Synthesis of environmentally friendly film-forming polymers based on 1,3-pentadiene

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Abstract. The use of traditional paints and varnishes containing organic solvents in their composition causes significant harm to human health and leads to environmental pollution. In this regard, an actual problem is the creation of new environmentally friendly paints and varnishes that are applied to the painted surface without the use of organic solvents. As a result of the research, a method has been developed for producing 1,3-pentadiene polymers, which can be used in the manufacture of thermoplastic paints for road marking. The method consists in carrying out the process of cationic polymerization of 1,3-pentadiene using a catalytic system based on ethylaluminum sesquichloride. It was found that the polymer chain of the synthesized poly-1,3-pentadiene consists mainly of 1,4-trans- and 1,2-trans-units and is characterized by reduced unsaturation. The introduction of a modifier, diisopropyl ether, into the catalytic system makes it possible to obtain completely soluble 1,3-pentadiene polymers with the required softening point temperature.

1. Introduction
Piperylene (1,3-pentadiene) is a large-scale by-product of petrochemistry, formed in the processes of cracking of hydrocarbons or isoprene production via isopentane dehydrogenation [1]. One of the methods for the utilization of 1,3-pentadiene is the polymerization of this monomer using cationic catalytic systems to obtain low molecular weight polymers, for example, oligopiperylene rubber of trade mark SKOP [1-3]. This low molecular weight rubber is used in the production of traditional paints and varnishes containing organic solvents. The use of such paints and varnishes leads to environmental pollution. Particularly dangerous for living organisms and humans are the emissions of aromatic hydrocarbons, such as toluene and xylene, which contained the variety of paint materials, for example, in paints for road marking [4, 5].

The aim of this study is to develop a method for obtaining new environmentally friendly thermoplastic polymer materials based on 1,3-pentadiene, which can be applied in road marking paint without the use of organic solvents.

To achieve this goal, it is necessary to solve the following tasks:
1) to develop methods for the production of poly-1,3-pentadiene, which make it possible to exclude the formation of a crosslinked insoluble fraction (IF) in the polymer;
2) to investigate the possibility of synthesis 1,3-pentadiene polymers with a softening point temperature in the range from 80 to 100°C, which is necessary for the production of thermoplastic paints for road marking.
2. Materials and Method
The 1,3-pentadiene produced by JSC Sintezkauchuk (Sterlitamak) had the following composition (%): trans-1,3-pentadiene - 61.2, cis-1,3-pentadiene - 35.9, cyclopentene - 1.8, 2- methyl-2-butene - 0.8; cyclopentadiene - 0.1, saturated hydrocarbons - 0.2. Before polymerization experiments, 1,3-pentadiene was washed with water, dried with NaX molecular sieves, and then distilled over CaH₂ in an argon flow.

Methylene chloride (CH₂Cl₂, Biosolve, 99.8%), 2-chloro-2-methylbutane ( tert-butyl chloride, Fluka, 99.5%) were distilled over CaH₂ in an argon flow. Diethyl ether (Fluka, 99.8%), methyl tert-butyl ether (Fluka, 99.5%) and diisopropyl ether (Fluka, 99.8%) were treated with KOH for 24 hours and distilled over CaH₂ in an argon flow. Titanium tetrachloride (Aldrich, 99.9%), diphenyl ether (Fluka, 99.9%) were used as received. Ethylaluminum sesquichloride (EASC, Al(C₂H₅)₃Cl, s) was obtained by mixing equimolar amounts of Al(C₂H₅)₃Cl (Aldrich, 99.5%) and Al(C₂H₅)Cl₂ (Aldrich, 99.0%).

The methods for preparing catalytic systems and carrying out of 1,3-pentadiene polymerization are described in [6, 7]. The content of insoluble fraction in poly-1,3-pentadiene was determined by Soxhlet extraction of polymer in toluene for 24 hours. The molecular characteristics of poly-1,3-pentadiene (M₆ and Mₘ are the number-average and weight-average molecular weights, respectively, Mₘ/M₆ is the polydispersity) were determined by gel permeation chromatography (GPC) on a Waters Alliance GPCV-2000 liquid chromatograph equipped with a refractometric and viscometer detectors and a set of four Waters styrogel columns with pore sizes of 500 (HR-2), 10⁴ (HR-3), 10⁵ (HR-4) and 10⁶ (HR-5) Å. Eluent - toluene, temperature 30°C, elution rate of 0.5 ml per minute. The calculation of molecular characteristics was based out on polystyrene standards Waters [8].

