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V. A. Rozentsvet^a; V. G. Kozlov^a; E. F. Ziganshina^a; N. P. Boreiko^a

^a Institute of Ecology of Volga River Basin, Russian Academy of Sciences, Togliatti, Russia

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Molecular Heterogeneity of Cationic Polyisoprene

V. A. Rozentsvet, V. G. Kozlov,
E. F. Ziganshina, and N. P. Boreiko

Institute of Ecology of Volga River Basin,
Russian Academy of Sciences, Togliatti, Russia

Abstract: The effect of polymerization conditions on the molecular parameters and unsaturation of cationic polyisoprene synthesized with the $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ -trichloroacetic acid catalytic system has been studied. It has been shown that regardless of the initial monomer concentration, formation of the high-molecular-mass fraction in the polymer was observed when the first characteristic (threshold) concentration of the polymer was achieved. Further transformation of this fraction into the insoluble fraction took place when the second characteristic concentration of the polymer was achieved. The level of threshold concentrations of the polymer was determined by the component ratio in the catalytic system and the temperature of polymerization.

Keywords: Branched fraction; Cationic polymerization; ^{13}C NMR; Insoluble fraction; Isoprene; Microstructure

INTRODUCTION

Poly(1,3-dienes) prepared by cationic polymerization are characterized by reduced unsaturation and, in many cases, by the presence of branched and cross-linked structures.^[1–6] In the synthesis of cationic

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Correspondence: Victor A. Rozentsvet, Institute of Ecology of Volga River Basin, Russian Academy of Sciences, ul. Komzina 10, Togliatti 445003 Russia.
E-mail: rozentsvet@mail.ru

poly(1,3-dienes), the control of the molecular heterogeneity is a complex problem.

In Audisio et al.^[7] and Priola et al.^[8] the cationic polymerization of isoprene was catalyzed by equimolar complexes of BF_3 with H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{COOH}$, or H_3PO_4 . The resulting polyisoprene was characterized by low number-average molecular mass and reduced unsaturation. The latter was explained in these studies by the formation of cyclic structures in polymer chains during polymerization. This fact was suggestive of a complex mechanism governing the formation of molecular heterogeneity of the polymer.

The goal of this work was to study the effect of polymerization conditions on the molecular heterogeneity of cationic polyisoprene synthesized with the $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ -trichloroacetic acid (TCAA) catalytic system.

EXPERIMENTAL SECTION

Isoprene purchased from ZAO Togliattikauchuk had the following composition (wt.%): isoprene, 99.4; 2-methyl-2-butene, 0.3; 2-methyl-1-butene, 0.2; and 3-methyl-1-butene, 0.1. Before experiments, isoprene was washed with water, dried on NaX molecular sieves, and distilled over CaH_2 in argon flow. The content of microadmixture in isoprene was (wt.%): water, less than 1×10^{-3} ; cyclopentadiene, 1×10^{-4} ; dimethoxymethane, 5×10^{-4} ; carbonyl compounds (calculated with respect to acetone), 2×10^{-3} ; and acetylenic compounds, 1×10^{-3} . Methylene chloride (Fluka) used as a solvent was distilled over CaH_2 in argon flow. TCAA (Fluka) and $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (Fluka) were used as received.

Polymerization was carried out in glass ampoules that were heated under high vacuum in purified argon medium before experiments. The catalytic complex was prepared separately in a glass ampoule by mixing desired amounts of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and TCAA solutions.

The catalyst was deactivated by addition of propylene oxide and methanol mixture (1:1, vol.). The polymer was isolated by distillation of the solvent and unreacted monomer from the ampoules under vacuum at 40°C.

It is important to note that, due to a high initial rate of the cationic isoprene polymerization, it is necessary to maintain isothermal conditions, especially at the initial stage. In this work, temperature variations during the whole polymerization process did not exceed 1°–2°C. This was assured by decreasing the general volume in the ampoules down to 0.5–1 mL and a high stirring speed. Monomer conversion reproducibility in the kinetic experiments was ± 2 rel.%.

