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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Cationic Polyisoprene: Synthesis, Structure, and Some Properties

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Abstract—The effect of the catalyst composition and temperature on the cationic polymerization of isoprene in the presence of the catalytic system $TiCl_4$–trichloroacetic acid was examined. The molecular heterogeneity, microstructure, and some properties of the resulting cationic polymer were determined.

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Cationic polymerization of isoprene under the action of various Lewis acids yields, as a rule, cross-linked polymers insoluble in organic solvents [1–5]. In the initial step, the polymerization rate is the highest, which is followed by a period in which the reaction practically ceases [2, 3]. The use of aromatic solvents in isoprene polymerization results in a considerable decrease in the molecular weight of the polymer due to the chain-terminating effect of the solvent. The final yield of polyisoprene remains low [2–4].

At the same time, cationic polyisoprene can find wide use in paint-and-varnish industry as a film-forming polymer, and also as an effective plasticizer for rubber stocks in tire production [6]. Therefore, search for efficient procedures for preparing polyisoprene with the required molecular characteristics is an important problem.

In this study we examined cationic polymerization of isoprene on the catalytic system $TiCl_4$–trichloroacetic acid (TCAA), regular trends in variation of molecular characteristics of the resulting polyisoprene, and its microstructure and properties. The procedure that we suggest for preparing cationic polyisoprene allows synthesis of the polymers with the required molecular parameters in a high yield.

EXPERIMENTAL

In our study we used polyisoprene produced by the Tol'yattikauchuk Private Company, of 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. Prior to polymerization, isoprene was washed with water, dried over NaX zeolites, and distilled from CaH_2 in an argon flow. The content of microimpurities in the isoprene, determined according to TU (Technical Specification) 38.103659–88, was as follows (wt %): water $<1 \times 10^{-3}$, cyclopentadiene 1×10^{-4}, dimethoxymethane 5×10^{-4}, carbonyl compounds (counting on acetone) 2×10^{-3}, and acetylenic compounds 1×10^{-3}.

The procedures for polymerization and purification of solvents (methylene chloride, toluene) and catalyst components are described in [7, 8].

The molecular parameters of the soluble (sol) fraction of the polymer were determined with a Waters-Alliance GPCV-2000 liquid chromatograph equipped with three Styrogel columns: HR-2, HR-4, and HR-6. The eluent was toluene, and elution rate, 1 ml min^{-1}. The microstructure of polyisoprene was analyzed by IR and NMR spectroscopy using Bruker Vector-33 and Bruker AM-500 spectrometers, respectively [7]. The onset temperature of the polymer degradation was determined with a Setaram thermal analyzer at a heating rate of 15 deg min^{-1}.

Polymerization of isoprene under the action of $TiCl_4$ without TCAA addition is slow (Fig. 1, curve *1*), in agreement with published data [2, 3]. Introduction of TCAA as a proton donor into the catalytic complex leads to appreciable acceleration of the polymerization (Fig. 1, curves *2*–*5*). The reaction rate is the highest in the initial step. Then, as the monomer is exhausted, the polymerization rate noticeably decreases, but the process does not cease fully, so that a high monomer conversion can be attained. Substantial activation of the process on adding TCAA to the catalyst is apparently associated

Monomer conversion, GF content, and molecular parameters of SF of the polymer at various temperatures and times of the polymerization. Conditions: –20°C, $[TiCl_4] = 0.005$, [TCAA] = 0.01, and $[C_5H_8] = 2.0$ M; solvent CH_2Cl_2

T, °C	τ, min	Isoprene conversion, wt %	GF content, wt %	Molecular parameters of SF		
				$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
+20	0.25	21.3	0	2.2	6.2	2.8
	5.00	33.8	0	3.4	10.9	3.2
	60.00	48.4	0	4.8	21.1	4.4
	240.00	60.3	0	5.3	64.6	12.2
	480.00	78.9	0	5.4	217.6	40.3
	1440.00	98.2	1.9	4.9	158.2	32.3
–20	0.25	24.5	0	4.1	16.0	3.9
	1.00	30.9	0	5.1	23.0	4.5
	5.00	35.0	0	5.5	29.2	5.3
	15.00	42.4	0	6.7	71.4	10.7
	180.00	55.5	0	7.7	606.4	78.4
	1440.00	77.1	54.0	4.8	162.7	33.9
–70	0.15	19.6	0	8.4	98.7	11.8
	2.00	32.9	0	10.9	157.0	14.4
	5.00	35.8	0	14.4	233.0	16.2
	10.00	37.5	0	16.2	348.3	21.5
	30.00	41.4	20.3	8.2	102.4	12.5
	1440.00	53.4	91.4	6.0	21.3	3.6

with an increase both in the concentration of active polymerization centers and in their stability.