¹H and ¹³C NMR spectra of poly-1,3-pentadiene were recorded on a Bruker Avance III spectrometer with an operating frequency of 400.13 MHz at ¹H and 100.62 MHz at ¹³C, solvent CDCl₃. The number of acquisitions was 16 and 10500, the relaxation delay between pulses was 5 and 10 s, respectively for the ¹H and ¹³C NMR spectra. The Overhauser effect was minimized by recording ¹³C NMR spectra in the "inverse gate decoupling" mode. The softening point temperature (Tₛ) of 1,3-pentadiene polymers was determined by the "ring and ball" method according to GOST 11506-73.

3. Results and Discussion
A characteristic feature of the cationic polymerization of conjugated dienes is the occurrence of side reactions leading to the production of crosslinked insoluble polymers, which greatly complicates the practical use of such polymers. It is known that in the cationic polymerization of 1,3-pentadiene using catalytic systems based on titanium and vanadium chlorides, the formation of an insoluble fraction in the polymer is observed, as a rule, at high degrees of monomer conversion [1-3].

In this regard, at the first stage of the work, the possibility of modifying of the model catalytic system TiCl₄ – CF₃COOH by diethyl, methyl tert-butyl, diphenyl, and diisopropyl ether was investigated in order to regulate the molecular characteristics of the resulting polymer and eliminate the formation of an insoluble fraction in the poly-1,3-pentadiene (table 1).

As can be seen from the data in the table, the process of 1,3-pentadiene polymerization has a pronounced unsteady character. The highest polymerization rate is observed at the initial stage of the process. Thus, in the absence of a modifier in the system the monomer conversion is 51.5%, in 1 min of the process (table 1). That is, during this time, more than half of the initial 1,3-pentadiene is converted into a polymer. Practically complete conversion of the monomer (96.8%) is achieved only after 24 hours of the process.

As shown in our works [1, 6, 7, 9], a sharp decrease in the rate of cationic polymerization of 1,3-dienes with an increase in monomer conversion is explaining by the deactivation of a significant part of the active centers of polymerization during the process.

With an increase in the duration of the polymerization process, the values of average molecular weights of 1,3-pentadiene polymers increase (table 1).
Table 1. Results of polymerization of 1,3-pentadiene (1,3-PD) using the catalytic system TiCl₄ – CF₃COOH modified by ethers. Polymerization conditions: [C₅H₈] = 4.0 mol/l, [TiCl₄] = 1.0 \cdot 10^{-2} mol/l, CF₃COOH/TiCl₄ = 2.0, 20 °C, methylene chloride

| Ether   | Ether TiCl₄ (mol/mol) | Time (min) | Conversion 1,3-PD (%) | Content IF (%) | Molecular characteristics of the polymer |
|---------|----------------------|------------|-----------------------|---------------|-----------------------------------------|
|         |                      |            |                       |               | Mn \cdot 10^{-3} (g/mol) | M_w \cdot 10^{-3} (g/mol) | M_w/M_n |
| –       | 0                    | 1.0        | 51.5                  | 0             | 4.1 | 35.4 | 8.6 |
|         |                      | 5.0        | 61.6                  | 0             | 4.2 | 62.8 | 15.0 |
|         |                      | 30.0       | 72.1                  | 0             | 4.4 | 284.5 | 64.6 |
|         |                      | 240.0      | 89.8                  | 0             | 4.5 | 930.3 | 206.7 |
|         |                      | 1440.0     | 96.8                  | 46.4          |      |      |     |
| (C₂H₅)₂O | 1.0                 | 1440.0     | 45.2                  | 0             | 3.5 | 8.5 | 2.4 |
|         | 5.0                 | 1440.0     | 32.3                  | 0             | 2.5 | 5.4 | 2.2 |
|         | 10.0                | 1440.0     | 30.5                  | 0             | 2.7 | 5.1 | 1.9 |
|         | 1.0                 | 1440.0     | 74.1                  | 0             | 3.0 | 17.9 | 5.9 |
| (C₆H₅)₂O | 5.0                 | 1440.0     | 72.3                  | 0             | 3.3 | 16.8 | 5.1 |
|         | 10.0                | 1440.0     | 65.8                  | 0             | 3.5 | 12.9 | 3.7 |
|         | 1.0                 | 1440.0     | 95.2                  | 0             | 4.2 | 21.3 | 5.0 |
| (i-C₃H₇)₂O | 5.0                 | 1440.0     | 94.7                  | 0             | 4.0 | 16.6 | 4.2 |
|         | 10.0                | 1440.0     | 94.0                  | 0             | 3.1 | 8.5 | 2.7 |