The content of the insoluble fraction in the polymer was determined by Soxhlet extraction in boiling toluene for 24 h. The soluble part of the polymer (soluble fraction) was separated from the insoluble fraction in a centrifuge using a polymer solution in hexane. The molecular parameters of the polymer soluble fraction were measured at 30°C using a Waters-Alliance GPC V-2000 liquid chromatograph equipped with two detectors (viscometer and refractometer) and a set of Styrogel columns having pore sizes of 500 (HR-2), 10^3 (HR-3), 10^4 (HR-4), and 10^6 (HR-6) Å. Toluene was used as an eluent; the rate of elution was 1 mL/min.

Polymer unsaturation and polyisoprene microstructure were determined by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy using a Bruker AM-500 spectrometer operated at 500 and 125 MHz frequencies, respectively. Before spectroscopic analyses, the residual catalyst was removed from all polymer samples by means of column chromatography using Fluka Silica gel 60 with particle sizes from 0.063 to 0.2 mm. Polymer unsaturation was calculated from ^{13}C NMR spectra by comparing the intensities of signals due to olefin and aliphatic carbons. The microstructure of polyisoprene was calculated using olefinic regions of ^1H and ^{13}C NMR spectra as described by Rozentsvet et al.^[9]

RESULTS AND DISCUSSION

The molecular parameters of polyisoprene were significantly affected by the initial concentration of the isoprene and its conversion (Table I).

It was found that, regardless of the initial monomer concentration, average molecular mass and polydispersity increase with the duration of the process. At monomer concentrations of 1.0 and 2.0 mol/L, number-average (M_n) and weight-average (M_w) molecular masses and polydispersity (M_w/M_n) of the polymer evenly increase up to high conversions of isoprene (Table I). At an initial monomer concentration of 4.0 mol/L and a conversion of 94.8%, the values of M_w and polydispersity grow appreciably, whereas the values of M_n remain practically invariable. At initial monomer concentrations of 6.0 and 8.0 mol/L, a similar jump in M_w and polydispersity was observed at conversions of 66.4 and 49.9%, respectively. Moreover, at monomer concentrations of 6.0 and 8.0 mol/L, the insoluble fraction formed at conversions of 97.4 and 77.5%, respectively. The above data indicate that with an increase in the initial monomer concentration, a jumpwise rise in M_w and formation of insoluble fraction (IF) were observed at a lower conversion. The concentration of the polymer, calculated per monomer unit of polyisoprene, at which a jumpwise rise in M_w and M_w/M_n took place was calculated from the data in Table I. Regardless of the initial concentration of isoprene in the system, the calculated concentration

Table I. Conversion of isoprene, content of the insoluble fraction (IF), and parameters of the soluble fraction (SF) of polyisoprene as a function of the time of polymerization at various initial monomer concentrations

[C ₅ H ₈] ₀ , mol/L	Time, min	Conversion, wt. %	Molecular parameters of SF		
			$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
1.0	0.5	32.9	0.6	1.9	3.2
	5.0	70.4	0.7	2.3	3.3
	30.0	92.8	0.8	2.8	3.5
2.0	0.5	25.8	0.8	2.5	3.1
	5.0	46.5	0.8	2.8	3.5
	30.0	71.4	0.9	3.0	3.3
	300.0	94.3	1.0	3.9	3.9
4.0	0.5	18.0	0.8	2.3	2.9
	5.0	27.9	0.8	2.6	3.3
	120.0	65.2	1.0	4.1	4.1
	300.0	72.0	1.2	5.3	4.4
	720.0	94.8	1.6	13.6	8.5
	1440.0	99.6	2.1	27.0	12.9
	6.0	0.5	12.2	1.0	3.4
6.0	30.0	40.6	1.3	5.9	4.5
	90.0	52.2	1.5	7.9	5.2
	300.0	66.4	1.9	16.0	8.4
	1440.0	97.4 ^a	90.5	3.4	26.8
8.0	0.5	5.9	0.9	2.9	3.2
	30.0	21.0	1.1	3.7	3.4
	480.0	49.9	1.5	10.8	7.2
	1440.0	59.8	2.0	42.6	21.3
	4320.0	77.5 ^b	2.3	102.3	44.5

Conditions: 20°C, [BF₃ · O(C₂H₅)₂] = 1.5 × 10⁻², [TCAA] = 7.5 × 10⁻² mol/L, methylene chloride.

^aContent of IF in the polymer is 39.7 wt. %.

