butyl bromide (^{t}BuBr, Aldrich, >99%), 2-chloro-2-methylbutane (**CMB**, Aldrich, >99%), and *n*-butyl chloride (^{n}BuCl, Aldrich, >99.5%) were distilled over CaH_2 under argon flow. Diethylaluminum chloride (Et_2AlCl, Acros Organic, 99%, 1.0 M in *n*-hexane), ethylaluminum dichloride ($EtAlCl_2$, Aldrich, 99%, 1.0 M in *n*-hexane), N-isopropyl-N’-phenyl-1,4-phenylenediamine (Lanxess, 99.9%), propylene oxide (Aldrich, >99.5%), methanol (Reachim, >99.8%) were used as received.

2.2. Polymerizations and characterization

Polymerization was performed in glass ampules (10 mL) equipped with magnetic stirrer under an argon atmosphere. In a typical polymerization, the ampule was charged by 1 mL (10 mmol) of isoprene, *tert*-butyl chloride (0.28 mL, 2.6 mmol) and 3.5 mL of CH_2Cl_2 and was thermostated at 20 °C under agitation for 5–7 min. Polymerization was initiated by the addition of 0.22 mL of solution of Et_2AlCl (3.02 mg, 0.025 mmol) in CH_2Cl_2. After a predetermined time, the reaction was terminated by 0.1 mL mixture of propylene oxide with methanol. Then, the solution of N-isopropyl-N’-phenyl-1,4-phenylenediamine (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 °C up to constant weight. Polymer yields were determined gravimetrically in respect to isoprene.

The content of insoluble fraction (IF) in the polymer was determined by Soxhlet extraction in toluene for 24 h. Before analyses, all polyisoprene 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. The number-average (M_n) and weight-average (M_w) molecular weights as well as polydispersity (M_w/M_n) 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}. The polyisoprene samples for the analysis were prepared in toluene at the concentration of 2-4 mg/mL. The calculation of number-average, weight-average molecular weights and polydispersity was performed using universal calibration in respect to polystyrene standards (Waters).

^{1}H (400.1 MHz) and ^{13}C (100.6 MHz) NMR spectra of polyisoprenes in $CDCl_3$ were recorded at the Center for Magnetic Resonance, St.-Petersburg State University Research Park using Bruker Avance III 400 spectrometer according to methodologies developed in works.[18,31] The numbers of scans were 16 and 8000, and the relaxation delays were 5 or 10 s in the case of ^{1}H and ^{13}C spectra, respectively. Chemical shifts were calibrated using the signals of chloroform as internal secondary standard (set to 7.27 and 76.91 ppm for ^{1}H and ^{13}C spectra, respectively). For suppression of Overhauser effect, ^{13}C NMR spectra were recorded using inverse-gated decoupling mode. ^{1}H, ^{13}C HSQC and ^{1}H, ^{13}C HMBC 2D NMR spectra were recorded using methodologies described in.[31] The calculation of the chemical shifts for carbon atoms in ^{13}C NMR spectrum was made using prediction parameters of Grant and Paul.[32]

The calculation of unsaturation (H_c) of polyisoprene, the monomer conversion as well as the content of head and end groups were performed based on ^{13}C NMR spectra according to the methodologies developed in this work and presented in Supplemental Material.

Differential scanning calorimetry (DSC) was performed using simultaneous thermal analyzers NETZSCH DSC 204 F1 Phoenix and NETZSCH STA 449 F3 Jupiter. The measurements were performed in closed Al crucible and helium flow (70 mL·min^{-1}). Data were recorded during the heating run (from −80 to 140 °C) at a heating rate of 10 °C·min^{-1}. The glass transition temperature (T_g) was given by the inflection point of the transition (Figure S1). The softening point (T_s) of polyisoprene was determined using ring-and-ball method according to ASTM E28-18. The thermomechanical properties of the polymer were recorded on a NETZSCH 402 F1 Hyperion thermomechanical analyzer at a load of 2.8 g· mm^{-2} and a heating rate of 5°C·min^{-1}.

3. Results

The efficient methods for the preparation of solid thermoplastic polymers from butadiene and 1,3-pentadiene were described in our previous works.[18,28] Such polymers were synthesized *via* cationic polymerization of corresponding 1,3-diene using alkyl aluminum halides as co-initiators in conjunction with aliphatic secondary alkyl halides such as isopropyl chloride or 2-chlorobutane. Therefore, the synthesis of solid thermoplastic polyisoprenes was initially performed using similar initiating systems.

3.1. Isoprene polymerization with ^{i}PrCl/Et_2AlCl and ^{n}BuCl/Et_2AlCl initiating systems

The cationic polymerization of isoprene in the presence of Et_2AlCl in CH_2Cl_2 without an addition of alkyl halides (AH) proceeds with extremely low rate converting only 3.0 wt% of the monomer into polymer for 4 h (Table 1).

This behavior coincides with the earlier report on similar initiating system and confirms the high degree of purification of solvent and isoprene from protic impurities such as water and other oxygen-containing compounds.[11] The introduction into the system of primary alkyl chloride (^{n}BuCl) does not improve the yield of polyisoprene independently on the molar ratio of ^{n}BuCl to Et_2AlCl (Table 1, Figure 1, curve 4). On the contrary, the use of secondary AH (^{i}PrCl) instead of primary one results in the anticipated increase of the reaction rate (Tables 1 and S1): yield of 62.6% is achieved in 15 min at optimal ^{i}PrCl to Et_2AlCl ratio equals to 100.

One of the features of the cationic polymerization of isoprene with ^{i}PrCl/Et_2AlCl initiating system are the presence of induction period with duration of 2–3 min (Tables 1 and S1, Figure 1, curve 3). According to our earlier works,[18,28] the induction period observed in the cationic polymerization of butadiene and 1,3-pentadiene with secondary AH/Et_2AlCl initiating systems is connected with the *in situ* generation of stronger Lewis acid ($EtAlCl_2$) during initiation step *via* interaction of ^{i}PrCl with Et_2AlCl. This explanation is consistent with the absence of induction period during the cationic polymerization of isoprene with ^{i}PrCl/$EtAlCl_2$ initiating system (Figure 1, curve 2). After completion of induction period, the cationic polymerization of isoprene proceeds with the high rate up to 50–60% of the polymer

Table 1. Cationic polymerization of isoprene with ^{n}BuCl/Et_2AlCl and ^{i}PrCl/Et_2AlCl initiating systems in CH_2Cl_2 at 20°C^a.

AH	$\frac{[AH]}{[Et_2AlCl]}$	Time (min)	Polymer Yield ^{b} (%)	IF ^{c} (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	M_w/M_n	H_c ^{d} (mol%)	T_g ^{e} (°C)
–	0	30	1.7	0	–	–	–	–	–
		240	3.0	0	–	–	–	–	–
^{n}BuCl	100	240	3.1	0	–	–	–	–	–
	500	240	2.5	0	–	–	–	–	–
^{i}PrCl	100	2	12.5	0	3.9	11.3	2.9	52	12
		5	47.3	0	4.3	58.6	13.6	45	52
		10	56.3	0	4.5	158.1	35.1	44	55
		15	62.6	0	4.6	500.7	108.8	41	58
		30	74.8	28.8	–	–	–	–	–
	500	2	7.1	–	–	–	–	–	–
		5	21.5	0	3.9	12.3	3.2	51	29
		15	42.4	0	4.4	33.7	7.7	46	50
		20	55.4	0	4.7	152.3	32.4	44	56
		30	67.4	0	5.1	520.6	102.1	41	59
		40	73.3	27.3	–	–	–	–	–

^{a}Conditions: $[C_5H_8] = 2.0$ M, $[Et_2AlCl] = 5.0 \times 10^{-3}$ M. ^{b}Polymer yield: determined gravimetrically in respect to isoprene ^{c}IF: insoluble fraction, ^{d}H_c–unsaturation of polyisoprene: determined by ^{13}C NMR spectroscopy (see Supplemental Material for details). ^{e}T_g–glass transition temperature: determined by DSC.