At the same time, a significant increase in the values of the weight average molecular weights (M_w) and polydispersity (M_w/M_n) is observed, while the values of the number average molecular weights (M_n) increase insignificantly.

Figure 1 shows the GPC traces of 1,3-pentadiene polymers synthesized at various monomer conversions.

![Figure 1](image1.png)

Figure 1. GPC traces of poly-1,3-pentadiene synthesized at monomer conversion 51.5 (1), 61.6 (2), 72.1 (3), and 89.8 (4)%.

As can be seen from the data in figure 1, with an increase in the conversion of the monomer, the proportion of the high molecular weight fraction significantly increases in the composition of the
polymer. This explains the significant increase in the values of the weight average molecular weight and, accordingly, the polydispersity of the polymer. As shown in [1, 6, 7, 9], the appearance and increase in the proportion of the high-molecular fraction in the composition of polydiene in the course of cationic polymerization is associated with the occurrence of a side reaction of growing chain transfer to the double bond of the polydiene. This leads to a decrease in the unsaturation of the polymer, the formation of branched macromolecules, and in some cases a crosslinked insoluble fraction in the polymer. Indeed, when the monomer conversion is 96.8%, the IF content in the resulting poly-1,3-pentadiene is 46.4% (table 1).

The literature describes some methods for suppressing the formation of an insoluble fraction during the cationic polymerization of 1,3-dienes. One of the most effective methods is the modification of cationic catalytic systems with ethers [1, 3, 10, 11].

Indeed, as shown by the experiments carried out in this work, the introduction of diethyl or diphenyl ether into the TiCl$_4$ – CF$_3$COOH catalytic system makes it possible to exclude the formation of IF in the composition of the synthesized 1,3-pentadiene polymers (table 1). However, this significantly decreases the yield of the resulting polymer. Thus, at a molar ratio of diethyl ether to TiCl$_4$ equal to 1 to 1, the conversion of 1,3-pentadiene decreases from 96.8% to 45.2% in 24 hours of the process and at ratio of component equal to 10 to 1, respectively, – 30.5% (table 1). When diphenyl ether (DPO) is used at a molar ratio of DPO to TiCl$_4$ equal to 10 to 1, the monomer conversion decreases from 96.8% to 65.8%. When methyl tert-butyl ether (MTBE) was introduced into the TiCl$_4$ – CF$_3$COOH catalytic system in a molar ratio of MTBE to titanium tetrachloride in the range from 0.5 to 5.0, a significant decrease in the 1,3-pentadiene polymerization rate and polymer yield was also observed. In the case of modification of the TiCl$_4$ – CF$_3$COOH catalytic system with diisopropyl ether (DIPE), a slight decrease in the monomer conversion is observed (table 1). So, with a molar ratio of (i-C$_3$H$_7$)$_2$O to TiCl$_4$ equal to 1 to 1, the conversion of 1,3-pentadiene in 24 hours of the process decreases to 95.2%, and at a molar ratio of ether to titanium tetrachloride equal to 10 to 1, the polymer yield decreases to 94.0% (table 1). It is important to note that regardless of the content of diisopropyl ether in the catalyst, the resulting polymer does not contain IF in its composition, wherein with an increase in the content of ether in the system, the values of the average molecular weights and polydispersity of the polymer decrease (table 1).

Thus, the optimal results on the modification of the TiCl$_4$ – CF$_3$COOH catalytic system were obtained using diisopropyl ether. The introduction of this modifier makes it possible to completely exclude the formation of IF in the composition of the synthesized poly-1,3-pentadiene with a slight decrease in the polymer yield. It should be noted that the 1,3-pentadiene polymers synthesized under the conditions of table 1 have a low softening point temperature (T$_s$), ranging from 20 to 40 °C, which is apparently due to the relatively high unsaturation of the polymers. This does not allow the use of these 1,3-pentadiene polymers in the production of environmentally friendly thermoplastic paint materials.

