Cationic Polymerization of 1,3-Pentadiene Coinitiated by Zinc Halides

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ABSTRACT: Technology of industrial production of liquid rubber under trademark "SKOP" is based on the cationic polymerization of 1,3-penadiene (piperylene) in the presence of $TiCl_4$ or $AlCl_3$-based catalytic systems. The disadvantage of these catalytic systems is the high probability of formation of branched and insoluble fractions due to the chain transfer to polymer. This deteriorates the useful qualities of SKOP. Here we propose the new initiating systems for the cationic polymerization of 1,3-pentadiene based on the homogeneous (dissolved in a minimal amount of diethyl ether) zinc halides ($ZnCl_2$ and $ZnBr_2$) as coinitiators and hydrochloric acid, *tert*-butyl chloride or trichloroacetic acid as initiators. These initiating systems allow to synthesize fully soluble low molecular weight (M_n = 1000–3000 g mol^{-1}) poly(1,3-pentadiene)s with relatively narrow molecular weight distribution (M_w/M_n < 2.0), which do not contain any high molecular weight and insoluble fractions in the whole range of monomer conversion. The polymers synthesized in the presence of zinc halides possess the same microstructure that those prepared with $TiCl_4$ as coinitiator. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The 1,3-pentadiene (piperylene) is a large-scale byproduct of processes of isoprene production via dehydrogenation of isopentane or cracking of hydrocarbons. In Russia, this monomer is used for the production of liquid rubber SKOP (synthetic caoutchouc oligomer of piperylene), which is intensively used in paint and varnish industry.[1,2] The technology of production of SKOP is based on the cationic polymerization of 1,3-pentadiene using $H_2O/TiCl_4$[1] or $AlCl_3 \times O(C_6H_5)_2$[2] initiating systems. The main disadvantage of these catalytic systems is the high probability of formation of insoluble fraction (IF) in the course of polymerization of 1,3-pentadiene leading to the deterioration of useful qualities of SKOP. Different additives such as olefins,[3] acetone,[4] and other molecular weight regulators[2] were typically added to the polymerization system to suppress gel formation during the 1,3-pentadiene polymerization. However, this complicated the production of poly(1,3-pentadiene)s with defined molecular.

The chain transfer to polymer is a main feature of cationic polymerization of conjugated dienes.[2,5–7] This leads to the appearance in the polymer of branched high molecular weight fraction (HMWF) and then insoluble fraction, while resulting poly(diene)s are characterized by reduced unsaturation (for a detailed review on cationic polymerization of 1,3-dienes, see Ref. 2). The formation of HMWF and IF is observed during the cationic polymerization of 1,3-pentadiene using the initiating systems based on $AlCl_3$,[7–15] $FeCl_3$,[16] $SnCl_4$,[17] $TiCl_4$,[1–6,18–20] and $VOCl_3$.[21] Depending on the nature of Lewis acid used, the appearance of HMWF and IF is revealed at the different stages of the polymerization process. For example, HMWF and IF were formed at the beginning of the polymerization with $AlCl_3$ as coinitiator,[8–15] while in the presence of $TiCl_4$ and $VOCl_3$ HMWF and IF were observed only when certain concentrations of polymer were achieved in the reaction medium.[2,18–21]

Based on exhaustive analysis of the literature data it was unambiguously concluded that the intensity of chain transfer reaction to polymer during the cationic polymerization of 1,3-pentadiene increased with increasing acidity of Lewis acid used.[2] Therefore, the investigation of the polymerization of 1,3-pentadiene in the presence of weak Lewis acids such as, for example, zinc halides[22] is of considerable interest. However, data on the cationic polymerization of 1,3-dienes in the presence of zinc halides is limited to the work,[23] which describes the polymerization of cyclopentadiene with initiating system consisting of the HCl adduct of cyclopentadiene as initiator and ZnX_2 (X = Cl, Br, I)

as coinitiator. This initiating system induced slow cationic polymerization of cyclopentadiene (5–26 days) at relatively high Lewis acid concentration ($[ZnX_2] = 0.1$ M) and low temperature ($-78°C$) affording poly(cyclopentadiene)s with low molecular weight ($M_n = 4000$–6000 g mol^{-1}).[23]

This work is devoted to the investigation of the cationic polymerization of 1,3-pentadiene in the presence of initiating systems based on ZnCl$_2$ and ZnBr$_2$ with the aim to synthesize poly(1,3-pentadiene)s, which do not contain high molecular weight and insoluble fractions in the whole range of monomer conversions and polymerization conditions.

