The modification of cis-1,4-polybutadiene with copolymers of maleic anhydride and \( \alpha \)-olefin: the influence of the nature of the \( \alpha \)-olefin

I.G. Akhmetov, K.M. Kubanov, and E.F. Ziganshina

OAO “Nizhnekamskneftekhim” (Nizhnekamskneftekhim Open Joint Stock Company), Nizhnekamsk

INTRODUCTION

In 2011, the worldwide production of synthetic rubbers exceeded 14 million t\(^1\), the proportion of polybutadienes amounting to more than 22%. One of the butadiene rubbers in highest demand is cis-1,4-polybutadiene produced using a neodymium-containing catalytic system. The high processing and service properties of “neodymium” polybutadiene and its vulcanisates are determined primarily by its high stereoregularity. Furthermore, polybutadiene produced using a neodymium catalyst contains no toxic or ecologically harmful oligomers, and the production layout does not incorporate a catalyst residue washing-out stage because neodymium is not an oxidation catalyst. Rubber compounds based on these butadiene rubbers possess high dynamic properties and low hysteresis losses \(^2\)-\(^4\). The shortcomings of neodymium polybutadiene include the high cold flow of the rubber, which is determined by the linearity of its macromolecules. This problem is particularly acute in the case of the production of a polymer of narrow polydispersity. This leads to considerable difficulties in the isolation and storage of the rubber \(^5\). Therefore, work on lowering the cold flow of polybutadiene produced in the presence of a neodymium-containing catalytic system is fairly urgent, as borne out by the unwavering interest of researchers in this question \(^6\)-\(^10\). An analysis of the patent literature showed that the most effective method for reducing the cold flow of rubber is to modify the polymer at the final stage of the polymerisation process by the interaction of “living” macromolecules with functional groups of different reactive compounds \(^11\)-\(^14\).

Earlier, we examined the possibility of modifying neodymium polybutadiene with a copolymer based on maleic anhydride and \( C_{12-10} \) \( \alpha \)-olefin fraction. It was shown that the introduction of the modifier leads to a reduction in the cold flow of the polymer obtained through an increase in the average molecular weights of the polymer and the formation of branched, functionalised macromolecules \(^15\). The present work is devoted to a study of the influence of the nature of the \( \alpha \)-olefin in the copolymer on features of the modification process and on the properties of the cis-1,4-polybutadiene obtained.

EXPERIMENTAL AND DISCUSSION

A complex produced by the interaction of hydrocarbon solutions of neodymium neodecanoate, diisobutyaluminium hydride, hexachlorop-xylene, and methylalumoxane \(^16\) was used as the catalyst for butadiene polymerisation. Polybutadiene was synthesised in a metal reactor equipped with a stirrer, a sleeve for maintaining constant temperature, and devices for feeding the solution of monomer, catalyst, and modifier and for sampling the polymerisate. Hexane was used as the initial solvent, and the initial concentrations of monomer and catalyst (in terms of neodymium) in the reaction medium were 1.4 and 1.4 x 10\(^{4}\) mol/L respectively. The polybutadiene was modified, once a butadiene conversion of over 80% had been reached, by introducing toluene solutions of copolymers of maleic anhydride and \( \alpha \)-olefin into the reaction medium. Deactivation of the reaction mixture was carried out with ethanol, and the polybutadiene was stabilised with the
antioxidant Novantoks 8PFDA. The polymer obtained was isolated and dried to constant weight.

Modifiers (MDs) were obtained by radical copolymerisation of maleic anhydride and an \(\alpha\)-olefin from a series including decene-1, dodecene-1, tetradecene-1, and hexadecene-1. The products, kindly provided by OOO “Fosforos” (Fosforos LLC), comprised statistical copolymers with a molecular weight of 1000-1500 and an acid number in the range 300–350 mg KOH/g.