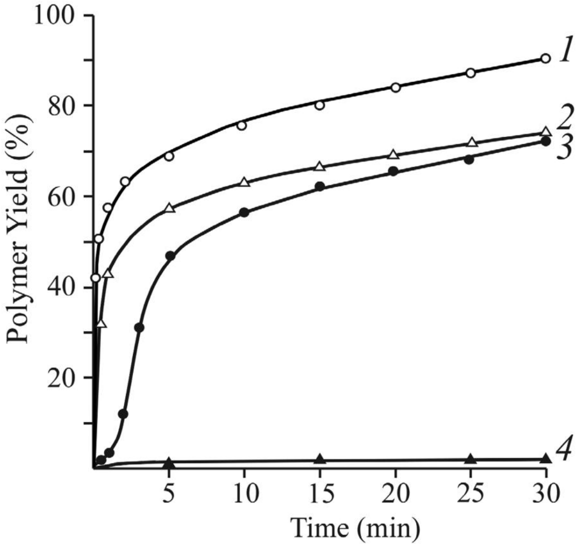


Figure 1. Polymer yield vs time dependences for the cationic polymerization of isoprene with $^tBuCl/Et_2AlCl$ (*1*), $^iPrCl/EtAlCl_2$ (*2*), $^iPrCl/Et_2AlCl$ (*3*) and $^nBuCl/Et_2AlCl$ (*4*) initiating systems. Conditions: $[C_5H_8] = 2.0$ M, $[Et_2AlCl] = [EtAlCl_2] = 5.0 \times 10^{-3}$ M, $[^tBuCl] = [^iPrCl] = [^nBuCl] = 0.5$ M, 20 °C, CH_2Cl_2.

yield and then the rate of polymerization is significantly decreased (Figure 1, curve 3, Tables 1 and S1). In fact, the first-order plots are not linear for all initiating system studied (Figure S2a). This indicates that the process of cationic polymerization of isoprene with $PrCl/Et_2AlCl$ initiating system is characterized by pronounced non-steady-state kinetics.

The decrease of the temperature from 20°C to −30°C results in sharp decrease in the rate of cationic polymerization of isoprene with $^iPrCl/Et_2AlCl$ initiating system, while the reaction is complete terminated at −78°C (Table S2).

In addition, the values of number- and weight -average molecular weights as well as polydispersity increase with increasing polymer yield independently on the ^iPrCl to Et_2AlCl molar ratio (Tables 1 and S1, Figure S2b). However, the observed significant increase of both M_w and M_w/M_n values of synthesized polymers is connected with the increase of the content of high molecular weight fraction in the polymer due to the chain transfer to polymer (Figure 2, curves 1–4).

Unsaturation of polyisoprenes decreased from level of 51–52 mol% to 41 mol% with the increase of the reaction time (Tables 1 and S1).

It is known from the literature that increase of M_w and M_w/M_n values in conjunction with the decrease of unsaturation is explained by the chain transfer to polymer *via* reaction of growing macrocations with the double bonds of poly(1,3-diene) chain with the generation of branched polymer chains.[7,10,16,18] As we showed earlier for the cationic polymerization of isoprene with $^tBuCl/TiCl_4$ initiating system, the probability of the chain transfer to polymer increased with the increase of monomer conversion due the depletion of the monomer.[9,10] Therefore, the resulting polyisoprene represents a set of macromolecules with different length and branching density that, in turn, leads to observed broad and multimodal molecular weight distribution. Evidently, the same mechanism of formation of polyisoprene with broad and multimodal molecular weight distribution (Figure 2) operated during the cationic polymerization of isoprene with $^iPrCl/Et_2AlCl$ initiating system.

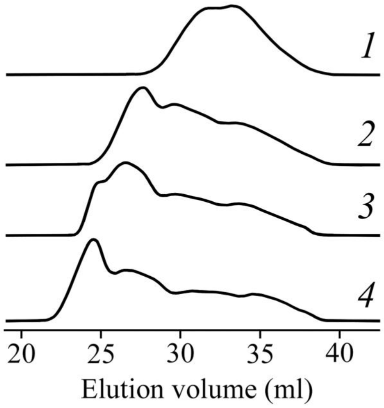


Figure 2. SEC traces of polyisoprenes synthesized with $^iPrCl/Et_2AlCl$ initiating system at different polymer yields (%): 12.5 (1), 47.3 (2), 56.3 (3) и 62.6 (4). Conditions: $[C_5H_8] = 2.0$ M, $[Et_2AlCl] = 5.0 \times 10^{-3}$ M, $^iPrCl/Et_2AlCl$ = 100, CH_2Cl_2, 20 °C.

Another important feature of the cationic polymerization of isoprene with $^iPrCl/Et_2AlCl$ initiating system is the formation of insoluble fraction (IF) at the reaching the level of 70–75% of polymer yield (Tables 1 and S1).

As it can be seen in Table 1, the reduction of unsaturation of polyisoprenes to level of 44–46 mol% and below results in sharp increase of their glass transition temperatures. Synthesized under such conditions polyisoprenes appear as solid thermoplastic polymers.

Taking into account these results and aiming at decreasing the content of IF, we used tertiary alkyl halides instead of secondary ones in further experiments. Indeed, according to literature, using tertiary alkyl halides as initiators of cationic polymerization of 1,3-dienes allowed to decrease the content of IF due to the competitive chain transfer of growing chain to the alkyl halide.[10,16,27,33]

3.2. Isoprene polymerization with tertiary alkyl halide/Et_2AlCl initiating systems

3.2.1. Effect of the initiator

Table 2 summarizes the results obtained during the investigation of $AlEt_2Cl$-co-initiated cationic polymerization of isoprene using different tertiary alkyl halides as initiators: *tert*-butyl chloride (^tBuCl), *tert*-butyl-bromide (^tBuBr) and 2-chloro-2-methylbutane (CMB).

According to data presented in Table 2 and Figure 1 (curve 1), the cationic polymerization of isoprene with tertiary alkyl halide/Et_2AlCl initiating system proceeds with high rate without an induction period for all tertiary alkyl halides studied. Interestingly, according to Table 2, the values of polymer yields are typically higher than monomer conversion. For example, for polyisoprene synthesized with $^tBuCl/Et_2AlCl$ initiating system after 960 min of reaction, the polymer yield is 105.3%, while the value of conversion of isoprene is 98.0% (Table 2). This difference is connected

Table 2. Effect of the nature of tertiary alkyl halide on the $AlEt_2Cl$-co-initiated cationic polymerization of isoprene at 20°C in CH_2Cl_2[a].

