Synthesis of new environmentally friendly thermoplastic polymers based on isoprene

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Abstract. A significant part of the roofing sealing materials produced in the industry contains organic solvents. The use of such roofing materials causes significant harm to the environment and human health. In this study, new thermoplastic isoprene polymers with a softening point temperature in the range from 80 to 120°C have been synthesized, which make it possible to manufacture roll roofing materials used in practice without solvents. The process of production of polymers is based on the cationic polymerization of isoprene using catalytic system ethylaluminum sesquichloride - tert-butyl chloride. Varying the polymerization conditions allows one to control the molecular characteristics and softening point temperature of the polymers. A pilot batch of rolled roofing material was produced on the basis of the obtained polymer. As a result of the tests, it was shown that for a number of physical and mechanical parameters, the pilot batch of roofing material surpasses the known compositions using aliphatic hydrocarbon resins of the trade mark "Hikorez".

1. Introduction
Currently, in Russia, a significant part of the manufactured roofing sealing materials contains organic solvents [1]. The use of such roofing compositions causes significant harm to human health and negatively affects the state of ecosystems [2]. In this regard, an actual problem is the creation of new environmentally friendly polymeric materials that reduce the risks of environmental pollution. One of the solutions to this problem is the development of methods for obtaining new thermoplastic polymers, which are applied to the roof surface without the use of organic solvents.

The aim of the study is to develop a process for preparation of new thermoplastic polymers based on an industrially produced diene monomer-isoprene. Another task of the present study is to produce a pilot batch of roofing roll material using new isoprene polymers and to study the physical and mechanical characteristics of the resulting composition.

2. Materials and Methods
Isoprene produced by JSC “Sintezkauchuk” (Sterlitamak) with a basic substance content of 97.5% was used in the work. Methylene chloride (Biosolve, 99.5%) and 2-methyl-2-chloropropane (tert-butyl chloride, TBC, Fluka, 99.5%) were distilled in the presence of CaH₂ in an argon flow. Ethylaluminium sesquichloride, Al(C₂H₅)₃Cl₁₅, was obtained by mixing equimolar amounts of Al(C₂H₅)₂Cl (Aldrich, 99.5%) and Al(C₂H₅)Cl₂ (Aldrich, 99.0%). The method for carrying out the process of isoprene polymerization is described in [3, 4].
Before conducting the experiments to determine the molecular characteristics and microstructure of polyisoprene, polymer samples were purified from catalyst residues by column chromatography on Silica gel 60 (Fluka), eluent – chloroform.

The molecular characteristics of polymers (Mₐ and Mₘ – number average and weight average molecular weights, respectively, Mₘ/Mₐ – polydispersity) were determined by gel permeating chromatography (GPC) on a Waters Alliance GPCV-2000 liquid chromatograph equipped with refractometric and viscometric detectors and a set of four styrogel columns "Waters" with pore sizes of 500 (HR-2), 10³ (HR-3), 10⁵ (HR-4) and 10⁷ (HR-5) Å. Eluent-toluene, temperature 30 °C, elution rate 0.5 ml per minute. The calculation of molecular characteristics was carried out on the basis of universal calibration according to the polystyrene standards "Waters" [5].

¹³C NMR spectra of polyisoprene were recorded on a Bruker Avance-600 spectrometer with a number of acquisitions 8000 and a relaxation delay 12 s. Samples were prepared as solutions in CDCl₃. The unsaturation and the content of structural units in the polymer were determined from the data of ¹³C NMR spectra according to the methods given in [6]. The softening point temperature (Tₛ) of polymers was determined by the "ring and ball" method according to GOST 11506-73. The density, penetration and water absorption of polymer compositions were measured according to GOST 25945-98, the breaking strength with concrete or metal was measured according to GOST 209-75.

3. Results and Discussion

A characteristic feature of the cationic polymerization of conjugated dienes is the high probability of passing a side reaction of the transfer of the growing chain to the double bond of the polydiene [7]. In some cases, this leads to the formation of a crosslinked insoluble fraction in the polymer, which looks like a solid glassy polymer particle. The presence of insoluble fraction in the polymer significantly complicates its practical application. In this regard, an important task of this work is to find the conditions for the production of completely soluble isoprene polymers that do not contain insoluble fraction (IF).

Table 1 presents the results of a study of the process of isoprene cationic polymerization using catalytic systems based on ethylaluminium sesquichloride (EASC).

As can be seen from the data in table 1, the polymerization of isoprene in the presence of EASC without the addition of tert-butyl chloride (TBC) to the reaction mixture proceeds at a low rate. The conversion of isoprene for 1 hour of the process is 35.7% (table 1). A completely soluble polymer is formed only when the monomer conversion is 25% and below. With an increase in the isoprene conversion to polymer, the formation of insoluble fraction is observed, the content of which increases with duration of the polymerization process (table 1). When tert-butyl chloride is introduced into the reaction mixture, the polymerization rate and the polymer yield increase significantly. Thus, in the absence of TBC, the conversion of isoprene for 5 minutes of the process is 10.8%. At a molar ratio of TBC to EASC equal to 10 to 1, the conversion of isoprene in 5 minutes of the process is 54.5%, at a ratio of 100 to 1 - 63.8%, at a ratio of 250 to 1 - 68.7% and at a ratio of 500 to 1 - 71.8% (table 1). The formation of an insoluble fraction in the polymer is observed only at molar ratios of TBC to EASC equal to 10 to 1 and 100 to 1. In the case of using higher concentrations of TBC in the reaction mixture, the formation of completely soluble polyisoprene is observed in studied range of monomer conversions.