EXPERIMENTAL

Materials

The 1,3-pentadiene purchased from OAO Nizhnekamskneftekhim had the following compositions (wt %): *trans*-1,3-pentadiene, 47.9; *cis*-1,3-pentadiene, 45.8; cyclopentene, 4.0; 2-methyl-2-butene, 0.1; 2-methyl-1-butene, 0.1; isoprene, 0.1; cyclopentadiene, 0.1, the rest—saturated hydrocarbons. Before experiments, 1,3-pentadiene was washed with water, dried on NaX molecular sieves, and then distilled over CaH$_2$ in argon flow. The content of trace impurities in 1,3-pentadiene was (wt %): water, $<3.0 \times 10^{-4}$; carbonyl compounds (calculated with respect to acetone), $<1.0 \times 10^{-3}$; peroxides (calculated with respect to active oxygen), $<1.0 \times 10^{-3}$; nitrogen-containing compounds (calculated with respect to dimethylformamide), $<5.0 \times 10^{-4}$.

CH$_2$Cl$_2$ (Biosolve, 99.9%), *n*-hexane (Reachim, 99.5%), toluene (Reachim, 99.9%), *tert*-butyl chloride (^{t}BuCl, Fluka, >99.5%) was distilled over CaH$_2$ under inert atmosphere before use. Diethyl ether (Fluka, >99.8%) was treated with KOH overnight and then distillated from CaH$_2$ under inert atmosphere. Acetone (Fluka, >99.7%), tetrahydrofuran (THF, Aldrich, 99.9%), ZnCl$_2$ (Merck, >98.0%), ZnBr$_2$ (Merck, >98.0%), and trichloroacetic acid (TCAA, Aldrich, >99.0%) were used as received.

Water was used in a form of saturated solution in monomer or solvents. The saturated solutions of water were prepared by vigorous mixing of monomer (solvent) with water. The content of water was determined by Karl–Fischer titration. The solution of HCl in CH$_2$Cl$_2$ was prepared through bubbling of dry gaseous HCl. The concentration of HCl was determined by titration.

Polymerization Procedure

Polymerizations were carried out under an argon atmosphere in baked glass ampoules of total volume 12 mL equipped with magnetic stirrer bar and a septum. As an example of a typical procedure, the ampoule was charged by 1,3-pentadiene (0.02 mol, 2 mL) and CH$_2$Cl$_2$ (7.7 mL) and then thermostated at desired temperature for 5–7 min. The reaction was initiated by addition of solution of catalytic complex in CH$_2$Cl$_2$ (0.30 mL), containing ZnCl$_2$ (1.0×10^{-4} mol, 0.0136 g), trichloroacetic acid (1.0×10^{-3} mol, 0.1635 g) and diethyl ether (7.7×10^{-4} mol, 0.0571 g) was added to ampoule via dry syringe. After a predetermined time, the reaction was terminated by addition to the ampoule about 0.2 mL of a mixture of propylene oxide with methanol (50:50 v/v). The solution of *N*-isopropyl-*N'*-phenyl-1,4-phenylenediamine was then immediately added as

an antioxidant to the reaction media. The polymer was isolated by evaporation of solvent and unreacted monomer from ampoules and dried in vacuum at 40°C up to constant weight. Monomer conversions were determined gravimetrically.

Characterizations

The insoluble fraction (IF) was separated by centrifugation from solution of polymer in toluene. The content of IF in the polymer was determined by additional Soxhlet extraction in boiling toluene for 24 h. Before analyses, soluble fraction of poly(1,3-pentadiene) was purified by column chromatography using Silica gel 60 from Fluka and chloroform as eluent. After purification, yield of polymer was 96–98% with respect to original (unpurified) polymer.

The number-average (M_n) and weight-average (M_w) molecular weights as well as molecular weight distribution (M_w/M_n) were measured by gel permeation chromatography using Waters-Alliance GPCV-2000 chromatograph equipped with two detectors (refractometric and viscometric) and set of Styrogel columns with pore size of 500 (HR-2), 10^3 (HR-3), 10^4 (HR-4), and 10^6 (HR-6) Å thermostated at 30°C. Toluene was used as eluent, the elution rate was 1 mL min^{-1}. The calculations were based on polystyrene standards (Waters).[18] Microstructure and unsaturation were determined by ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra, which were recorded in CDCl$_3$ at room temperature using Bruker AM-500 spectrometer according to methodology of Ref. 24 A pulse delay of 8–12 s was given for recording ^{13}C NMR spectra and 6000–8000 scans were accumulated.