AH	Time (min)	Polymer Yield[b] (%)	Isoprene Conv.[c] (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	M_w/M_n	H_c[d] (mol.%)	T_g[e] (°C)	T_s[f] (°C)
^tBuCl	0.08	41.6	39.8	1.9	6.5	3.4	53	14	<20
	0.5	54.2	51.6	2.2	9.0	4.1	50	30	76
	5	68.5	64.8	2.7	15.3	5.7	48	48	103
	30	88.3	83.7	3.6	38.9	10.8	44	56	117
	60	93.4	87.9	3.7	64.1	17.3	43	58	124
	960	105.3	98.0	4.6	264.5	57.5	42	59	128
	1440	107.1[g]	–	–	–	–	–	–	–
^tBuBr	0.08	55.5	50.1	1.1	3.2	2.9	52	8	<20
	0.5	66.8	60.6	1.2	3.8	3.2	50	24	47
	5	79.6	71.0	1.5	5.1	3.4	47	46	65
	60	99.1	89.6	2.1	10.1	4.8	44	56	102
	1440	109.0	98.9	2.4	15.9	6.6	43	60	109
CMB	0.08	36.2	34.3	1.9	5.9	3.1	53	6	<20
	0.5	48.4	46.2	2.4	8.4	3.5	51	18	41
	5	62.5	59.1	2.7	12.3	4.6	47	45	98
	30	79.5	75.4	3.2	24.6	7.7	45	52	104
	60	87.7	82.1	3.6	34.6	9.6	44	54	110
	1440	105.8	98.7	4.2	248.9	59.3	42	58	119

[a] Conditions: $[C_5H_8] = 2.0$ M, $[AlEt_2Cl] = 5.0 \times 10^{-3}$ M, $[^tBuCl] = [^tBuBr] = [CMB] = 0.5$ M.

[b] Polymer yield: determined gravimetrically in respect to isoprene. [c] Isoprene conversion: calculated from ^{13}C NMR spectra. [d] H_c–unsaturation of polyisoprene: determined by ^{13}C NMR spectroscopy. [e] T_g–glass transition temperature: determined by DSC. [f] Softening point: determined using ring-and-ball method. [g] Polymer contained insoluble fraction (40.8%).

Table 3. Effect of ^tBuCl to Et_2AlCl ratio on the cationic polymerization of isoprene with $^tBuCl/Et_2AlCl$ initiating system in CH_2Cl_2 at 20°C[a].

$\frac{[^tBuCl]}{[Et_2AlCl]}$	Time (min)	Polymer Yield[b] (%)	Isoprene Conv.[c] (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	M_w/M_n	H_c[d] (mol.%)	T_g[e] (°C)	T_s[f] (°C)
250	0.5	55.5	51.2	2.1	6.5	3.1	52	13	<20
	5	71.8	66.7	2.5	9.1	3.6	47	32	66
	60	95.7	88.8	3.3	20.6	6.2	43	59	120
	1440	108.5	99.5	3.8	55.4	14.6	41	60	125
450	0.5	61.4	55.1	1.8	4.9	2.7	53	14	<20
	5	79.0	72.0	2.2	6.9	3.1	46	36	84
	60	98.8	90.2	2.8	12.3	4.4	42	57	110
	1440	110.5	99.7	3.3	21.6	6.6	41	59	116

[a] Conditions: $[C_5H_8] = 2.0$ M, $[Et_2AlCl] = 5.0 \cdot 10^{-3}$ M. IF is absent in all samples. [b] Polymer yield: determined gravimetrically in respect to isoprene. [c] Isoprene conversion: calculated from ^{13}C NMR spectra. [d] H_c–unsaturation of polyisoprene: determined by ^{13}C NMR spectroscopy. [e] T_g–glass transition temperature: determined by DSC. [f] Softening point: determined using ring-and-ball method.

with the presence of *tert*-butyl head and chlorine end groups in the polymer chain. Note, that monomer conversion was calculated from ^{13}C NMR spectra of polyisoprene using special methodology (see Supplemental Material for details), which takes into account the content of *tert*-butyl head group and chlorine in end group in the total weight of polyisoprene. It is known that *tert*-butyl head groups are formed in the course of the initiation of cationic polymerization of 1,3-dienes by *tert*-butyl cations, while chlorine end groups were generated due to the chain transfer to *tert*-butyl chloride.[9,10,29,33] The difference between yield and conversion increased with increasing reaction time indicating the increase of the content of *tert*-butyl head and chlorine end groups, respectively (Table 2). The similar results were obtained for the polyisoprenes synthesized with $^tBuBr/Et_2AlCl$ and CMB/Et_2AlCl initiating systems.

All polyisoprenes synthesized with tertiary alkyl halides as initiators with the exception of polyisoprene prepared with $^tBuCl/Et_2AlCl$ initiating system in 24 h are fully soluble in organic solvents and do not contain insoluble fraction (Table 2). The increase in the molar ratio of ^tBuCl to Et_2AlCl from 100 to 250 or higher allows synthesizing fully soluble polyisoprenes also with $^tBuCl/Et_2AlCl$ initiating system (Table 3).

According to Tables 2 and 3, the values of molecular weight and polydispersity increased with the increase in the monomer conversion independently on the initiator nature. Besides, the increase of ^tBuCl to Et_2AlCl molar ratio results in some increase of polymer yield, whereas values of the molecular weight and poydispersity are decreased significantly. This indicates the increase of the rate of chain transfer of growing macrocations to initiator (^tBuCl) with raising its concentration. It is important to note that use of ^tBuBr instead of ^tBuCl allows decreasing significantly both the molecular weight and polydispersity of synthesized polyisoprenes due to the faster chain transfer to ^tBuBr (Table 2). Therefore, the molecular weight and polydispersity of polyisoprenes synthesized with tertiary alkyl halide/Et_2AlCl initiating systems could be easily controlled by both the nature of alkyl halide (e.g. ^tBuCl vs. ^tBuBr) and the ratio of alkyl halide to Lewis acid.

In addition, the decrease of unsaturation from 53–55 mol% to 41–43 mol% with the increase of monomer conversion is observed for all polyisoprene samples synthesized with tertiary alkyl halide/Et_2AlCl initiating systems (Tables 2 and 3). The reduction of unsaturation of polyisoprenes down to 44–45 mol% leads to sharp increase in their glass transition temperature and softening point (Tables 2 and 3), while synthesized polymers appear as solid thermoplastic polymers, which are fully soluble in hydrocarbons, aromatic and chlorinated solvents. Importantly, the cationic polymerization of butadiene and 1,3-pentadiene with tertiary alkyl halide/Et_2AlCl initiating systems, in strong contrast to polymerization of isoprene, results in polymers with much higher degree of unsaturation.[18,28]

3.2.2. Effect of temperature

It is known that the rate of cationic polymerization of 1,3-dienes with $^tBuCl/TiCl_4$ initiating system significantly increases with the decrease of temperature from 20°C to −78°C.[10,16,33] However, according to Table 4, the opposite dependence of polymerization rate on the temperature is observed for cationic polymerization of isoprene with $^tBuCl/Et_2AlCl$ initiating system. Indeed, yield of polymer for 30 min of polymerization decreases from 88.3% to 66.4% with decreasing of the temperature from 20°C to −78°C (Tables 2 and 4).

The similar decrease of polymer yields with reduction of the temperature is also observed for the cationic polymerization of isoprene with $^tBuBr/Et_2AlCl$ and CMB/Et_2AlCl initiating systems (Tables 2 and S3). Additionally, an induction period duration of 1–2 min is observed for isoprene polymerization with these initiating systems at −78°C (Tables 4 and S3). Interestingly, such of induction period is absent for the cationic polymerization of isoprene at −78 °C with $^{t}BuCl/EtAlCl_2$ initiating system under identical conditions.