The dependences of the content of the gel fraction (GF) and molecular parameters of the sol fraction (SF) of polyisoprene on the reaction temperature and monomer conversion are given in the table. The trends we observed are largely similar to those described previously for cationic polymerization of 1,3-pentadiene [8, 9].

At 20°C, in the initial period, the number-average (M_n) and weight-average (M_w) molecular weights

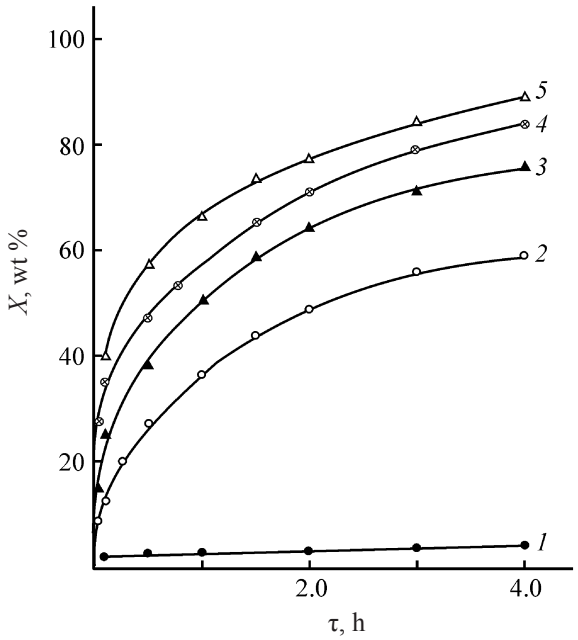

Fig. 1. Isoprene conversion *X* as a function of polymerization time τ. TCAA concentration, M: (*1*) 0, (*2*) 0.005, (*3*) 0.010, (*4*) 0.020, and (*5*) 0.040. Polymerization conditions: 20°C, $[TiCl_4] = 0.01$, $[C_5H_8] = 4.0$ M; solvent toluene.

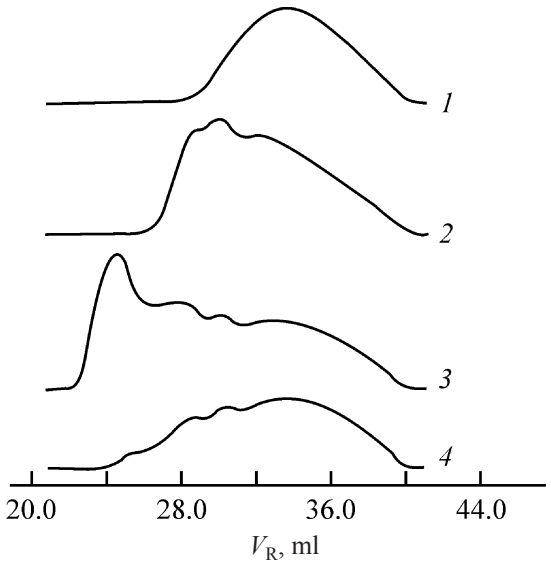

Fig. 2. Chromatograms of polyisoprene obtained at isoprene conversion of (*1*) 24.5, (*2*) 42.4, (*3*) 55.5, and (*4*) 77.1 wt %. Polymerization conditions: –20°C, $[TiCl_4] = 0.005$, [TCAA] = 0.01, and $[C_5H_8] = 2.0$ M; solvent CH_2Cl_2; the same for Fig. 3. (V_R) Retention volume.

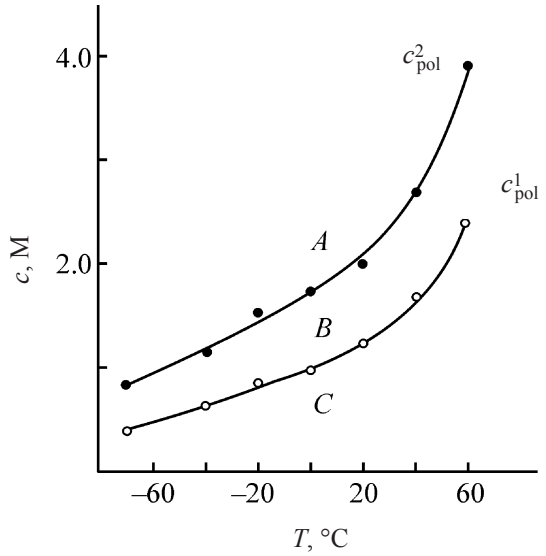

Fig. 3. First (c^1_{pol}) and second (c^2_{pol}) threshold concentrations of the polymer as functions of the polymerization temperature T. (c) Polyisoprene concentration counting on monomeric units.

and the polydispersity index (M_w/M_n) of the polymer somewhat increase with increasing process time. At a monomer conversion of 60.3 wt %, M_w and M_w/M_n increase considerably, which is due to appearance of a high-molecular-weight branched fraction (HBF) in the polymer [8]. At 98.9 wt % conversion of the monomer, the GF is formed, and the average molecular weights and polydispersity of SF decrease.