RESULTS

Polymerization of 1,3-Pentadiene Under Heterogeneous Conditions

The cationic polymerization of 1,3-pentadiene in the presence of ZnCl$_2$ and ZnBr$_2$ proceeded under heterogeneous conditions since zinc halides are not soluble in reaction media. Appreciable amounts of polymer were obtained only after 10 days of polymerization even in the presence of relatively high concentrations of zinc halide (Table I). The obtained poly(1,3-pentadiene)s contained essential amount of insoluble fraction. The number-average and weight-average molecular weights of soluble fraction were low; whereas molecular weight distribution (MWD) was relatively narrow ($M_w/M_n \leq 2.0$). The observed low activity of zinc halides in the polymerization of 1,3-pentadiene could be explained either by the heterogeneity of the polymerization system or lack of initiator.

Polymerization of 1,3-Pentadiene Under Homogeneous Conditions

Appropriate Initiator Search. The solubilization of zinc halides in diethyl ether allowed to conduct the polymerization of 1,3-pentadiene under homogeneous conditions. However, without an addition of initiator to the system the activity of homogeneous zinc halides remained quite low (see Table II).

The addition of water as an initiator to the polymerization system (in a form of saturated solution in monomer and solvent) did not improve the activity of zinc halides in the cationic polymerization of 1,3-pentadiene. This essentially distinguishes the behavior of ZnX$_2$-based (X = Cl, Br) initiating systems in the

Table I. Cationic Polymerization of 1,3-Pentadiene in the Presence of Zinc Halides (ZnX_2) in CH_2Cl_2 at 20°C: [IP] = 2.0M; [ZnX_2] = 5.0 × 10^{-2} M

ZnX_2	Time (days)	Conversion (%)	IF[a] (%)	$M_n \times 10^{-3}$[b] (g mol^{-1})	$M_w \times 10^{-3}$[b] (g mol^{-1})	M_w/M_n[b]
$ZnBr_2$	1.0	0.8	–	–	–	–
	10.0	7.5	12.6	1.4	2.7	1.9
	30.0	23.7	29.4	1.5	3.0	2.0
$ZnCl_2$	1.0	0.6	–	–	–	–
	10.0	6.9	21.3	1.5	2.9	1.9

[a]Insoluble fraction, [b]Determined for soluble fraction.

polymerization of 1,3-pentadiene from catalytic systems based on TiCl$_4$, where the addition of water dramatically increased the rate of cationic polymerization of 1,3-dienes.[1–4,17,25] Probably, it could be explained by the fact that zinc halides are considered as so-called "chlorophilic" Lewis acids, i.e., they interact strongly with a chlorine atom than with oxygen atom.[26,27] Indeed, the use of hydrogen chloride and *tert*-butyl chloride as initiators allowed to increase the reaction rate significantly (Table II). The increase of initiator/Lewis acid ratio led to the gradual increase of monomer conversion. Note, ^{t}BuCl/ZnX_2 initiating systems sowed higher activity than HCl/ZnX_2 initiating systems (Table II).

Another very important observation from Table II is the total absence of insoluble fraction in the poly(1,3-pentadiene)s prepared using homogeneous ZnX_2-based initiating systems in the whole range of monomer conversions. The obtained polymers were characterized by relatively low molecular weight (M_n = 1000 g mol^{-1}) and narrow molecular weight distribution (M_w/M_n = 2–3). Interestingly, the increase of initiator to Lewis acid ratio almost did not influence the molecular weight or MWD of synthesized polymers (Table II).

Polymerization of 1,3-Pentadiene with Trichloroacetic Acid/ ZnX_2 Initiating System. The use of trichloroacetic acid (TCAA) as initiator allowed to achieve the highest activity for zinc halides in the cationic polymerization of 1,3-pentadiene (see Table III). As we can see from Table III, the monomer conversion increased significantly with increasing of TCAA/$ZnBr_2$ molar ratio from 1 to 10. The further increase of initiator concentration almost did not influence the reaction rate.

The use of toluene or *n*-hexane as solvents instead of CH_2Cl_2 as we anticipated led to the considerable decrease of reaction rate due to reduction of the solvent polarity (dielectric constants are 8.9, 2.4, and 1.9 for CH_2Cl_2, toluene and *n*-hexane, respectively). It should be also noted that for the solubilization of $ZnBr_2$ a minimal amount of diethyl ether was used (9.2 × 10^{-2} M), while the addition to the system an excess of diethyl ether led to the dramatic decrease of monomer conversion (Table III) that is consistent with a possible deactivation of active cationic species through their interaction with base (diethyl ether).[2] Another explanation for this observation is the formation of complex of Lewis acid with diethyl ether, which exists in equilibrium with free Lewis acid, and an excess of ether shifts this