As it was anticipated, both the molecular weights (especially weight-average molecular weight) and polydispersities of polyisoprenes synthesized $^{t}BuCl/Et_2AlCl$ increase with decreasing of the reaction temperature (Tables 2 and 4). Indeed, polyisoprene with 57.1% of yield obtained at −78 °C is characterized by M_n and M_w of 4500 g mol^{-1} and 75400 g mol^{-1}, respectively (Table 4), whereas polymers with 54.2% of yield obtained at 20 °C show M_n and M_w of 2200 g mol^{-1} and 9000 g mol^{-1}, respectively (Table 2). Moreover, the cationic polymerization of isoprene with $^{t}BuCl/Et_2AlCl$ initiating system at −78°C is often accompanied by the formation of insoluble fraction. Indeed, IF is generated after 24 h and 0.5 h when polymerization of isoprene ($[^{t}BuCl]/[Et_2AlCl]$) is conducted at 20°C and −78°C, respectively (Tables 2 and 4, S3). In addition, all polyisoprenes synthesized at −78°C appear as viscous liquids with T_g below zero due to the relatively high degree of unsaturation (71–82 mol%, Table 4).

Table 4. Cationic polymerization of isoprene with $^{t}BuCl/Et_2AlCl$ initiating system in CH_2Cl_2 at − 78°C in CH_2Cl_2[a].

$\frac{[^{t}BuCl]}{[Et_2AlCl]}$	Time (min)	Polymer Yield [b] (%)	Isoprene Conv. [c] (%)	IF [d] (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	M_w/M_n	H_c [e] (mol.%)
100	0.25	7.8	–	0	1.8	4.7	2.6	–
	0.5	15.0	–	0	2.1	5.7	2.7	–
	2	38.0	36.6	0	3.3	12.1	3.7	80
	5	46.3	44.0	0	3.5	17.1	4.9	78
	15	57.1	54.0	0	4.5	75.4	16.8	72
	30	66.4	–	28.2	–	–	–	–
450	0.5	7.6	–	0	1.7	3.8	2.2	–
	2	21.2	19.5	0	2.0	5.0	2.5	82
	5	35.6	32.9	0	2.7	7.0	2.6	79
	15	55.7	51.2	0	3.3	11.5	3.5	75
	30	61.8	57.0	0	3.4	14.2	4.2	73
	60	67.6	62.4	0	3.9	20.5	5.3	71

[a]Conditions: $[C_5H_8] = 2.0$ M, $[Et_2AlCl] = 5.0 \cdot 10^{-3}$ M. [b]Polymer yield: determined gravimetrically in respect to isoprene. [c]Isoprene conversion: calculated from ^{13}C NMR spectra. [d]IF: insoluble fraction, [e]H_c–unsaturation of polyisoprene: determined by ^{13}C NMR spectroscopy.

Thus, conducting of the cationic polymerization of isoprene at negative temperatures results in decrease of polymer yield, appearance of insoluble fraction in polymer and, therefore, does not provide the synthesis of solid thermoplastic polymers.

3.3. The structure of polyisoprenes synthesized with alkyl halide/Et_2AlCl initiating systems

3.3.1. CMB/Et_2AlCl initiating system

Figure 3 shows aliphatic and olefinic parts of ^{13}C NMR spectrum of polyisoprene synthesized with CMB/Et_2AlCl

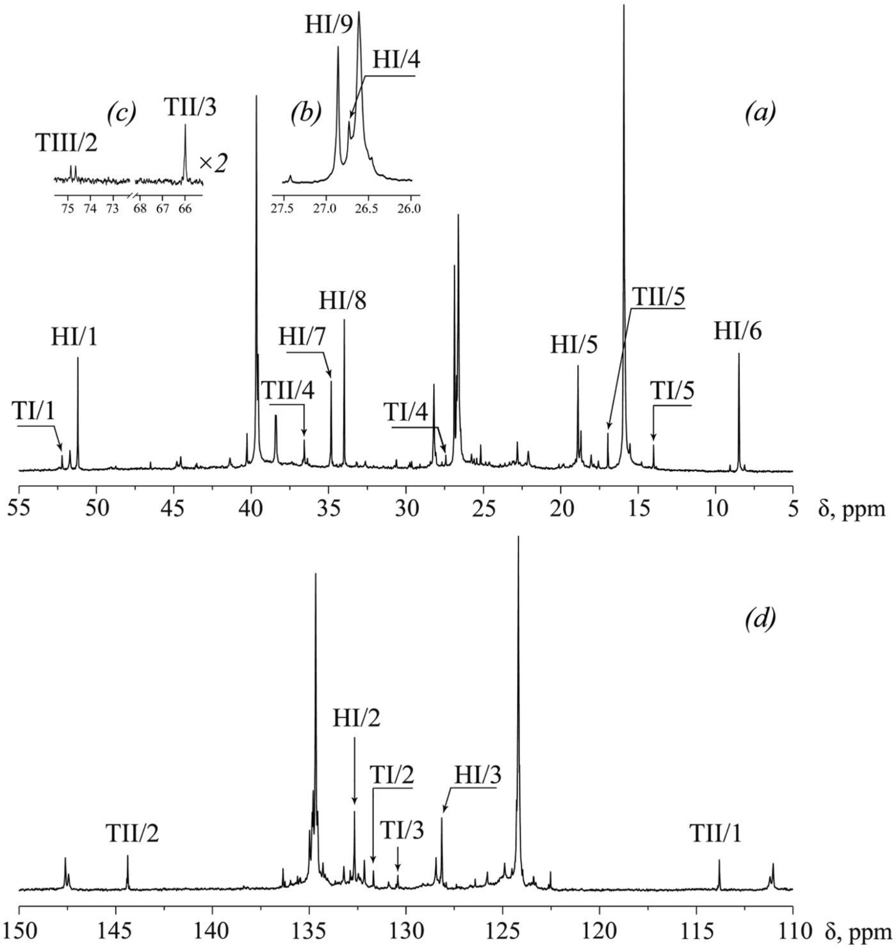
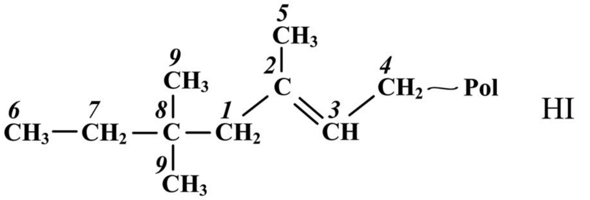


Figure 3. Fragments of (a, b, c) aliphatic and (d) olefinic parts of ^{13}C NMR spectrum of polyisoprene synthesized with CMB/Et_2AlCl initiating system. Conditions: $[C_5H_8] = 2.0$ M, $[Et_2AlCl] = 5.0 \times 10^{-3}$ M, CMB/Et_2AlCl = 100, CH_2Cl_2, −78 °C, time: 10 min, conv.= 41.4%, M_n=5.1 × 10^3 g mol^{-1}, M_w=35.6 × 10^3 g mol^{-1}, M_w/M_n=7.0. Here and hereinafter on Figures, only signals of carbon atoms in terminal units are labeled.



Scheme 1. Proposed structure of head group of polyisoprene synthesized with CMB/Et_2AlCl initiating system. Here and hereinafter the carbon atoms are designated by Arabic numbers.

Table 5. Calculated and experimental values of chemical shifts of spectral signals of carbon and hydrogen atoms in head groups of polyisoprene synthesized with CMB/Et_2AlCl initiating system (structure HI).