From the data in table 1, it can be seen that the practically complete degree of conversion of the monomer for a technologically convenient time (2 hours) is achieved only when the ratio of TBC to EASC is equal of 500 to 1 (table 1).

Regardless of the molar ratio of TBC to EASC, the values of the number average molecular weight of polyisoprene increase with increasing of polymer yield. At the same time, the values of the weight average molecular weights and polydispersity increase most significantly. Thus, when the molar ratio of TBC to EASC equal of 500 to 1, the values of the number average molecular weight of the polymer in the course of polymerization increase from 2600 to 5100 g/mol, i.e., approximately two times, while
the values of the weight average molecular weight of the polymer increase from 11300 to 364700 g/mol, i.e., more than an order of magnitude.

Table 1. Results of isoprene polymerization in the presence of the catalytic system Al(C₂H₅)₃.CCl₁₅ – (CH₃)₃CCl and characteristics of the resulting polymer. Polymerization conditions: [C₅H₈]=4.0 mol/l, [Al(C₂H₅)₃.CCl₁₅]=0.005 mol/l, 20 °C, methylene chloride.

| TBC (mol/mol) | Time (min) | Isoprene conversion (%) | Content of the IF (%) | Molecular characteristics of the polymer | Тₛ (°C) |
|---------------|------------|-------------------------|-----------------------|-----------------------------------------|---------|
| 0             | 5.0        | 10.8                    | 0                     | Mₑ·1₀⁻³ (g/mol) 19.6  Mᵦ·1₀⁻³ (g/mol) 3.4    Mₑ/Mᵦ <20   | <20     |
|               | 10.0       | 16.3                    | 0                     | 9.4  135.3  14.4    78                    |         |
|               | 15.0       | 20.8                    | 0                     | 14.9 504.7  33.9    92                    |         |
|               | 25.0       | 25.6                    | 0                     | –  –  –  –                 |         |
|               | 30.0       | 27.9                    | 27.4                  | –  –  –  –                 |         |
|               | 60.0       | 35.7                    | 77.9                  | –  –  –  –                 |         |
| 10            | 0.50       | 41.3                    | 0                     | 4.6  134.2  29.2    96                    | 96      |
|               | 0.75       | 43.2                    | 0                     | 7.9  298.8  37.8    105                   |         |
| 100           | 1.0        | 45.9                    | 73.6                  | –  –  –  –                 |         |
|               | 2.0        | 47.3                    | 87.5                  | –  –  –  –                 |         |
|               | 5.0        | 54.5                    | 90.1                  | –  –  –  –                 |         |
| 250           | 0.5        | 46.6                    | 0                     | 4.2  29.9  7.1     91                    | 91      |
|               | 1.0        | 49.4                    | 0                     | 4.4  47.1  10.7    93                    |         |
|               | 2.0        | 52.7                    | 0                     | 4.9  82.4  16.8    98                    |         |
|               | 4.0        | 60.3                    | 0                     | 5.5  333.8  60.7    104                   |         |
|               | 5.0        | 63.8                    | 19.3                  | –  –  –  –                 |         |
| 500           | 1.0        | 55.3                    | 0                     | 3.5  19.8  5.7     67                    | 67      |
|               | 5.0        | 68.7                    | 0                     | 3.9  32.9  8.4     79                    |         |
|               | 30.0       | 76.4                    | 0                     | 4.3  87.0  20.2    96                    |         |
|               | 60.0       | 88.3                    | 0                     | 4.8  129.6  27.0    104                   |         |
|               | 120.0      | 90.8                    | 0                     | 5.5  378.7  68.9    115                   |         |
| 500           | 0.5        | 58.7                    | 0                     | 2.6  11.3  4.3     63                    |         |
|               | 2.0        | 67.4                    | 0                     | 2.9  17.1  5.9     73                    |         |
|               | 5.0        | 71.8                    | 0                     | 3.4  22.2  6.5     80                    |         |
| 500           | 15.0       | 79.1                    | 0                     | 3.6  47.7  13.3    93                    |         |
|               | 30.0       | 85.3                    | 0                     | 3.9  95.2  24.4    103                   |         |
|               | 60.0       | 91.6                    | 0                     | 4.5  274.8  61.1    112                   |         |
|               | 120.0      | 99.6                    | 0                     | 5.1  364.7  71.5    120                   |         |

Figure 1 shows the GPC traces of isoprene polymers obtained at different conversions of isoprene.

As can be seen from the GPC traces, with an increase in the conversion of isoprene, the contents of the high molecular weight fraction in the resulting polymer significantly increase on the molecular mass distribution curves (figure 1). This explains the observed significant increase in the values of Mₑ and, respectively, Mₑ/Mᵦ during the polymerization process.

