The influence of the properties of the catalytic system on the properties of cis-1,4-polybutadiene modified with a copolymer of maleic anhydride and hexadecene-1

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Cis-1,4-polybutadiene continues to be one of the most in-demand synthetic rubbers [1]. The high demand for this polymer is promoting new research on improving the properties of cis-1,4-polybutadiene and vulcanisates based on it. An analysis of literature and patent data has shown that the optimum characteristics are possessed by polybutadienes with reduced polydispersity and a high (over 96%) content of cis-1,4-units [2-6]. However, a polymer of this kind possesses high cold flow, which causes considerable difficulties at the stages of formation and drying [3]. A possible solution is to modify cis-1,4-polybutadiene by the interaction of “living” macromolecules with polyfunctional reactive compounds at the final stage of the polymerisation process [7-10]. Earlier we showed that copolymers of maleic anhydride and α-olefin can be used as such modifiers [11]. The use of these compounds makes it possible to lower considerably the cold flow of the cis-1,4-polybutadiene obtained. The high effectiveness of the modifier is due to its good hydrocarbon solubility and consequently its uniform distribution in the reaction medium [12].

As the catalyst for butadiene polymerisation, the indicated studies used a neodymium-containing catalytic system modified with methylaluminoxane (MAO). It is known that the MAO content in the reaction medium determines the proportion of active centres in relation to the neodymium introduced, and consequently the number of “living” macromolecules [13]. In this work a study was made of the influence of the concentration of methylaluminoxane in the catalytic system on features of the process of interaction of “living” macromolecules of cis-1,4-polybutadiene and a copolymer of maleic anhydride and hexadecene-1 at the final stage of the polymerisation process.

As the catalyst for butadiene polymerisation, use was made of a complex obtained as a result of the interaction of hydrocarbon solutions of neodymium neodecanoate (NN), diisobutylaluminium hydride (DIBAH), hexachlorop-xylene (HCPX), and methylaluminoxane [14]. In order to retain the specified level of molecular weights of the obtained cis-1,4-polybutadiene with variation in the methylaluminoxane concentration, the content of diisobutylaluminium hydride was changed little.

The synthesis of polybutadiene was conducted in a metal reactor equipped with a stirrer, a sleeve for maintaining constant temperature, and devices for introducing the solution of monomer, catalyst, and modifier and sampling the polymerisate. Hexane was used as the solvent, and the initial concentration of monomer and catalyst (in terms of neodymium) in the reaction medium amounted to 1.4 and 1.4 x 10⁻⁴ mol/L respectively. The polymerisation temperature was 50°C. Once a butadiene conversion of over 80% had been reached, the polybutadiene was modified by introducing into the reaction medium a toluene solution of a copolymer of maleic anhydride and hexadecene-1 at a temperature of 50°C. The molar ratio of modifier (in terms of maleic anhydride) to Nd was 1.5. The reaction mixture was deactivated with ethanol, and the polybutadiene was stabilised with the antioxidant Novantox 8PFDA. The
obtained polymer was separated and dried to constant mass.

The molecular parameters of polybutadiene were assessed by gel permeation chromatography on an Alliance GPCV-2000 liquid chromatograph (Waters) equipped with two detectors (refractometric and viscometric) and a set of styrogel columns (Waters) with a pore size of 500 Å (NT-2), 10³ Å (NT-3), 10⁴ Å (NT-4), and 10⁶ Å (NT-6). Calibration of the instrument was carried out according to narrowly disperse standard specimens of polystyrene (\(M_\text{w}/M_\text{n} = 1.1\)) covering the entire range of measured molecular weights on the given set of columns. The eluent was toluene, the elution rate was 1 mL/min, and the temperature was 30°C. The cold flow and Mooney viscosity of the polymers were determined according to the GOST 19920.18-74 and GOST 10722-76 standards respectively.

According to earlier investigations, increase in the MAO content in a catalytic system based on neodymium neodecanoate leads to an increase in its activity [15]. The results presented in Table 1 indicate that increase in the initial polymerisation rate is due to increase in the effective growth rate constant \(k_g\) and in the proportion of active centres in relation to the neodymium introduced \(y_a\).

Taking into account the mechanism of modification of cis-1,4-polybutadiene by copolymers of maleic anhydride and hexadecene-1 [16-18], it was assumed that increase in \(y_a\) and consequently increase in the concentration of “living” macromolecules in the reaction medium should have an influence on the effectiveness of the modifier.

Figure 1 shows the dependence of the plastoelastic characteristics of modified cis-1,4-polybutadiene on the MAO:Nd molar ratio in the catalytic system. It can be seen that modification leads to a considerable increase in Mooney viscosity and to a greater than fourfold reduction in the cold flow of the polymer formed. In the range of MAO:Nd molar ratios of 5-16 there is a considerable increase in the Mooney viscosity and a practically constant level of cold flow values of the modified cis-1,4-polybutadiene. Subsequent increase in the MAO concentration in the system is not accompanied with any significant changes in the plastoelastic properties of the polymer.