Number of carbon atoms	Type of carbon atom	Signal	Chemical shift (ppm)		
			^{13}C NMR		^{1}H NMR [b] (experimental)
			calculated	experimental[a]	
1	CH_2	HI/1	52.8	51.2	1.92
2	C	HI/2	133.5	132.7	–
3	CH	HI/3	127.6	128.2	5.11
4	CH_2	HI/4	26.8	26.7	2.04
5	CH_3	HI/5	18.3	18.9	1.65
6	CH_3	HI/6	8.2	8.5	0.87-0.89
7	CH_2	HI/7	35.0	34.8.	1.26
8	C	HI/8	33.0	34.0	–
9	CH_3	HI/9	27.5	26.9	0.86-0.88

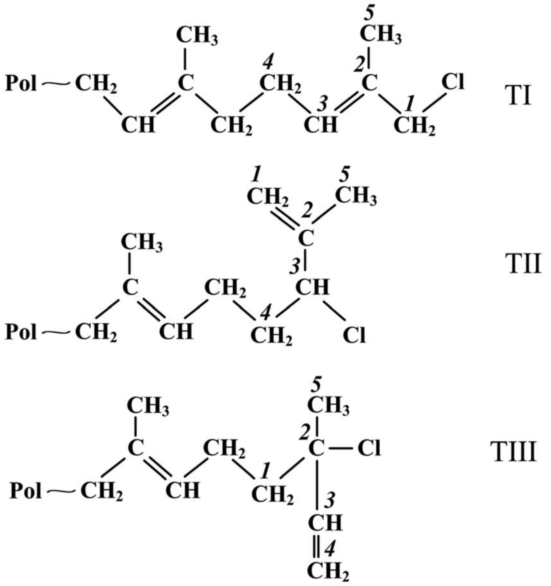
[a]See Figures 3 and S5 for details. [b]See Figure S5 for details.

initiating system (see ^{1}H NMR spectrum of polymer in Figure S3).

The position of carbon atoms in structural units of polyisoprene main chain synthesized *via* cationic mechanism was studied earlier by us in details.[10,31] As it can be seen from Figure 3, *trans*-1,4 units with regular head-to-tail enchainment are dominant structure of unsaturated part of polyisoprene chain (signal of carbon atoms at 15.9, 26.6, 39.7, 124.2 and 134.7 ppm).[31] Besides, the signals of carbon atoms of *trans*-1,4 units with inverse *tail-to-tail* (28.2 ppm) and *head-to-head* (38.4 ppm) enchainment as well as low intensity signals of carbon atoms of 1,2- (22.1, 40.3, 51.7, 111.0 and 147.6 ppm) and 3,4-units (18.8, 32.6, 44.8, 111.2 and 147.5 ppm) were presented in the structure of polyisoprene chain.[31] The quantitative calculation of the content of different structural units in polyisoprene main chain performed based on the methodology of work gives the following values: *trans*-1,4: 93 mol%; 1,2-units: 3 mol%; 3,4-units: 4 mol%.[31]

The signals of carbon atoms of *cis*-1,4 units,[31] conjugated terminal units as well as six-membered cyclic structures,[9,17,31] which can be formed in the course of intramolecular cyclization,[11−15] are totally absent in the structure of synthesized with CMB/Et_2AlCl initiating system polyisoprene.

The identification of the carbon atoms of head group of polyisoprene synthesized with CMB/Et_2AlCl initiating system (HI in Scheme 1) was performed for the first time. This head group generated in the course of initiation of the polymerization of isoprene by 2-chloro-2methyl-butane and represents dimethyl propane fragment of initiator connected with *trans*-1,4 unit of polyisoprene (scheme 1):



Scheme 2. Structure of chlorine-containing end groups with *trans*-4,1 (TI) and 4,3- (TII) and 1,2- (TIII) structures of polyisoprene synthesized CMB/Et_2AlCl initiating system.

Calculated and experimentally determined values of chemical shifts of carbon atoms in structure HI are presented in Table 5.

As it can be seen in Table 5, a good correlation between calculated and experimental values of chemical shifts of carbon atoms of structure HI is observed in ^{13}C NMR spectrum (Figure 3). According to DEPT-135° ^{13}C NMR spectrum (Figure S4*a*) signals with chemical shifts 8.5 (HI/6), 18.9 (HI/5), 26.9 (HI/9), 128.2 (HI/3) ppm have positive increment and therefore belong to methyl or methine carbon atoms, whereas signals at 26.7 (HI/4), 34.8 (HI/7) and 51.2 (HI/1) ppm are characterized by negative increment and belong to methylene carbon atoms. Signals at 34.0 (HI/8) and 132.7 (HI/2) are absent on DEPT-135° ^{13}C NMR spectrum and, therefore, belong to quaternary carbon atoms. This confirms the correctness of assignment of signals of carbon atoms in head group of structure HI. Additional confirmation of the structure of head group HI was performed with the help of ^{1}H, ^{13}C HSQC 2D (Figure S5) and ^{1}H, ^{13}C HMBC 2D NMR spectroscopy (Figure S6 and discussion therein). It should be noted that signals of head group in which dimethyl propane fragment of initiator connected with *trans*-4,1, 1,2- or 3,4-units were not detected in ^{1}H and ^{13}C NMR spectra of polyisoprene synthesized with CMB/Et_2AlCl initiating system.

Apart from signals of head group, the signals corresponding to three types of chlorine-containing end groups with *trans*-4,1 (TI), 4,3- (TII) and 1,2- (TIII) structures were found in NMR spectra of polyisoprene prepared with CMB/Et_2AlCl initiating system (Scheme 2).

The position of signals of carbon atoms of structures TI and TII in NMR spectra was determined in our earlier work devoted to the investigation of structure of polyisoprene prepared with $^{t}BuCl/TiCl_4$ initiating system.[31] Signals at 52.3 (TI/1), 131.7 (TI/2), 130.5 (TI/3), 27.4 (TI/4) and 14.0 (TI/5) ppm belonging to carbon atoms of structure TI and signals