The molecular parameters of the copolymers of maleic anhydride and \(\alpha\)-olefin were assessed by the ebullioscopic method [17], and those of butadiene by gel-permeation chromatography on an Alliance GPCV-2000 liquid chromatograph (Waters) equipped with two detectors (refractometric and viscometric detectors) and a set of Waters styrogel columns with a pore size of 500 Å (NT-2), 10^3 Å (NT-3), 10^4 Å (NT-4), and 10^6 Å (NT-6). The instrument was calibrated to narrowly dispersed standard specimens of polystyrene \((M_w/M_n = 1.1)\), which cover the entire region 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 the Mooney viscosity of the polymers were determined according to the GOST 19920.18-74 and GOST 10722-76 standards respectively.

Figure 1 presents the dependences of change in the Mooney viscosity of polybutadiene on the content of copolymer of maleic anhydride and \(\alpha\)-olefin in the reaction medium with variation in the component composition of the modifier. It can be seen that, irrespective of the type of \(\alpha\)-olefin in the copolymer, rapid growth of the curves is observed in the range of MD:Nd molar ratios from 0.25 to 1.5. Increase in the molecular weight of the \(\alpha\)-olefin in the modifier is accompanied with more dynamic increase in the viscosity of the polymer formed. The growth of the curves is slowed down at an MD:Nd molar ratio of 1.5. The maximum change in viscosity of the polybutadiene in all cases examined amounted to ~20 Mooney units. The exception was the dependence obtained with the use of a modifier based on decene-1, which was characterised by the minimum values of change in viscosity and a practically monotonic growth in this index in the entire MD:Nd range examined.

The effect of modification of the polybutadiene with copolymers of maleic anhydride and \(\alpha\)-olefins on the cold flow of the polymer formed is presented in Figure 2. Similarly to the Mooney viscosity, the cold flow values change considerably in the range of MD:Nd molar ratios of 0.25-1.5. Thus, the reduction in cold flow of the rubber in the indicated range amounts to more than 15 mm/h for practically all specimens. Further increase in the copolymer content in the system does not lead to any significant change in this index. In contrast to the dependences presented in Figure 1, polybutadiene modified with a copolymer based on decene-1 with an MD:Nd molar ratio of only 2.0 approaches, in cold flow value, polymer specimens obtained using the other modifiers examined.

The obtained results indicate that the nature of the \(\alpha\)-olefin in the copolymer has a significant influence on its modifying capacity. Let us consider the reasons for this. Firstly, change in the structure of the copolymer could promote an “easier” interaction of the functional group of the modifier with the growing polymer chain. At the same time, as shown by the results of experiments, the copolymers can be placed in the following order of effectiveness as modifiers: decene-1 < dodecene-1 < tetradecene-1 < hexadecene-1, which suggests increasing steric hindrances in chemical interactions. Secondly, increase in the molecular weight (MW) of the alkyl radical of \(\alpha\)-olefin could lead to a corresponding increase in the MW of the modified polymer. However, the values of the molecular weights of the polybutadiene and modifier differ by two orders of magnitude, and therefore changes in the MW of elementary units for copolymers of maleic anhydride and different \(\alpha\)-olefins

![Figure 1. The dependence of change in the Mooney viscosity (\(\Delta\)) on the MD:Nd molar ratio when copolymers based on decene-1 (1), dodecene-1 (2), tetradecene-1 (3), and hexadecene-1 (4) are used.](Image)

![Figure 2. The dependence of cold flow on the MD:Nd molar ratio when copolymers based on decene-1 (1), dodecene-1 (2), tetradecene-1 (3), and hexadecene-1 (4) are used.](Image)
cannot have any significant effect on the characteristics of the modified polymer. Thirdly, with increase in the mass fraction of olefin fragments in the modifier, its solvation in the reaction medium can be improved by reducing the copolymer-solvent interaction. To check this hypothesis, a study was made of the solubility of the investigated copolymer specimens in hydrocarbon solvents and the influence of the modification time and the nature of the copolymer on the molecular weight characteristics of the polybutadienes formed.