^bContent of IF in the polymer is 20.2 wt. %; in other samples, the IF is absent.

of the polymer proved to be in the range 3.8–4.0 mol/L. At initial monomer concentrations of 1.0 and 2.0 mol/L, such polymer concentration is unattainable in the system even at 100% conversion; as a result, no jumpwise increase in M_w and M_w/M_n was observed. On the basis of the results in Table I, polymer concentration corresponding to the onset of formation of the insoluble fraction was also calculated. Regardless of the initial concentration of the monomer, the polymer concentration was at a level of 5.9–6.0 mol/L.

Figure 1 shows the size exclusion chromatography (SEC) chromatograms of polyisoprene prepared at an initial monomer concentration

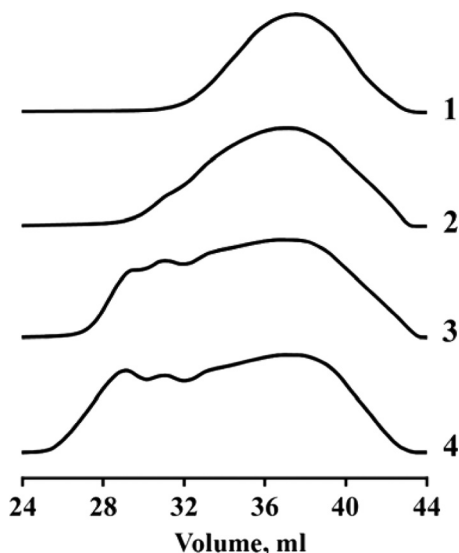


Figure 1. SEC chromatograms of polyisoprene synthesized at monomer conversions of (1) 21.0 wt.%, (2) 49.9 wt.%, (3) 59.8 wt.%, and (4) 77.5 wt.%. Conditions: 20°C, $[C_5H_8] = 8.0$, $[BF_3 \cdot O(C_2H_5)_2] = 1.5 \times 10^{-2}$, and $[TCAA] = 7.5 \times 10^{-2}$ mol/L, methylene chloride.

of 8.0 mol/L and various monomer conversions. At a conversion of 21.0%, the polymer was characterized by monomodal distribution. When the conversion increased to 49.9%, a new fraction appeared in the high-molecular-mass region of the chromatogram. With the increasing monomer conversion, the content of the high-molecular-mass fraction (HMF) in the polymer became more noticeable. In accordance with Rozentsvet and Kozlov^[10] and Rozentsvet et al.,^[11] the formation of HMF in the cationic polymerization of 1,3-dienes is associated with the appearance of branched structures due to chain transfer to the polymer. Upon further increase in monomer conversion, the polymer concentration in the system increased, while the rate of polymerization decreased, and, accordingly, the probability of chain termination on the polymer became higher. Eventually, this effect was responsible for formation of the insoluble fraction.

As the content of TCAA in the system increased, while the content of $BF_3 \cdot O(C_2H_5)_2$ remained invariable, a certain reduction in average molecular masses and polydispersity took place, provided other conditions were the same (Table II). Moreover, the conversions of the monomer corresponding to an abrupt change in the values of M_w and polydispersity of the polymer decreased. The character

Table II. Molecular parameters of polyisoprene as a function of monomer conversion at various TCAA : $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (mol/mol) ratios in the catalytic system

TCAA: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$	Conversion, wt. %	Molecular parameters		
		$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
0	5.9	0.9	2.0	2.2
	31.0	1.1	3.3	3.0
	57.6	1.4	7.1	5.1
	65.2	2.1	18.4	8.8
	92.2	2.8	357.8	127.8
1.0	11.4	0.8	2.3	2.9
	29.5	1.0	3.0	3.0
	55.0	1.2	5.7	4.8
	79.7	1.9	17.5	9.2
	99.2	2.5	96.7	38.7
10.0	28.1	0.9	2.8	3.1
	39.9	0.9	2.8	3.1
	64.3	1.0	3.3	3.3
	80.4	1.4	6.4	4.6
	99.8	1.7	14.4	8.5

Conditions: 20°C , $[\text{C}_5\text{H}_8] = 4.0$, $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2] = 1.5 \times 10^{-2}$ mol/L, methylene chloride.

of the change in molecular characteristics with the increasing ratio TCAA/ $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ in the catalytic system leads us to propose that TCAA is involved in the reactions of chain transfer.