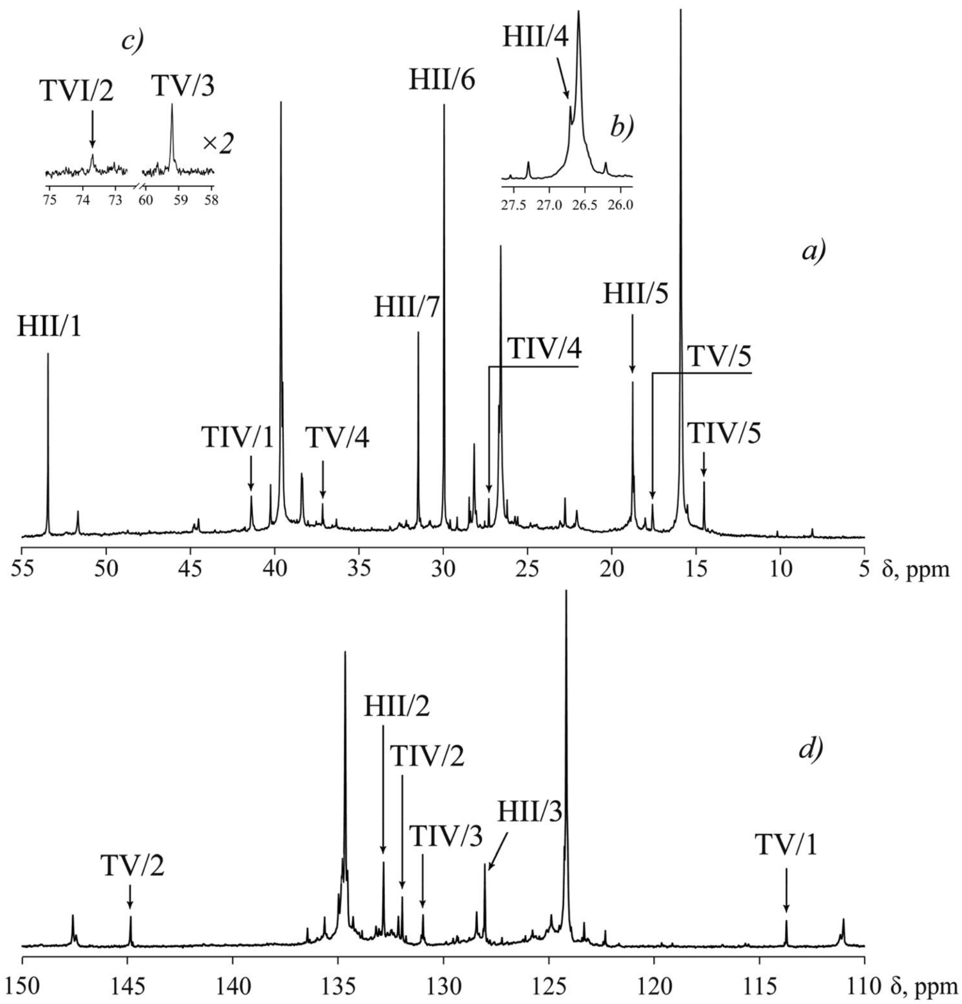


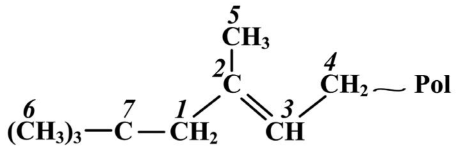
Figure 4. Fragments of (a, b, c) aliphatic and (d) olefinic parts of ^{13}C NMR spectrum of polyisoprene synthesized with ^{t}BuBr/Et$_2$AlCl initiating system. Conditions: [C$_5$H$_8$] = 2.0 M, [Et$_2$AlCl] = 5.0 × 10^{-3} M, ^{t}BuBr/Et$_2$AlCl = 100, CH$_2$Cl$_2$, −78 °C, time: 60 min, conv.= 60.7%, M_n=3.5 × 10^3 g mol^{-1}, M_w=17.3 × 10^3 g mol^{-1}, M_w/M_n=4.9.

at 113.8 (TII/1), 144.4 (TII/2), 66.1 (TII/3), 36.3 (TII/4) and 17.0 (TII/5) ppm belonging to carbon atoms of structure TII are detected in ^{13}C NMR spectrum of polyisoprene obtained with CMB/Et$_2$AlCl initiating system (Figures 3 and S5).[31] Besides, the signals in the region between 74–75 ppm, which can be tentatively attributed to chlorine-containing end group with 1,2-structure (structure TIII in Scheme 2), are also found in ^{13}C NMR spectrum of synthesized polyisoprene (Figure 3c).

The identification of carbon atoms of structure TIII is performed for the first time in this work. Calculated values of the signal of carbon atom TIII/2 is 73.8 ppm that correlates well with the experimentally determined values of the chemical shifts of two spectral signals at 74.6 and 74.9 ppm (Figure 3c). In addition, these signals disappeared in DEPT-135° ^{13}C NMR spectrum (Figure S4*a*) that confirms their belonging to quaternary carbon atoms. Due to the very low intensity of the signals at 74.6 and 74.9 ppm in comparison with intensities of signals of carbon atoms in structures TI and TII (Figure 3a and c), the signals of other carbon atoms of structure TIII could not be unambiguously identified in ^{13}C NMR spectrum of polyisoprene.

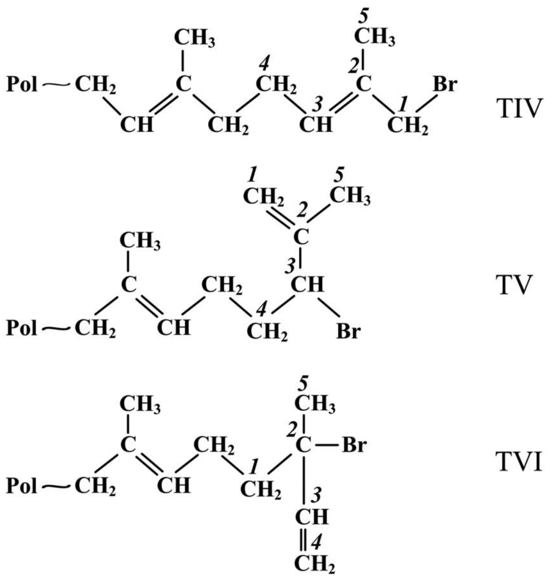
3.3.2. ^{t}BuBr/Et$_2$AlCl initiating system

Figure 4 shows aliphatic and olefinic regions of ^{13}C NMR spectrum of polyisoprene synthesized with ^{t}BuBr/Et$_2$AlCl initiating system (see Figure S7 for ^{1}H NMR spectrum). The comparative analysis of ^{13}C NMR spectra presented in Figures 3 and 4 reveals the identical structure of main chain of polyisoprene, obtained with ^{t}BuBr/Et$_2$AlCl and CMB/Et$_2$AlCl initiating systems. The head group of polisoprene synthesized with ^{t}BuBr/Et$_2$AlCl initiating system represents *tert*-butyl group from initiator connected with *trans*-1,4 unit of polyisoprene (structure HII):



HII

The position of signals of carbon atoms in structure HII was determined in our earlier work.[31] In fact, intensive signals at 53.5 (HII/1), 132.9 (HII/2), 128.1 (HII/3), 26.7 (HII/4), 18.8 (HII/5), 30.0 (HII/6) and 31.5 (HII/7) ppm are detected in ^{13}C NMR spectrum confirming that initiation of the



Scheme 3. Proposed structure of terminal bromine-containing units of *trans*-4,1 (TIV), 4,3- (TV) and 1,2- (TVI) structures.

Table 6. Calculated and experimental values of chemical shifts of spectral signals of carbon and hydrogen atoms in terminal groups of polyisoprene synthesized with ^{t}BuBr/Et$_2$AlCl initiating system (TIV and TV)

				Chemical shift (ppm)		
				^{13}C NMR		
Structure	Number of carbon atoms	Type of carbon atom	Signal	calculated	experimental[a]	^{1}H NMR[b]
TIV	1	CH$_2$	TIV/1	41.7	41.5	3.98
	2	C	TIV/2	134.3	132.0	–
	3	CH	TIV/3	128.8	131.0	5.63
	4	CH$_2$	TIV/4	27.3	27.3	2.08
	5	CH$_3$	TIV/5	14.9	14.5	1.78
TV	1	CH$_2$	TV/1	114.6	113.7	4.90, 5.08
	2	C	TV/2	146.1	144.9	–
	3	CH	TV/3	57.9	59.2	4.56
	4	CH$_2$	TV/4	37.0	37.2	1.94, 2.06
	5	CH$_3$	TV/5	18.3	17.6	1.89

[a]See Figures 4 and S9 for details. [b]See Figure S9 for details.

polymerization of isoprene with ^{t}BuBr/Et$_2$AlCl initiating system proceeds *via tert*-butyl cations. End groups of polyisoprene represent bromine-containing groups of different structure, which are generated in the course of chain transfer of the growing macrocation to ^{t}BuBr. The identification of the positions of the signals of carbon atoms in these end groups is performed for the first time in the present study. By analogy with the known structure of the terminal chlorine-containing units, it can be assumed that in the polyisoprene synthesized using the ^{t}BuBr/Et$_2$AlCl initiating system, the terminal units will have the TIV, TV, and TVI structures (Scheme 3):

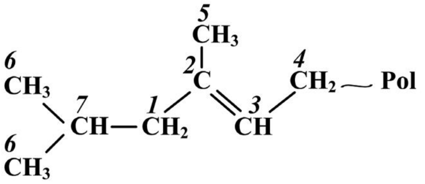
Table 6 shows calculated and experimentally determined values of the chemical shifts of carbon and hydrogen atoms in structures TIV, TV and TVI.