Table II. Effect of Initiator Nature and Concentration on the Cationic Polymerization of 1,3-Pentadiene in the Presence of Zinc Halides as Coinitiators in CH_2Cl_2 at 20°C: [C_5H_8] = 2.0M; [ZnX_2] = 2.0 × 10^{-2} M; [Et_2O] = 1.8 × 10^{-1} M, and 1.5 × 10^{-1} M for $ZnBr_2$ and $ZnCl_2$, Respectively

ZnX_2	Initiator (mM)	Time (h)	Conversion (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	M_w/M_n
$ZnBr_2$	–	96	0.9	–	–	–
	H$_2$O (3)	96	1.2	–	–	–
	H$_2$O (10)	96	2.8	–	–	–
	HCl (40)	1	10.2	0.9	2.2	2.4
	HCl (100)	1	22.6	0.9	2.2	2.4
	HCl (200)	1	39.4	0.8	2.4	3.0
	^{t}BuCl (20)	1	14.5	1.0	2.3	2.3
	^{t}BuCl (200)	1	66.4	1.1	2.7	2.5
	^{t}BuCl (1000)	1	99.3	1.2	2.8	2.3
$ZnCl_2$	–	96	0.9	–	–	–
	H$_2$O (10)	96	1.7	–	–	–
	HCl (40)	1	7.3	1.0	2.4	2.4
	HCl (200)	1	30.6	0.9	2.5	2.8
	^{t}BuCl (200)	1	39.2	1.2	2.7	2.3

Table III. Effect of Solvent Nature, TCAA/ZnBr$_2$ Molar Ratio, and Electron Donor on the Cationic Polymerization of 1,3-Pentadiene with TCAA/ZnBr$_2$ Initiating System at 20°C for 1 h: [C$_5$H$_8$] = 2.0M; [ZnBr$_2$] = 1.0 × 10^{-2} M; [Et$_2$O] = 9.2 × 10^{-2} M

Solvent	TCAA/ZnBr$_2$ (mol mol^{-1})	Conversion (%)	M_n × 10^{-3} (g mol^{-1})	M_w × 10^{-3} (g mol^{-1})	M_w/M_n
CH$_2$Cl$_2$	1.0	12.6	1.8	3.4	1.9
	3.0	29.7	1.6	3.3	2.1
	5.0	42.5	1.7	3.5	2.1
	10.0	66.3	1.7	3.6	2.1
	10.0[a]	28.4	2.0	3.9	2.0
	10.0[b]	15.0	1.3	2.6	2.0
	20.0	70.5	1.8	3.7	2.1
Toluene	10.0	24.7	1.1	2.1	1.9
n-Hexane	10.0	21.8	1.3	2.7	2.1
Diethyl ether	10.0	2.8	–	–	–

[a]Acetone (7.1 × 10^{-2} M), [b]Tetrahydrofuran (7.8 × 10^{-2} M) were used instead of diethyl ether for solubilization of ZnBr$_2$.

equilibrium towards complex formation.[27] This led to the decrease of the concentration of free Lewis acid and, in turn, the rate of polymerization.[27] In addition, the use of acetone or tetrahydrofuran for the solubilization of zinc halides led to the less active catalytic systems in comparison with using diethyl ether (Table III). Finally, the solvent nature or TCAA/ZnBr$_2$ molar ratio only slightly influenced the molecular weight and polydispersity and all obtained polymers did not contain any insoluble fraction (see Table III).

The similar results were obtained for TCAA/ZnCl$_2$ initiating system, although the activity of this system was lower in comparison with TCAA/ZnBr$_2$ initiating system (curves 1 and 3 in Figure 1). The higher activity of ZnBr$_2$ as compared to ZnCl$_2$ was also observed in the cationic polymerization of cyclopentadiene coinitiated by zinc halides.[23] This difference is consistent with the increase of Lewis acidity and/or decrease of lattice

Figure 1. Conversion vs. time (1, 3) and ln[M]$_0$/[M] vs. time (2, 4) dependences for 1,3-pentadiene polymerization with TCAA/ZnBr$_2$ (1, 2) and TCAA/ZnCl$_2$ (3, 4) initiating systems at 20°C in CH$_2$Cl$_2$: [C$_5$H$_8$] = 2.0 M; [ZnCl$_2$] = [ZnBr$_2$] = 1.0 × 10^{-2} M; [TCAA] = 1.0 × 10^{-1} M. Diethyl ether concentration: 9.2 × 10^{-2} M and 7.7 × 10^{-2} M for ZnBr$_2$ and ZnCl$_2$, respectively.