Figure 2 shows how the characteristics of the molecular-weight-distribution (MWD) of the polymer vary with increasing conversion at a polymerization temperature of –20°C. At 24.5 wt % conversion, the polymer still has a unimodal MWD (Fig. 2, curve *1*), but at 42.4 wt % conversion the formation of HBF is clearly manifested in the MWD curve (Fig. 2, curve *2*). The molecular-weight distribution of polyisoprene becomes polymodal. With an increase in the monomer conversion, the HBF content in the polymer increases until GF appears (Fig. 2, curve *3*), after which the average molecular weights and polydispersity decrease (curve *4*) owing to cross-linking of HBF macromolecules to form GF.

When the polymerization is performed at –70°C, HBF appears already at 19.6 wt % conversion, and GF starts to form at 41.4 wt % conversion (see table).

Thus, HBF and GF are formed at all the examined temperatures, and with decreasing polymerization temperature the degree of conversion at which HBF and GF start to form clearly decreases (see table). Hereinafter, the polymer concentration in the reaction mixture at which HBF starts to form is conventionally denoted as the "first threshold concentration of the polymer," c^1_{pol}. Correspondingly, the polymer concentration at which GF starts to form is conventionally denoted as the "second threshold concentration of the polymer," c^2_{pol}. Knowing the initial concentration and conversion of the monomer, we can readily calculate c^1_{pol} and c^2_{pol}. For example, at 20°C, c^1_{pol} = 1.21 M and c^2_{pol} = 1.96 M (for convenience, the polymer concentration is given in terms of the monomeric units).

Figure 3 shows the temperature dependence of the first and second threshold concentrations of the polymer. The c^1_{pol} and c^2_{pol} values exceeding 2.0 M were obtained in additional experiments performed at a higher monomer concentration (4.0 and 6.0 M). It can be seen that, with increasing temperature, the threshold concentrations of the polymer increase. The whole field of the process conditions is divided in Fig. 3 in three fields: A, B, and C. When the polymerization is performed in field C (below c^2_{pol} curve), the forming polyisoprene will have a unimodal MWD and will not contain HBF and GF. The level of average molecular weights in field C can be controlled by varying the process temperature (see table). In field B (below c^2_{pol} but above c^1_{pol}), the forming polymer will contain HBF and have a polymodal MWD, but will not contain GF. The HBF content can be controlled by varying the process temperature. In field A, the forming polymer will always contain GF.

Figure 4 shows the IR spectrum of a polyisoprene sample obtained at –20°C, with unimodal MWD. Although the IR spectrum of cationic polyisoprene does not furnish quantitative information on the polymer microstructure, the presence of absorption bands at 887,

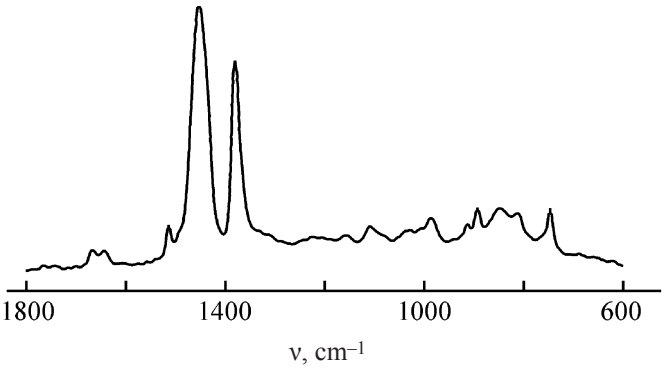

Fig. 4. IR spectrum of cationic polyisoprene. (ν) Wavenumber.

907, and 1153 cm^{-1} suggests the presence in polyisoprene of 3,4-, 1,2-, and 1,4-trans-units, respectively.

The ^1H and ^{13}C NMR spectra of this polyisoprene sample (Fig. 5) furnish more complete information on the content of structural fragments. In the "olefinic" part of the ^1H NMR spectrum, there are proton signals of methylene groups of the 3,4-unit at 4.6–4.8 ppm and 1,2-unit at 4.8–5.0 ppm, and of methine groups of the 1,4-unit at 5.0–5.2 ppm and 1,2-unit at 5.7–5.9 ppm (Fig. 5a). In the "aliphatic" part of the ^{13}C NMR spectrum, there is the major signal of the methyl carbon atom of the 1,4-*trans*-unit at 16.0 ppm and minor signals of methyl carbon atoms of the 3,4-unit at 18.8 ppm and 1,2-unit at 22.1 ppm (Fig. 5b). The signal of methyl carbon atoms of the 1,4-*cis*-unit (23.5 ppm) is absent. In the "olefinic" part of the ^{13}C NMR spectrum, there is a total signal of methylene carbon atoms of 1,2- and 3,4-units at 111.2 ppm, a signal of the methine carbon atom of the 1,4-*trans*-unit at 124.3 ppm, a signal of the quaternary carbon atom of the 1,4-trans-unit at 134.8 ppm, and a total signal of the methine carbon atom of the 1,2-unit and the quaternary carbon atom of the 3,4-unit at 147.7 ppm (Fig. 5c).