As it can be seen in Table 6, a good correlation between calculated and experimentally determined chemical shifts of carbon atoms of terminal bromine-containing groups is observed. According to DEPT-135° ^{13}C NMR spectrum (Figure S8), signals at 14.5 (TIV/5), 131.0 (TIV/3), 17.6 (TV/5), 59.2 (TV/3) ppm have positive increment and belong to methyl or methine carbon atoms, whereas signals at 41.5 (TIV/1), 27.3 (TIV/4), 113.7 (TV/1) 37.2 (TV/4) ppm have negative increment and can assigned to methylene carbon atoms. Moreover, signals at 132.0 (TIV/2) and 144.9 ppm (TV/2) are absent in DEPT-135° ^{13}C NMR spectrum (Figure S8) indicating their belonging to quaternary carbon atoms. Concerning bromine-containing end group of structure TVI, only the weak signal at 73.7 ppm belonging to quaternary carbon atom TVI/2 (Figure 4) is detected in ^{13}C NMR spectrum of polyisoprene due to the low intensity of signals of such structure. The position of this signals is correlated well with the calculated value (72.8 ppm).

3.3.3. ^{t}BuCl/Et$_2$AlCl and ^{i}PrCl/Et$_2$AlCl initiating systems

^{1}H and ^{13}C NMR spectra of polyisoprene synthesized with ^{t}BuCl/Et$_2$AlCl initiating system are presented in Figures S10 and S11, respectively. The analysis of obtained spectra revealed their similarity with NMR spectra of polyisoprene prepared with ^{t}BuCl/TiCl$_4$ initiating system.[31] Unsaturated part of polymer chain had the same structure as polyisoprene synthesized with CMB/Et$_2$AlCl and ^{t}BuBr/Et$_2$AlCl initiating systems. Head group of polyisoprene obtained with ^{t}BuCl/Et$_2$AlCl initiating system represents *tert*-butyl group connected with *trans*-1,4 unit of polyisoprene chain (structure HII), while the end groups are the chlorine-containing groups of the structure TI, TII and TIII.

^{1}H and ^{13}C NMR spectra, DEPT-135° ^{13}C NMR spectrum as well as ^{1}H, ^{13}C 2D HMBC NMR spectra of polyisoprene synthesized using ^{i}PrCl/Et$_2$AlCl initiating system are presented in Figures S12 – S15. Unsaturated part of polymer chain has the same structure as polyisoprene synthesized with CMB/Et$_2$AlCl initiating system (Figures 3 and S13). The head group represents isopropyl group connected with *trans*-1,4 unit of polyisoprene chain (structure HIII):



HIII

The identification of the signals of carbon atoms of the structure HIII presented in Table S4 and Figures S13–S15. The signals of carbon atoms of chlorine-containing end groups of structure TI, TII and TIII are absent in NMR spectra with the exception of low intensity signal at 52.3 ppm (Figure S13*a*).

3.4. Thermomechanical properties of synthesized polyisoprenes

Figure 5 shows the dependences of deformation on the temperature for polyisoprenes obtained at different polymerization time.

An increase in the values of flow temperature of polyisoprene samples with the increase of the duration of polymerization is observed that is consistent with the increase of

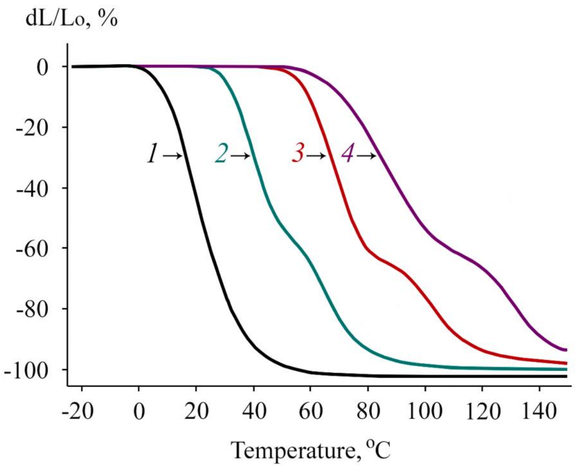


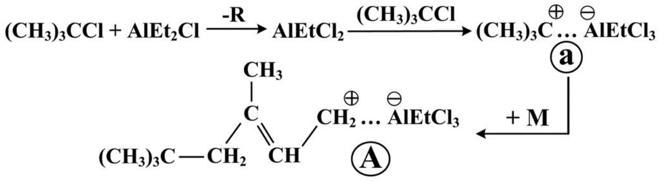
Figure 5. Deformation vs temperature dependences for polyisoprenes synthesized with ${}^tBuCl/Et_2AlCl$ initiating system at different polymerization time in CH_2Cl_2 at 20 °C.
Conditions: ${}^tBuCl/Et_2AlCl = 250$, $[C_5H_8] = 2.0$ M, $[Et_2AlCl] = 5 \times 10^{-3}$ M, time: 5 s (**1**), 5 min (**2**), 60 min (**3**) and 24 h (**4**).

their glass transition temperature and softening point, respectively (Figure 5, Table 3). The shape of thermomechanical plots confirms that synthesized polyisoprenes are thermoplastics and, therefore, can be processed by standard methods.

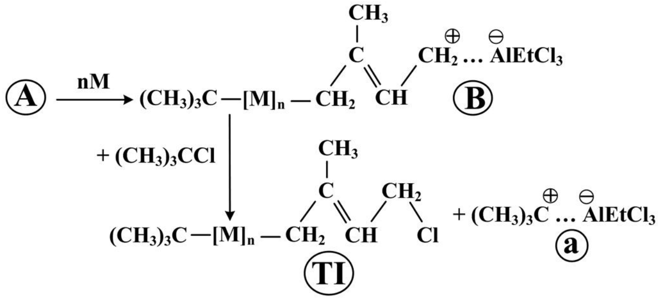
4. Discussion

The obtained results indicate that strategy for the synthesis of solid thermoplastic polymers from isoprene is similar to one developed for the synthesis of solid polymers of butadiene and 1,3-pentadiene.[18,28] This strategy consists in the purposeful decrease of unsaturation of polymer to the level of 40–50 mol% *via* polymerization of 1,3-diene with alkyl halide/alkyl aluminum halide initiating system using significant excess of alkyl halide over the Lewis acid. It should be noted that initiating systems based on secondary alkyl chlorides (isopropyl chloride, 2-chlorobutane) and alkyl aluminum chloride of different compositions are optimal for the preparation of solid polymers from butadiene and 1,3-pentadiene.[18,28] However, the cationic polymerization of isoprene with ${}^iPrCl/Et_2AlCl$ initiating system results in the formation of insoluble fraction independently on the ${}^iPrCl$ to Et_2AlCl ratio (Tables 1 and S1). On the other hand, solid thermoplastic polyisoprene without any insoluble fraction are synthesized using tertiary alkyl halides (${}^tBuCl$, ${}^tBuBr$ and CMB) in conjunction with Et_2AlCl (Tables 2 and 3). In contrast, the cationic polymerization of butadiene and 1,3-pentadiene with initiating system based on tertiary alkyl halides leads to liquid polymers with high degree of unsaturation.[16,18,33] To explain the observed differences in the polymerization of various 1,3-dienes, the mechanism of Et_2AlCl-co-initiated cationic polymerization of isoprene using tertiary (${}^tBuCl$) and secondary (${}^iPrCl$) alkyl chlorides will be briefly discussed below.