Analysis of the molecular parameters of the specimens indicates that change in the plastoelastic characteristics is due to an increase in the average molecular weights of the polymer. Figure 2 presents the time dependences of the number-average and weight-average molecular weights of cis-1,4-polybutadiene obtained at different stages of the modification process with variation of the composition of the catalytic system. It was established that, irrespective of the modification conditions, the form of the curves is retained. In the 0-60 s range there is an intense increase in the molecular weights of the polybutadiene; in this period, interaction of the main part of the “living” macromolecules with the copolymer of maleic anhydride and hexadecene-1 takes place. Increase in the modification time leads to a negligible change in \(M_\text{w}\) and \(M_\text{w}\). Here, over the entire course of interaction of “living” cis-1,4-polybutadiene with the modifier, increase in the MAO concentration in the reaction medium leads to the formation of specimens of greater molecular weight. Thus, with change in the MAO:Nd molar ratio in the catalytic complex from 5 to 25, there is an increase in \(M_\text{w}\) and \(M_\text{w}\) of the polymer produced at the final stage of modification from 155 x 10³ to 180 x 10³ and from 420 x 10³ to 540 x 10³ respectively.

Table 1. The kinetic parameters of butadiene polymerisation in the presence of an NN-DIBAH-HCPX-MAO catalytic system with different methylaluminoxane concentrations

<table>
<thead>
<tr>
<th>MAO:Nd molar ratio</th>
<th>(w_\text{p} (\text{mol/L min}))</th>
<th>(k_g (\text{L/mol min}))</th>
<th>(y_a (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.20</td>
<td>1614</td>
<td>60</td>
</tr>
<tr>
<td>8.0</td>
<td>0.22</td>
<td>2154</td>
<td>68</td>
</tr>
<tr>
<td>16.0</td>
<td>0.26</td>
<td>2450</td>
<td>76</td>
</tr>
<tr>
<td>25.0</td>
<td>0.31</td>
<td>2723</td>
<td>80</td>
</tr>
</tbody>
</table>

\(w_\text{p}\) – initial polymerisation rate  
\(k_g\) – rate constant of polymer chain growth  
\(y_a\) – proportion of active centres in relation to the neodymium introduced

\(\Delta_\text{nominal units} \longrightarrow \text{Cold flow, mm/h}\)

[Figure 1. The dependence of the cold flow and the change in Mooney viscosity (\(\Delta\)) of specimens of modified cis-1,4-polybutadiene on the MAO:Nd molar ratio (* unmodified specimen)]
Figure 3 shows curves of the molecular weight distribution of cis-1,4-polybutadiene specimens synthesised by the action of catalytic systems with an MAO:Nd molar ratio of 5 and 25 at different stages of the modification process. It can be seen that, before interaction with the copolymer of maleic anhydride and hexadecene-1, cis-1,4-polybutadiene specimens have similar MWD curves. However, increase in the MAO content in the catalytic system leads to the formation of a polymer with higher polydispersity. In Akhmetov and Akhmetova [19] it was shown that this is due to the participation of MAO in reactions of polymer chain growth constraint. This is confirmed by the observed increase in the proportion of low-molecular-weight fraction, but does not explain the broadening of the MWD in the region of high molecular weights. To all appearances, besides the participation of MAO in chain transfer reactions, “new” types of active centre with less likelihood of macromolecule growth constraint are formed. Increase in the level of $k_g$ values with increase in the MAO content in the catalyst points to this (Table 1).

The introduction of the copolymer of maleic anhydride and hexadecene-1 into the reaction medium leads to displacement of the MWD curves into the region of high molecular weights. Here, increase in the MAO content in the reaction medium determines the magnitude of the displacement of the MWD curve. It must also be pointed out that, in the range of inflection of the time dependences of the molecular weights, the MWD curves of cis-1,4-polybutadiene specimens “lose” their symmetry. Subsequent increase in the modification time is accompanied with the recovery of symmetry. It can be assumed that this is due to the presence in the reaction medium of “living” macromolecules possessing kinetic inhomogeneity. At the initial stage of modification, living macromolecules with a molecular weight ranging from $100 \times 10^3$ to $500 \times 10^3$ interact with the copolymer. Here, taking into account the data in Figures 2a and b, it can be said that “the main mass of the living polymer” possesses precisely this molecular weight, and recovery of the symmetry of the MWD is due to slower involvement of macromolecules with a low molecular weight in the process of modification.

Thus, it has been shown that increase in the proportion of active centres in relation to the neodymium introduced at the stage of synthesis of the “base” polymer leads to a greater increase in the Mooney viscosity without having any significant effect on the level of cold flow of cis-1,4-polybutadiene modified with a copolymer of maleic anhydride anhydride and hexadecene-1. Changes in

Figure 2. The dependence of the number-average molecular weight $M_n$ (a) and the weight-average molecular weight $M_w$ (b) on the duration of modification ($\tau$) with an MAO:Nd molar ratio of 5 (1), 8 (2), 16 (3), and 25 (4)

Figure 3. The form of the MWD curves of polybutadiene with an MAO:Nd molar ratio of 25 (a) and 5 (b) at different stages of the modification process
the plastoelastic characteristics of polybutadiene in the process of modification are due to increase in the average molecular weights, with greater dynamics for $M_w$. The nature of change in the MWD of cis-1,4-polybutadiene in the process of modification may indicate an increase in the kinetic inhomogeneity of the catalytic system with increase in the MAO concentration in the reaction medium.

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