energy of corresponding metal halide (MX$_n$, M = metal, X = Cl, Br, I) in a series: MCl$_n$ < MBr$_n$ < MI$_n$.[28] In other words, among all investigated in this work ZnX$_2$-based initiating system homogeneous TCAA/ZnBr$_2$ initiating system showed the highest activity in the cationic polymerization of 1,3-pentadiene, which is comparable with the activity of most active catalytic system based on TiCl$_4$.[1–4,17,18–20] or VOCl$_3$.[21]

The cationic polymerization of 1,3-pentadiene using TCAA/ZnX$_2$ (X = Cl or Br) initiating system showed strongly pronounced unsteady-state kinetics (Figure 1) that is a general feature of cationic polymerization 1,3-dienes.[1–5,15,17–21,25] Indeed, as it can be seen from Figure 1, the first order plots are not linear.

Influence of Polymerization Temperature. It is known that relationship of the rate of cationic polymerization of 1,3-pentadiene on the polymerization temperature is quite complicated and often depends on the nature of catalytic system (Lewis acid).[2,4,5,19,21] For investigated in the present study TCAA/ZnX$_2$ (X = Cl, Br) initiating systems the reaction rate increased with increasing reaction temperature (Figure 2).

At –78°C, the cationic polymerization of 1,3-pentadiene almost did not proceed (the monomer conversion was <2.0% after 10 days of polymerization), while the maximal rate of polymerization was achieved at 60°C (Figure 2). The completely different behavior was observed for the catalytic system based on TiCl$_4$[2,4,19] or VOCl$_3$.[21] For example, for TiCl$_4$-coinitiated cationic polymerization of 1,3-pentadiene the maximal initial rate was observed at –70°C, while the rise of temperature up to 60°C led to the considerably reduction of the initial rate of reaction.[19] Probably, the observed behavior of homogeneous ZnX$_2$-based initiating system could be explained by the increase of tightness of the complex of Lewis acid with diethyl ether with decreasing temperature that led to the decrease of the instantaneous concentration of free Lewis acid and, in turn, the reaction rate.[29,30]

Importantly, poly(1,3-pentadiene)s synthesized even at low temperatures did not contain IF and were fully soluble in common
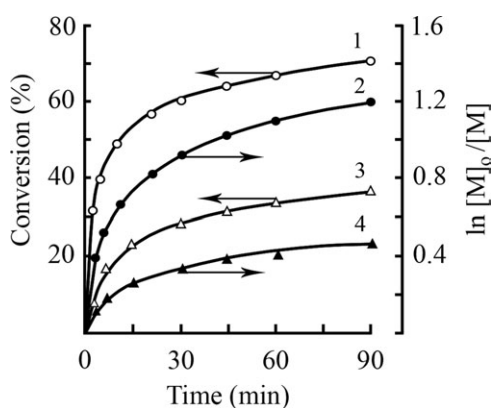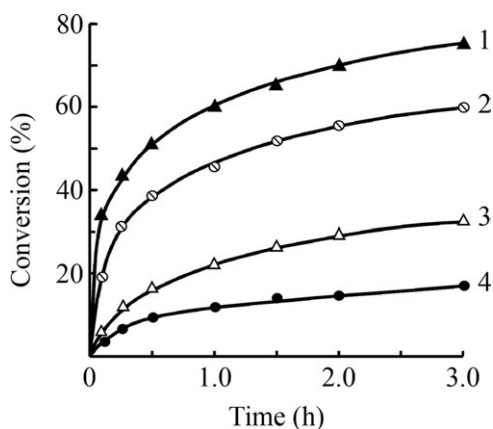
Figure 2. Conversion vs. time plots for 1,3-pentadiene polymerization with TCAA/ZnCl$_2$ initiating system in CH$_2$Cl$_2$ at different polymerization temperatures: [C$_5$H$_8$] = 2.0 M; [ZnCl$_2$] = 1 × 10^{-2} M; [TCAA] = 1.0 × 10^{-1} M; [Et$_2$O] = 7.7 × 10^{-2} M. Polymerization temperature: (1) 60°C; (2) 40°C; (3) 5°C; (4) −15°C.

organic solvents. It is known that in the cationic polymerization of 1,3-dienes the formation of HMWF and IF fractions is more pronounced at low temperatures.[2,19,21] As we can see

from Table IV, the increase of the reaction temperature led to some decrease of molecular weight and narrowing of molecular weight distribution. The similar trend was also observed for majority of known initiating system of cationic polymerization of 1,3-dienes.[2,4,5,19,21,25] The low molecular weight ($M_n < 500$ g mol^{-1}) reaction product obtained at −78°C was supposed to be not a polymer of 1,3-pentadiene (see Figure 3 and discussion therein for more details).