In this regard, the polymerization of 1,3-pentadiene using the catalytic systems based on ethylaluminum sesquichloride (EASC) was investigated. As shown by preliminary experiments, the polymerization of 1,3-pentadiene in the presence of Al(C$_2$H$_5$)$_3$Cl$_{1.5}$ without the addition of modifiers leads to the formation of a crosslinked insoluble polymer even at the initial stages of the polymerization process. In the case of the introduction of tert-butyl chloride into the reaction mixture, the formation of an insoluble fraction in poly-1,3-pentadiene is observed at a monomer conversion of 88% and higher (table 2).

In order to exclude the side reaction of the formation of an insoluble fraction in the polymer, the Al(C$_2$H$_5$)$_3$Cl$_{1.5}$ - (CH$_3$)$_2$CCl catalytic system was modified by the addition of diisopropyl ether. At a molar ratio of diisopropyl ether to EASC equal to 1 to 1, the formation of an insoluble fraction in the polymer occurs at a 1,3-pentadiene conversion of 93.5% and higher (table 2).
A completely soluble polymer is formed only when the molar ratio of diisopropyl ether to ethylaluminum sesquichloride is 5 to 1 (Table 2). It should be noted that the introduction of such amount of ether into the system practically does not affect the activity of the catalytic system during the cationic polymerization of 1,3-pentadiene. Thus, in the absence of diisopropyl ether in the system, the monomer conversion in 2 hours of the process is 97.5%. In the case of the introduction of diisopropyl ether into the catalytic system at a molar ratio to EASC equal to 5 to 1, the conversion of 1,3-pentadiene in 2 hours of the process is at the level of 96.0% (Table 2).

The softening point temperature of the synthesized 1,3-pentadiene polymers increases with an increase in the monomer conversion from 84 to 101°C. According to the literature [2, 4], the required level of softening temperatures of thermoplastic polymers used in paints for road marking should be in the range from 80 to 100°C.

The structure of poly-1,3-pentadiene obtained on the catalytic system Al(C₂H₅)₃.Cl₁.₅ - (CH₃)₃Cl - (i-C₃H₅)₂O was studied based on the analysis of the ¹³C NMR spectrum of the polymer. Figure 2 shows the aliphatic and olefinic regions of the ¹³C NMR spectrum of the polymer.

Comparative analysis of the position of signals of carbon atoms in the studied spectrum and published data [12, 13] allows us to conclude that the unsaturated part of the polymer chain of poly-1,3-pentadiene consists mainly of 1,4-trans-units. Thus, intense signals with chemical shifts (δ) of 20.0, 36.8, 40.3, 126.5, and 137.2 ppm belong to the carbon atoms of the 1,4-trans-unit with regular "head-to-tail" addition of monomer units. In addition, the spectrum of poly-1,3-pentadiene contains signals of carbon atoms of 1,4-trans-units with inverse "head-to-head" (δ 32.9 ppm) and "tail-to-tail" (δ 17.6 and 18.9 ppm) additions, as well as 1,4-trans-units connected with 1,2-structures (δ 21.9-22.4 ppm) [13].

Table 2. Results of polymerization of 1,3-pentadiene using the catalytic system Al(C₂H₅)₃.Cl₁.₅ - (CH₃)₃Cl. Polymerization conditions: [C₂H₅] = 6.0 mol/l, [Al(C₂H₅)₃.Cl₁.₅] = 0.010 mol/l, molar ratio (CH₃)₃Cl/Al(C₂H₅)₃.Cl₁.₅ = 10, 20 °C, methylene chloride.