Table III lists the molecular characteristics of polyisoprene synthesized at various polymerization temperatures. As the temperature was lowered, higher average molecular masses were achieved at similar monomer conversions. Moreover, at a temperature of -70°C , the HMF formed at the lowest monomer conversion (22%). It should be noted that, at this temperature (-70°C), the rate of polymerization was the lowest; therefore, even after 20 days, conversions higher than 26.3% were not achieved. As the temperature was increased to -20°C , conversion at which the HMF formed increased to 48.8%. Continuation of polymerization at a given temperature resulted in formation of the IF at a monomer conversion of 57.5%. Further increase in isoprene conversion at which high-molecular-mass and insoluble fractions (45.5 and 99.2%, respectively) formed was observed at a polymerization temperature of 20°C . At this temperature, formation of the IF took place at an almost maximally possible monomer conversion; therefore, in the

Table III. Content of IF and molecular parameters of SF of polyisoprene as a function of monomer conversion at various temperatures of polymerization

Temperature, °C	Conversion, wt.%	Molecular parameters		
		$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
-70	13.1	4.2	19.6	4.7
	18.2	4.5	27.3	6.1
	23.7	4.9	123.8	25.3
	26.3	5.0	173.2	34.6
-20	16.7	1.9	6.1	3.2
	25.1	2.2	9.7	4.4
	36.2	2.4	18.0	7.5
	52.4	2.7	206.1	76.3
	58.0 ^a	2.3	25.4	11.0
20	23.1	1.2	3.3	2.8
	39.4	2.7	10.3	3.8
	72.6	2.8	314.1	112.2
	98.1 ^b	1.7	10.7	6.3
	99.9 ^c	1.5	9.9	6.6
40	25.4	1.3	4.1	3.1
	49.9	1.6	5.1	3.2
	66.3	1.8	8.3	4.6
	77.1	1.9	11.7	6.2
	94.5	2.3	30.0	13.0

Conditions: 20°C, $[\text{C}_5\text{H}_8] = 8.0$, $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2] = 3.0 \times 10^{-2}$ mol/L, TCAA/ $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 = 5.0$.

^aContent of IF in the polymer is 10.2 wt.%.

^bContent of IF in the polymer is 50.6 wt.%.

^cContent of IF in the polymer is 60.7 wt.%; in other samples, the IF is absent.

polymerization of isoprene at 40°C, no insoluble fraction formed even at full conversion of the monomer. However, at 40°C, the formation of the HMF in the polymer was observed at a conversion of 77.1% (Table III). The inconsistency between monomer conversions at which HMF and IF formed at the same monomer concentration (8.0 mol/L) and at a temperature of 20°C (Tables I and III) can be explained by the fact that in the latter case, the concentration of the catalyst was higher by a factor of 2. Accordingly, the content of TCAA in the system increased and, as a result, the polymer concentration at which HMF and IF formed became higher. This was additional evidence that TCAA served as a chain transfer agent.

An increase in molecular mass with the decreasing polymerization temperature suggested a reduction in the role of chain transfer processes.

On the other hand, with the decreasing temperature, branched and cross-linked structures formed in the system at a lower concentration of the polymer. This can be associated with a relative change in the probability of chain transfer to the polymer compared to the corresponding chain transfer to other agents. This may cause a change in the type and character of branching, for example, in the number of branching junctions.^[12]

Figure 2 shows the ^{13}C NMR spectra of polyisoprene prepared in the temperature range from -70° to 20°C . In the aliphatic part of the spectra (Figure 2(a)), a dominant signal due to methyl carbons of 1,4-trans units of regular head-to-tail addition was observed at 16.0 ppm. In addition, minor signals due to methyl carbons of 1,2-units were detected at 18.8 ppm and signals due to 3,4-units were observed at