Microstructure and Unsaturation of Synthesized Poly(1,3-pentadiene)s. Poly(1,3-pentadiene)s synthesized in the presence of zinc halides are characterized by reduced but relatively high (74–84 mol %) unsaturation, which slightly increased with decreasing of reaction temperature (see Table V).

The dominant structure of unsaturated part of poly(1,3-pentadiene) chain is *trans*-1,4-units of regular head-to-tail addition:
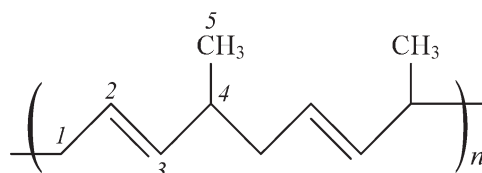

Table IV. Influence of Reaction Temperature on the Molecular Characteristics of Poly(1,3-pentadiene)s Obtained with TCAA/ZnBr$_2$ and TCAA/ZnCl$_2$ Initiating Systems in CH$_2$Cl$_2$: [C$_5$H$_8$] = 2.0M; [ZnBr$_2$] = [ZnCl$_2$] = 1.0 × 10^{-2} M; [TCAA] = 1.0 × 10^{-1} M; [Et$_2$O] = 9.2 × 10^{-2} M and 7.7 × 10^{-2} M for ZnBr$_2$ and ZnCl$_2$, Respectively

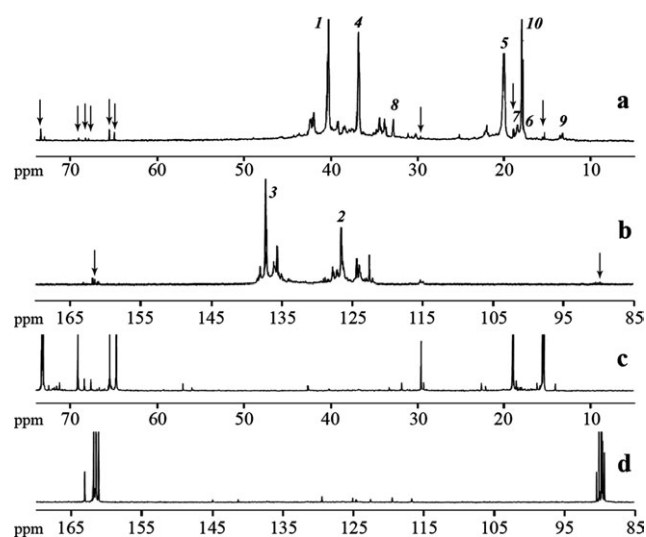| Lewis acid	Temperature (°C)	Conversion (%)	$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	M_w/M_n
ZnBr$_2$	60	32.8	1.5	2.7	1.8
		63.3	1.5	2.8	1.9
		73.6	1.4	2.7	1.9
		87.2	1.4	2.6	1.9
	20	24.5	1.9	3.6	1.9
		39.7	1.8	3.4	1.9
		51.8	1.7	3.6	2.1
		84.1	1.9	3.7	2.0
		85.8[a]	2.1	4.2	2.0
	−15	10.5	2.0	3.9	2.0
		47.4	2.1	4.2	2.0
		57.3	2.1	4.4	2.1
		66.7	2.0	4.4	2.2
	−78	2.0	<0.5	–	–
ZnCl$_2$	60	22.5	1.5	2.8	1.9
		43.4	1.4	2.8	2.0
		65.1	1.4	2.7	1.9
		84.7	1.5	2.8	1.9
	−15	12.4	2.3	4.1	1.8
		25.0	2.5	4.2	1.7
		34.1	2.3	4.2	1.8
		41.3	2.2	4.4	2.0

[a][C$_5$H$_8$] = 4.0 M.

Figure 3. ^{13}C NMR spectra of poly(1,3-pentadiene)s (a, b) and low molecular weight product (c, d) obtained with the TCAA/ZnBr$_2$ initiating system in CH$_2$Cl$_2$ at -15 and -78°C, respectively: [C$_5$H$_8$] = 2.0M; [ZnBr$_2$] = 1.0 $\times$ 10^{-2}M; [TCAA] = 1.0 $\times$ 10^{-1}M; [Et$_2$O] = 9.2 $\times$ 10^{-2}M.