According to the data presented in Table 1, modifiers based on decene-1 and dodecene-1 are insoluble in hexane, modifiers based on tetradecene-1 have limited solubility in hexane, and modifiers based on hexadecene-1 have good solubility in hexane. For the copolymers studied, toluene is a better solvent, but the dependence of the solubility of the modifier on the nature of the \( \alpha \)-olefin within it that was found for hexane is retained.

**Figure 3** presents the influence of the modification time and the nature of the copolymer on the molecular weight characteristics of polybutadienes obtained at an MD:Nd molar ratio of 1.5. Common to the obtained relationships is a rapid growth in the weight-average molecular weight of the polymer in the range from 0 to 60 s. Growth then slows down, and the curves flatten out. The maximum increase in MW from \( 330 \times 10^3 \) to \( 425 \times 10^3 \) is observed for a copolymer based on hexadecene-1. Change in the nature of the \( \alpha \)-olefin in the order hexadecene-1–tetradecene-1–dodecene-1–decene-1 is accompanied with a reduction in the MW of the specimens of modified polybutadiene. On the whole, the nature of the obtained curves is similar to the dependences we found earlier with a different MD:Nd molar ratio. It was shown that increase in the modifier concentration in the reaction medium led to growth in the average molecular weights of the polybutadiene, while stabilisation of the MW level was observed with a modification time of 60 s or more [15].

The results obtained indicate that a key factor during the interaction of reactive polybutadiene macromolecules with the copolymer is the “effective” concentration of functional groups of the modifier, which is determined primarily by the degree to which the copolymer and the reaction medium combine. Copolymers based on higher-molecular-weight \( \alpha \)-olefins appear to be distributed uniformly in the reaction mass in the form of individual macromolecules. By contrast, copolymers based on dodecene-1 and decene-1 are present in the reaction medium in the form of agglomerates, the effectiveness of which primarily depends on their linear size and not on the content of the functional groups.

To assess the effectiveness of the copolymers examined, we will use a parameter proposed earlier – the rate of change in the weight-average molecular weight of polybutadiene at the initial (up to 30 s) stage of modification [15]. From the data presented in **Figure 4** it can be seen that the effectiveness of the copolymer is increased considerably on switching from decene-1 to tetradecene-1. The use of modifiers based on hexadecene-1 is accompanied with the maximum rate of change in the weight-average molecular weight of polybutadiene at the initial stage. It is evident that further increase in the molecular weight of the \( \alpha \)-olefin in the copolymer will promote an increase in the effectiveness of modification. At the same time, the mass fraction of maleic anhydride (reactive functional groups) in the modifiers is inversely proportional to the molecular weight of an elementary unit of the copolymer and decreases linearly among the modifiers investigated (decene-1 < dodecene-1 < tetradecene-1 < hexadecene-1) (**Figure 4**). Therefore, in our view, the

![Figure 3. The dependence of the weight-average molecular weight (\( M_w \)) on the modification time (\( \tau \)) with an MD:Nd molar ratio of 1.5 when copolymers based on decene-1 (1), dodecene-1 (2), tetradecene-1 (3), and hexadecene-1 (4) are used](image)

<table>
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<tr>
<th>Solvent</th>
<th>( \alpha )-olefin</th>
<th>Decene-1</th>
<th>Dodecene-1</th>
<th>Tetradecene-1</th>
<th>Hexadecene-1</th>
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<td>Hexane</td>
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<td>—</td>
<td>—</td>
<td>2.2</td>
<td>&gt;8.0</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>0.1</td>
<td>2.0</td>
<td>4.2</td>
<td>&gt;8.0</td>
</tr>
</tbody>
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optimum modifier in the synthesis of polybutadiene with a neodymium-containing catalytic system is a copolymer based on maleic anhydride and hexadecene-1.

CONCLUSIONS

Thus, it has been shown that the nature of the α-olefin in the modifier has a considerable influence on the effectiveness of interaction of functional groups of the copolymer and “living” macromolecules of cis-1,4-polybutadiene. It is suggested that the effectiveness of the copolymer as a modifier depends primarily on the degree to which it combines with the reaction medium. Analysis of the results obtained indicates that the optimum is the use of a copolymer based on hexadecene-1.

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