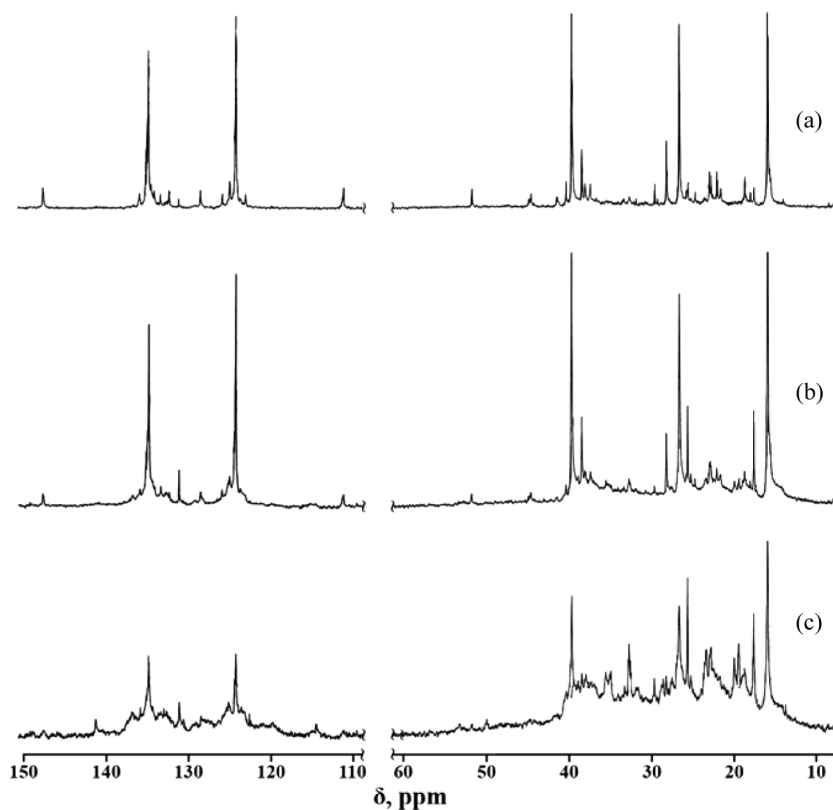


Figure 2. ^{13}C NMR spectra of cationic polyisoprenes synthesized at temperatures of (a) -70° , (b) -20° , and (c) 20°C .

22.1 ppm. The signal of the methylene carbon at 28.3 ppm corresponded to the inverse addition of 1,4-trans units according to the tail-to-tail type, while the signal at 38.5 ppm was assigned to the head-to-head addition. The contents of structural units, which were calculated as described in Rozentsvet et al.,^[9] were as follows: 68 mol% of 1,4-trans units of regular addition, 21 mol% of 1,4-trans units of inverse addition, 6 mol% of 3,4-units, and 5 mol% of 1,2-units. The unsaturation of polyisoprene synthesized at -70°C was 92 mol%; at -20°C , 72 mol%; and at 20°C , 55 mol% of the theoretical value. For polymers synthesized at -20°C and 20°C , characteristic signals were situated on the so-called pedestals. This complicated the correct calculation of the microstructure of the concerned samples of polyisoprene. With an increase in the temperature of polymerization, the level of pedestals in the spectra of polyisoprene increased. This phenomenon is usually explained by the presence of branched structures in polymers.^[13] It is suggested that such a character of evolution in the spectra indicated that the number of branching junctions increased with the temperature of polymerization. Accordingly, with a decrease in the temperature of polymerization, a gain in the molecular mass of branches in branched macromolecules was observed. Eventually, this was the reason for the appearance of a high-molecular-mass fraction at lower concentrations of the polymer in the system with decreasing polymerization temperature.

CONCLUSION

The above data give us grounds to make the following conclusions. In the cationic polymerization of isoprene carried out in the presence of the $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ -TCAA catalytic system, branched and cross-linked structures appear at strictly defined concentrations of the polymer in the system. The level of these concentrations is determined by the ratio of components in the catalytic system and the temperature of polymerization. With increase in the content of TCAA in the system and in the temperature of polymerization, the concentration of the polymer at which branched and cross-linked structures form tends to increase. At the lower temperature of polymerization, the overall unsaturation of the cationic polyisoprene becomes higher. This is apparently associated with a reduction in the number of branching junctions and an increase in the molecular mass of branches in branched macromolecules. The above-described relationships make it possible to select synthesis conditions for the cationic polymerization of isoprene that ensure production of the polymer with desired molecular parameters and free of the undesirable insoluble fraction.

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