The characteristic resonances of carbon atoms of this structure appeared at 20.0 ppm (5), 36.8 ppm (4), 40.3 ppm (1), 126.5 ppm (2) and 137.3 ppm (3) (see spectra (a) and (b) in Figure 3) that is in good agreement with the assignment made in Ref. 24 The signals of carbon atoms of methyl groups of *trans*-1,4-units with inverse tail-to-tail addition of monomer unit were detected at 17.6 and 18.5 ppm (signals 6, 7, Figure 3), for *meso*- and *racemic*-configurations of polymer chain, respectively,[24] while the signal at 32.9 ppm (signal 8, Figure 3) was attributed to methylene carbon atoms of *trans*-1,4-units with inverse head-to-head enchainment:
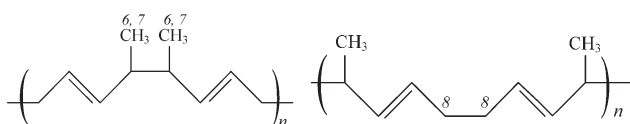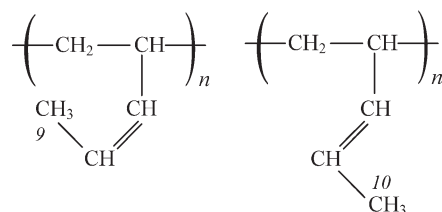

In addition, the signals of methyl carbon atoms of 1,2-*cis* (13.3 ppm, signal 9) and 1,2-*trans* (17.9 ppm, signal 10) were also detected in ^{13}C NMR spectrum of polymer [see Figure 3(a)]:

Besides, a set of new minor signals (see arrows in spectra (a) and (b) in Figure 3), which were not observed earlier in the polymers obtained with titanium halides[24] or VOCl$_3$,[21] was detected in ^{13}C NMR spectra of synthesized poly(1,3-pentadiene)s. As we can see from Figure 3 (spectra (c) and (d)) these signals corresponded to the low molecular weight product synthesized at -78°C.

Taking into account a careful purification of obtained polymers from traces of catalyst by column chromatography, one can be supposed that this by-product is adduct of monomer, TCAA and diethyl ether. Because the amount of this low molecular weight by-product did not exceed 2 mol %, we did not consider it due to the calculation of microstructure of unsaturated part of polymer chain. As it can be seen from Table V, the relative content of structural units in the poly(1,3-pentadiene)s prepared using zinc halides as coinitiators did not depend on the nature of zinc halide, reaction temperature, and monomer conversion. The microstructure of poly(1,3-pentadiene)s synthesized in the presence of zinc halides does not differ from one polymers obtained with titanium halides[2,24] or VOCl$_3$[21] as coinitiator. In other words, the microstructure of cationic poly(1,3-pentadiene)s does not depend on the nature of Lewis acid used in the polymerization.

DISCUSSION

To demonstrate the efficiency of new ZnX$_2$-based initiating system in the cationic polymerization of 1,3-pentadiene, a compar-

Table V. The Dependence of Unsaturation (H_H) and Microstructure of Poly(1,3-pentadiene)s Obtained with TCAA/ZnX$_2$ (ZnX$_2$ = ZnCl$_2$ and ZnBr$_2$) Initiating System on the Lewis Acid, Temperature, and Monomer Conversion: [C$_5$H$_8$] = 2.0M; [ZnBr$_2$] = [ZnCl$_2$] = 1.0 $\times$ 10^{-2} M; [TCAA] = 1.0 $\times$ 10^{-1} M; [Et$_2$O] = 9.2 $\times$ 10^{-2} M, and 7.7 $\times$ 10^{-2} M for ZnBr$_2$ and ZnCl$_2$, Respectively

ZnX$_2$	Temperature (°C)	Conversion (%)	H_H[a] (%)	Trans-1,4-units (%)			Trans-1,2-units (%)	Cis-1,2-units (%)
				Regular	Inverse	1,4(1,2)-[b]		
ZnBr$_2$	-15	57.3	84	48	10	11	24	7
	20	24.5	82	47	9	11	26	7
		51.8	80	47	11	10	26	6
		71.2	80	46	11	11	26	6
	40	58.4	77	47	10	11	26	6
	60	63.3	74	46	11	11	27	6
ZnCl$_2$	-15	41.3	83	48	9	11	25	7
	20	56.0	73	46	10	11	27	6

[a]Determined by ^{1}H NMR spectroscopy, [b]Trans-1,4-units connected with 1.2-units.