In general, the cationic polymerization of 1,3-dienes with aliphatic alkyl halide/Lewis acid initiating systems includes the following key steps: (i) initiation, (ii) propagation, (iii) chain transfer to alkyl halide, (iv) chain transfer to "own" or "alien" macromolecule and (v) termination.[9,10,16,18,28] Initiation of the polymerization of isoprene with ${}^tBuCl/Et_2AlCl$ initiating system is accompanied by *in situ* formation of $EtAlCl_2$ and mixture of isobutane, dimethylbutane and isooctane (**R** in Scheme 4).[34] The ionization of ${}^tBuCl$ by $EtAlCl_2$ followed by the monomer addition completes the initiation step (Scheme 4):



Scheme 4. Initiation in the cationic polymerization of isoprene with ${}^tBuCl/Et_2AlCl$ initiating system (**M:** isoprene; **R:** mixture of saturated hydrocarbons).



Scheme 5. Propagation and chain transfer to *tert*-butyl chloride in the cationic polymerization of isoprene with ${}^tBuCl/Et_2AlCl$ initiating system.

The observed induction period in the cationic polymerization of isoprene with ${}^tBuCl/Et_2AlCl$ initiating system at −78°C (Table 4) is consistent with much lower rate of *in situ* generation of $EtAlCl_2$ at such low temperature as compared to the polymerization performed at 20 °C where the induction period was absent (Tables 2 and 3). The absence of induction period during isoprene polymerization with ${}^tBuCl/EtAlCl_2$ at −78°C confirms the *in situ* generation of $EtAlCl_2$ at the initiation step (Scheme 4).

Propagation occurs *via* consecutive monomer addition to active center **A** formed during the initiation step (Scheme 5).

The competitive to propagation reaction is the chain transfer to initiator (*tert*-butyl chloride) used in high excess to Lewis acid leading to formation of chlorine-containing end groups of structures of TI, TII and TIII (Figures 3 and S11) and regeneration of active center of polymerization (**a** in Scheme 4). As we showed earlier,[10,27] such regeneration of the active center allows to reach high monomer conversions during the cationic polymerization of 1,3-dienes initiated by tertiary alkyl halides. Another chain transfer reaction, which operates in the cationic polymerization of isoprene under investigated conditions, is the chain transfer to polymer with the formation of branched or partially cross-linked macromolecules with reduced unsaturation. Mechanism of such reaction was investigated in our earlier works in details and is presented in Scheme S1.[10,16,18,35]

The initiation of cationic polymerization of isoprene with ${}^iPrCl/Et_2AlCl$ initiating system proceeds in the same way as initiation with $^tBuCl/Et_2AlCl$ initiating system *via in situ* generation of $EtAlCl_2$ followed by ionization of ^iPrCl by Lewis acid with the formation of isopropyl cation (Scheme S2). Indeed, the signals of carbon atoms of isopropyl head group connected with *trans*-1,4 unit of poyisoprene was identified in ^{13}C NMR spectra of polymer (Figures S13–S15). Importantly, the signals of chlorine-containing end groups TI, TII and TIII (Figures S13 and S14) are almost absent in ^{13}C NMR spectrum indicating the low intensity of chain transfer to isopropyl chloride (Scheme S3). This reduced ability of ^iPrCl to participate in chain transfer reaction results in the formation of cross-linked insoluble polyisoprene during the cationic polymerization of isoprene with $^iPrCl/Et_2AlCl$ initiating system (Tables 1 and S1) as well as of lower polymer yield in comparison with one obtained using tertiary alkyl halides as initiators (Tables 2–4).

The comparative analysis of the variation of molecular weight, polydispersity and unsaturation during the cationic polymerization of isoprene (Tables 1–4), butadiene and 1,3-pentadiene with the same initiating system based on secondary and tertiary alkyl halides is then performed.[18,28] This analysis reveals much higher reactivity of main chain double bonds in polyisoprene in the chain transfer reaction to polymer as compared to other poly(1,3-dienes). In fact, the formation of insoluble fraction did not occur during the cationic polymerization of butadiene and 1,3-pentadiene with $^iPrCl/Et_2AlCl$ initiating system up to complete monomer conversion,[18,28] whereas IF was generated in the course of polymerization of isoprene after reaching the level of 70–75% of polymer yield (Tables 1 and S1). On the other hand, the poly(1,3-diene)s obtained during the cationic polymerization of butadiene and 1,3-pentadiene using ^tBuCl as an initiator in conjunction with different Lewis acids ($TiCl_4$, $VOCl_3$ or Et_2AlCl) are viscous liquids with relatively high degree of unsaturation ($\geq$70 mol%) and low glass transition temperature (<0 °C).[16,18,27,33] According to Tables 2 and 3 polyisoprenes obtained in similar conditions are characterized by much lower unsaturation (41–48 mol%) and, consequently, much higher values of glass transition temperature (52–60 °C) and softening point (100–128°C). Apart from relatively high values of T_g, the synthesized polyisoprenes contains significant amount of chlorine- or bromine-containing terminal units that would improve their adhesive properties[36] and facilitate their further modification *via* nucleophilic substitution reactions of chloroallyl or bromoallyl end-functional polyisoprene.[37,38] Synthesized polyisoprenes with bromoallyl end groups could be potentially used as macroinitiators for ATRP of radically polymerized vinyl monomers such as, for example, methyl methacrylate. Indeed, Faust et al. reported the successful using of polyisobutylene with allyl halide end group as macroinitiator for ATRP of methyl methacrylate to prepare corresponding block copolymers.[39]

5. Conclusions

In this work, the Et_2AlCl-co-initiated cationic polymerization of isoprene in the presence of different alkyl halides, e.g. secondary (isopropyl chloride) and tertiary (2-chloro-2-methylbutane, ^tBuCl and ^tBuBr) was investigated. We have demonstrated here that cationic polymerization of isoprene with $^iPrCl/EtAlCl_2$ initiating system, in strong contrast to polymerization of butadiene and 1,3-pentadiene, results in ill-defined polyisoprene containing large amount of insoluble fraction due to the intensive chain transfer to polymer owing to the higher reactivity of main chain double bonds of polyisoprene as compared to polybutadiene and poly(1,3-pentadiene). In contrast, well defined solid thermoplastic polyisoprenes with reduced unsaturation (41–48 mol%) and relatively high glass transition temperature (52–60 °C) can be obtained using tertiary alkyl halide/Et_2AlCl initiating system. We also clearly showed in this study that not only the nature of alkyl group (secondary vs tertiary) but also halide (Cl vs Br) in alkyl halide had dramatic effect on the polymerization: substitution of ^tBuCl by ^tBuBr leads to considerable decrease of both molecular weight and polydispersity.

The developed in this study protocol allowed to prepared chloroallyl or bromoallyl end-functional polyisoprene, which can be easily modified *via* nucleophilic substitution reactions that opens new possibilities in the synthesis of functionalized poly(1,3-diene)s. In addition, polyisoprenes with bromoallyl end groups could be potentially used as macroinitiators for ATRP of radically polymerized vinyl monomers such as methyl methacrylate.

Disclosure statement

The authors declare no conflict of interest.

Author contributions

Victor A. Rozentsvet: Conceptualization, supervision, methodology, project administration, resources, writing-original draft, writing-review and editing. **Daria M. Ulyanova:** Investigation, formal analysis, data curation. **Nelly A. Sablina:** Investigation, data curation, software, visualization. **Sergei V. Kostjuk:** Formal analysis, writing-original draft, writing-review and editing. **Nina V. Sidorenko:** Investigation. **Peter M. Tolstoy:** Investigation, methodology, formal analysis.

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