As shown in [3, 4, 6-8], the sharp increase in the Mₑ and Mₑ/Mᵦ values during the cationic polymerization of conjugated dienes is explained by the occurrence of a side reaction of the growing chain transfer to the double bond of polyisoprene macromolecules with the formation of a high molecular weight branched fraction in the polymer. At low ratios of TBC to EASC, this leads to the formation of a crosslinked insoluble fraction in the polymer (table 1). At the ratios of TBC to EASC
equal of 250 and 500 to 1, the formation of a crosslinked insoluble fraction during polymerization does not occur, since TBC is an effective transfer agent of the growing chain [3, 8].

As can be seen from the data in table 1, the values of the softening point temperatures of the synthesized isoprene polymers increase with an increase in the monomer conversion, which is associated with a decrease in the unsaturation of the resulting polymers [3, 4, 9]. At high degrees of isoprene conversion, the softening point temperatures of the synthesized polymers are in the range from 80 to 120 °C (table 1), which is necessary for practical use in roofing materials.

Figure 2 shows the $^{13}$C NMR spectrum of polyisoprene synthesized using the EAS-TBC catalytic system.

As can be seen from figure 2, the unsaturated part of the polyisoprene polymer chain consists predominantly of 1,4-trans units with regular "head-to-tail" addition of monomer units. The carbon atoms of this structural unit of polyisoprene correspond to intense signals on the $^{13}$C NMR spectrum with the following chemical shifts (δ): 15.9, 26.6, 39.7, 124.2, and 134.7 ppm [6]. In addition, signals of 1,4-trans units with inverse "tail-to-tail" (δ 28.2 ppm) and "head-to-head" (δ 38.4 ppm) attachment of monomer units were identified in the spectrum of polyisoprene.

The $^{13}$C NMR spectrum shows relatively weak signals of 1,2-units (δ 22.6, 40.3, 41.4, 111.0, and 147.6 ppm), as well as 3,4-units (δ 18.8, 29.7, 44.8, 111.2, and 147.5 ppm) [6]. The signals with δ 30.0 and 31.5 ppm belong to the carbon atoms of the initial tert-butyl group connected with polyisoprene polymer chain, and the signals with δ 52.3 and 66.1 ppm belong to the carbon atoms of end chlorine containing units with 1, 4-trans and 4,3-structure, respectively [6].

The calculation of the content of structural units in the unsaturated part of the polymer chain of polyisoprene, carried out according to the method in the paper [6], gives the following results: 1,4-trans-units – 94 mol%, 1,2-units – 3 mol%, 3,4-units – 3 mol%. The unsaturation of polyisoprene is 54 mol% from theoretical. The reduced unsaturation of the synthesized polyisoprene and, the predominantly, 1,4-trans-structure of the polymer chain indicate that the polymerization of isoprene using EASC-TBC catalytic system proceeds by a cationic mechanism [7].

To test polyisoprene in roofing compositions, a pilot batch of polyisoprene was produced under the following polymerization conditions: the molar ratio of TBC to EASC is 500 to 1, the initial isoprene concentration is 4.0 mol/l, the process temperature is 20 °C, and the duration of process is 2 hours. The obtained polyisoprene was tested as a "thixotropic" component of a polymer composition for roll roofing materials based on butyl rubber (table 2).
Figure 2. Aliphatic (a) and olefinic (b) regions of the $^{13}$C NMR spectrum of polyisoprene synthesized using the catalytic system Al$(C_2H_5)_{1.5}$Cl$_{1.5}$ – (CH$_3$)$_3$CCl.

From the data in Table 2 it can be seen that the experimental polymer composition using the synthesized polyisoprene is superior to the control composition obtained with the aliphatic resin "Hikorez C-1100" in terms of breaking strength with concrete or metal.

Table 2. Physical and mechanical characteristics of the polymer composition for roll roofing material using "cationic" polyisoprene.

| Quality indicators                      | Control composition using "Hikorez" | Experimental composition using polyisoprene |
|-----------------------------------------|-------------------------------------|--------------------------------------------|
| Density (kg / m$^3$)                    | 1570                                | 1480                                       |
| Penetration (mm)                        | 7.5                                 | 6.2                                        |
| Water absorption (%)                    | 0.1                                 | 0.1                                        |
| Breaking strength with concrete (kg / cm$^2$) | 0.47                                | 0.51                                       |
| Breaking strength with metal (kg / cm$^2$)   | 0.41                                | 0.58                                       |
4. Conclusions
Thus, the cationic polymerization of isoprene using the catalytic system ethylaluminium sesquichloride-tert-butyl chloride makes it possible to synthesize soluble thermoplastic isoprene polymers with a softening point temperature in the range from 80 to 120 °C. Using synthesized isoprene polymers, a pilot batch of polymer composition for roll roofing materials was made, which showed higher physical and mechanical characteristics compared to the control composition prepared using Hikorez resin. The use of roll roofing materials, which are applied to the surface of roofs without the use of organic solvents, reduces the risks of environmental pollution.

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