Table VI. The Comparison of Activity of Various Lewis Acids in the Cationic Polymerization of 1,3-Pentadiene in CH_2Cl_2 at 20°C

Lewis acid (mM)	[C_5H_8] (M)	Time (min)	Conversion (%)	IF^a (%)	$M_n \times 10^{-3b}$ (g mol^{-1})	M_w/M_n^b	Ref.
$ZnBr_2^c$ (15)	2.0	30	82.0	0	1.9	1.9	$_-^d$
		120	96.8	0	2.1	2.0	
$AlCl_3$ (23)	1.6	120	83.0	3.0	2.8	25.9	14
$FeCl_3^e$ (130)	2.0	30	81.0	27.0	2.0	9.3	16
$VOCl_3$ (15)	4.0	30	76.6	0	6.5	161.0	21
		120	88.0	31.6	3.0	50.8	
$TiCl_4^f$ (27)	9.6	1	13.2	0	3.5	218.8	1
		30	41.4	7.5	3.6	186.1	
		120	59.3	21.0	3.5	197.7	

[a]Insoluble fraction, [b]Determined for soluble fraction, [c]TCAA (150 mM) was used as initiator, [d]This work, [e]n-Hexane was used as solvent, [f]H_2O (10 mM) was used as initiator, polymerization was conducted in toluene at 50°C.

ative analysis with the results obtained with other (reported to date) catalyst was performed (see Table VI). First of all, TCAA/$ZnBr_2$ initiating system showed the same or even higher activity in the cationic polymerization of 1,3-pentadiene in comparison with the well-known initiating system based on $AlCl_3$, $TiCl_4$, $VOCl_3$, or $FeCl_3$: the relatively high monomer conversion was achieved after 30 min of polymerization. Other very important feature of the present initiating system is the possibility to synthesize desired low molecular weight poly(1,3-pentadiene)s with relatively narrow molecular weight distribution ($M_w/M_n \leq 2.0$) in the whole range of monomer conversions and polymerization conditions, in other words the obtained polymers do not contain any high molecular weight and insoluble fractions. Indeed, as we can see from Table VI, none of the known initiating systems allow to obtain fully soluble in common organic solvents poly(1,3-pentadiene)s with such narrow molecular weight distribution, especially at high monomer conversions. For example, IF in poly(1,3-pentadiene)s synthesized with $AlCl_3$ or $VOCl_3$ is appeared at high monomer conversions, while very broad MWD indicates the presence of HMWF. During the polymerization of 1,3-pentadiene using industrial $H_2O/TiCl_4$ initiating system HMWF is appeared even at the low monomer conversions (ca. 13%) that initially leads to the significant broadening of MWD ($M_w/M_n = 218.8$) and then to the appearance of IF (see Table VI).

It should be also noted that ZnX_2-based initiating systems allowed to synthesize fully soluble poly(1,3-pentadiene)s with low polydispersity ($M_w/M_n < 2.5$) even at low reaction temperatures (see Table IV for details), although it is known that probability of the formation of HMWF and IF is increased with decreasing reaction temperature.[2,19,21] In addition, it is very important from industrial point of view that ZnX_2-based initiating systems could be also used in such nonpolar solvents as toluene and n-hexane without any deleterious effects on the molecular weight and polydispersity (see Table III). Finally, it was also shown that even at higher monomer concentration ([M] = 4 M, see Table IV), the synthesized polymers are characterized by relatively narrow MWD and do not contain high molecular weight and insoluble fractions.

To summarize, ZnX_2-based initiating systems are characterized by several advantages over known catalysts used in the polymer-

ization of 1,3-pentadiene and could be a good alternative to currently used in industry $AlCl_3$- and $TiCl_4$-based initiating systems.

CONCLUSIONS

The new effective initiating systems for the cationic polymerization of 1,3-pentadiene based on zinc halides ($ZnBr_2$ and $ZnCl_2$) were proposed. The high polymerization rate is achieved by using of homogeneous (dissolved in a minimal amount of diethyl ether) zinc halides and hydrochloric acid, *tert*-butyl chloride and, especially, trichloroacetic acid as initiators. The unsaturation of obtained poly(1,3-pentadienes) was relatively high (74–84 mol %), does not depend on the monomer conversion and slightly increased with decreasing reaction temperature. The unsaturated part of polymer chain possesses predominantly 1,4-*trans* microstructure with regular and inverse addition of monomer units as well as significant amount of 1,2-*trans* isomer, while 1,2-*cis* isomer is present in a minor amount.

An interesting feature of zinc halide-based initiating system is the possibility to synthesize low molecular weight polymers of 1,3-pentadiene with relatively narrow molecular weight distribution and without high molecular weight and insoluble fractions in the whole range of monomer conversions. Practically, these catalytic system allows to synthesize fully soluble in common organic solvents poly(1,3-pentadiene)s without necessity to use special molecular weight regulators.

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