| DIPE | Time (min) | Conversion 1,3-PD (%) | Content IF (%) | Molecular characteristics of the polymer | Tₛ (°C) |
|------|------------|----------------------|---------------|-----------------------------------------|---------|
|      |            |                      |               | Mn·10⁻³ (g/mol) | Mₙ·10⁻³ (g/mol) | Mₙ/Mₙ |
| 0    | 1.0        | 48.7                 | 0             | 2.6          | 30.4          | 11.7  |
|      | 2.0        | 63.9                 | 0             | 2.7          | 382.9         | 141.8 |
|      | 5.0        | 69.1                 | 0             | 2.8          | 647.7         | 231.3 |
|      | 30.0       | 87.8                 | 13.3          | –            | –             | –     |
|      | 60.0       | 92.0                 | 57.1          | –            | –             | –     |
|      | 120.0      | 97.5                 | 72.5          | –            | –             | –     |
| 1.0  | 1.0        | 45.1                 | 0             | 2.4          | 18.3          | 7.6   |
|      | 2.0        | 65.4                 | 0             | 2.5          | 75.6          | 30.2  |
|      | 5.0        | 70.8                 | 0             | 2.6          | 480.3         | 184.7 |
|      | 30.0       | 87.9                 | 0             | 2.7          | 699.4         | 259.0 |
|      | 60.0       | 93.5                 | 26.4          | –            | –             | –     |
|      | 120.0      | 97.9                 | 39.9          | –            | –             | –     |
| 5.0  | 1.0        | 42.7                 | 0             | 2.2          | 11.7          | 5.3   |
|      | 2.0        | 59.6                 | 0             | 2.2          | 15.8          | 7.2   |
|      | 5.0        | 66.6                 | 0             | 2.3          | 33.0          | 14.3  |
|      | 30.0       | 85.4                 | 0             | 2.4          | 107.2         | 44.7  |
|      | 60.0       | 91.1                 | 0             | 2.7          | 198.2         | 73.4  |
|      | 120.0      | 96.0                 | 0             | 2.8          | 287.6         | 102.7 |
Figure 2. Aliphatic (a) and olefinic (b) regions of $^{13}$C NMR spectrum of poly-1,3-pentadiene

The $^{13}$C NMR spectrum of poly-1,3-pentadiene shows distinct signals of 1,2-trans-units ($\delta$ 17.9, 38.2, 42.4, 123.8 and 135.6 ppm) and 1,2-cis-units ($\delta$ 13.1-13.5, 33108, 41.8, 122.5, 138.1 ppm). In addition, the signals of carbon atoms of the initial tert-butyl groups ($\delta$ 29.2, 30.8 ppm) connected with the 1,4-trans-unit of poly-1,3-pentadiene, as well as the terminal chlorine-containing 4,1-trans-unit ($\delta$ 45.4 ppm) were identified in the spectrum [13].

The calculation of the content of structural units in the unsaturated part of the polymer chain, carried out according to the method of [13], gives the following results (mol%):

1) 1,4-trans-units with regular attachment "head-to-tail" – 48;
2) 1,4-trans-units with tail-to-tail attachment – 8;
3) 1,4-trans-units with head-to-head attachment – 7;
4) 1,4-trans-units connected with 1,2-structures – 8;
5) 1,2-trans-units – 23;
6) 1,2-cis-units – 6.

The total unsaturation of poly-1,3-pentadiene is 59 mol. % of theoretical value. The predominant 1,4-trans- and 1,2-trans-structure of the polymer chain and the reduced unsaturation of the polymer unambiguously indicate the cationic mechanism of the studied process of 1,3-pentadiene polymerization using the Al(C$_2$H$_5$)$_{1,5}$Cl$_{1,5}$ - ($\text{CH}_3$)$_2$CCl - (i-C$_3$H$_7$)$_2$O catalytic system.

Thus, carrying out the process of cationic polymerization of 1,3-pentadiene on the three-component catalytic system Al(C$_2$H$_5$)$_{1,5}$Cl$_{1,5}$ - ($\text{CH}_3$)$_2$CCl - (i-C$_3$H$_7$)$_2$O at a molar ratio of the components equal to 1: 10: 5, respectively, allows to synthesize completely soluble 1,3-pentadiene polymers with the required softening point temperatures. A pilot batch of thermoplastic poly-1,3-pentadiene with a
softening point temperature of 96 °C has been produced, which is currently being tested during the production of road marking paint.

4. Conclusions
The optimal conditions for obtaining completely soluble thermoplastic polymers of 1,3-pentadiene with the required level of softening point temperatures have been established. The process of production of poly-1,3-pentadiene with optimal characteristics is based on the cationic polymerization of 1,3-pentadiene using three-component catalytic system consisting of ethylaluminum sesquichloride, tert-butyl chloride and diisopropyl ether. It was shown that the synthesized 1,3-pentadiene polymers are characterized by reduced unsaturation and contain mainly 1,4-trans and 1,2-trans-units in the unsaturated part of the polymer chain.

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