For quantitative calculation of the content of units in polyisoprene, we developed a new procedure. First, from the ^1H NMR spectrum we determined the ratio of the 1,2- and 3,4-units in the polymer. Then from the "olefinic" part of the ^{13}C NMR spectrum we calculated the content of the 1,4-*trans*-units and the total content of the 1,2- and 3,4-units. Knowing their ratio, we calculated the amount of each kind of units in the polymer. The following results were obtained (mol %): 1,4-*trans*-units 94, 1,2-units 3, and 3,4-units 3. It should be noted that these data concern only the unsaturated part of the polyisoprene chain. The total unsaturation of this polymer sample, evaluated from the ^{13}C NMR spectrum, is 51 mol % of the theoretical level.

Cationic polyisoprene synthesized by polymerization under the conditions of field C (Fig. 3) is a viscous colorless liquid with a density of 0.904 g cm^{-3} (20°C), n_D^{20} = 1.534. The polymer is completely soluble in aromatic and chlorinated solvents. In aliphatic solvents, it is completely soluble only at temperatures above 40°C. The polymer is insoluble in water, methanol, ethanol, and acetone. Cationic polyisoprene on glass plates forms hard and strong film coatings within the drying time of 12–16 h at 20 ± 5°C. The onset temperature of polyisoprene degradation is 280–300°C.

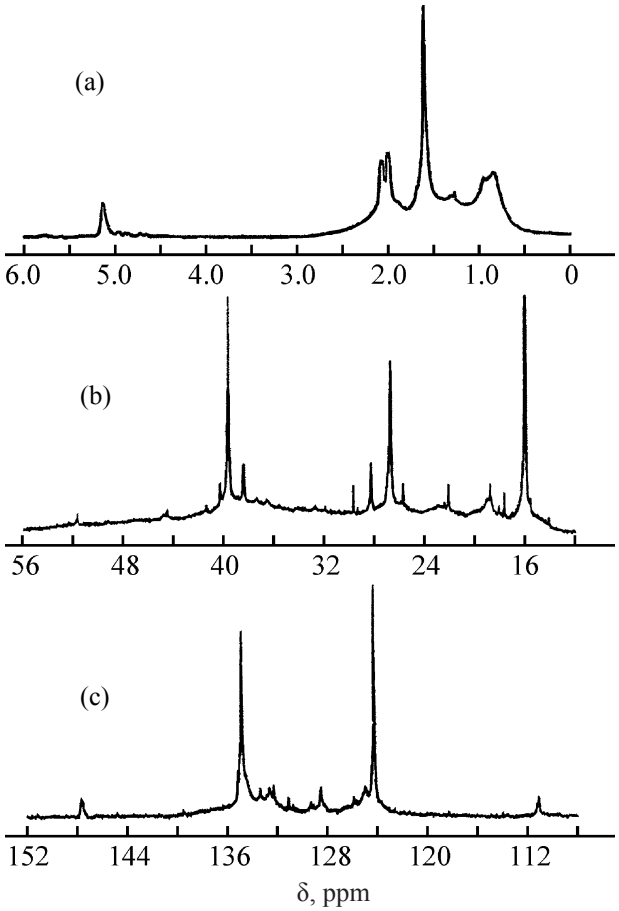

Fig. 5. (a) ^1H and (b, c) ^{13}C NMR spectra of cationic polyisoprene. (δ) Chemical shift. Carbon atoms: (b) aliphatic and (c) olefinic.

CONCLUSIONS

(1) Additions of trichloroacetic acid to the catalytic system based on $TiCl_4$ considerably activate the cationic polymerization of isoprene.

(2) With an increase in the monomer conversion, on reaching the threshold concentrations of the polymer in the reaction mixture c^1_{pol} and c^2_{pol}, the high-molecular-weight and gel fractions, respectively, appear in the polymer. With decreasing process temperature, c^1_{pol} and c^2_{pol} decrease.

(3) The unsaturated part of the polyisoprene chain contains 94 mol % 1,4-*trans*-units, 3 mol % 1,2-units, and 3 mol % 3,4-units.

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