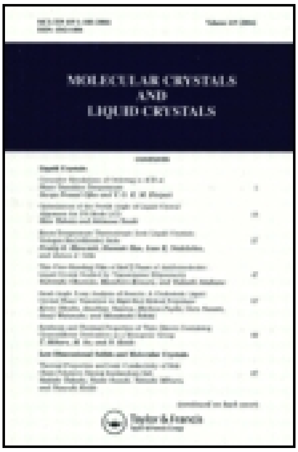

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Oligomer Obtained from the By-Products of Polybutadiene Production as a Rubber Plasticiser

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Waste products from polybutadiene rubber production can be used as a feedstock for obtaining oligomers containing styrene. It was demonstrated that styrene-based oligomers can be used in the production of butadiene rubber.

Keywords Copolymerisation; oligomers; polybutadiene; rubber; styrene

Introduction

The petrochemical industry has recently been focusing on the elaboration of low-waste and non-waste technological processes that make it possible to treat the waste and by-products produced with the aim of using them in the same technological process in which they were produced.

Obtaining polybutadiene by butadiene polymerisation in the presence of a metal complex catalyst in solution is an example of such usage. This process uses unsaturated compounds as by-products–dimers and trimers of butadiene. The main ones are: 4-vinylcyclohexene (VCH); n-dodecatetraene-2,4,6,10 (NDT); cyclododecatriene-1,5,9 (CDT), etc. These products form stillage bottoms after the refinement process by distillation of return solvent (toluene) extracted by aqueous degassing.

The formation of VCH, CDT and NDT was also observed in some other processes of organic synthesis [1] containing butadiene.

Nikulin et al. [2–4] have shown that free radical copolymerisation in a mixture of butadiene dimers and trimers contained in the by-product of butadiene rubber production allowed copolymers with low molecular mass to be obtained. However, the product yield of copolymers was lower than those produced with the use of silica-alumina catalysts. Investigations by these researchers demonstrated that the additional introduction of easily disposable monomers such as styrene resulted in an increase in the copolymer yield and enhancement of dimer and trimer conversion. However, rather large amounts of non-polymerised compounds were present in the product obtained (polymerisate).

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A radical initiator has now been introduced and is being widely used in the synthetic rubber industry–pinane hydroperoxide (PH). Nikulin et al. [5] considered PH as a possible reactant for the synthesis of low-molecular copolymers based on by-products formed in the production of butadiene rubber. However, they considered only one PH dosage (6.0 mass %), but the copolymer yield did not exceed 70 mass %, even when the styrene content of the monomer base mixture was 90 mass %. Moreover, the areas of application for the copolymer obtained were not determined by these researchers.

The object of our investigation was to study the free radical copolymerisation process of unsaturated compounds contained in the by-products of butadiene rubber production with styrene in the presence of the radical initiator, PH.

Experimental

The by-products of butadiene rubber production were studied which involved (in mass %): toluene – ~35.0; VCH – ~47.0; CDT, NDT and other high-boiling compounds – ~18.0. The base batch for polymerisation was obtained by introducing styrene into the by-product mixture formed during butadiene rubber production.

Low-molecular copolymers were obtained in the following way. 100 g of a hydrocarbon batch with different styrene contents was loaded into a leak-proof pile and then PH was added. The styrene content in the reaction mixture varied from 0 to 90 mass % relative to the unsaturated compounds. The total content of the polymerised compounds in the batch (styrene, VCH, CDT, NDT and others) was kept within a range of 50 to 60 mass % by diluting them with a calculated amount of solvent, namely toluene. The concentration of the polymerised compounds had to be kept constant due to the effect of excluding the concentration factor on the process of oligomer recovery from the by-products of butadiene rubber and styrene production.

The process was carried out at 100 ± 2°C for 50 h. Samples were taken after certain periods of time and the copolymer content was measured by gravimetric analysis. To accomplish this, the solvent and other low-boiling products were removed from the copolymer obtained and then the residual solids were weighed.

IR spectra were obtained with an FT-02IR Fourier Transform spectrometer. PMR spectra were measured with a Brucker unit (the solvent was deuterated chloroform). The molecular mass was determined by gel-penetrating chromatography on a Waters chromatograph supplied with standard chromatographic columns filled with Ultrastyrogel. The elution rate was approximately 1 ml/min. Tetrahydrofuran (Russian standard 6-02-621-81) was used as solvent. The concentration of the polymer solution investigated was less than $2 \cdot 10^{-3}$ g/ml.

Results and Discussion

Oligomer Synthesis

Table 1 presents the results of the investigations into the effect of styrene in a hydrocarbon batch, as well as the effect of the duration of the oligomerisation process on the yield of low-molecular copolymers. The amount of PH added was 5.0, 7.0 and 9.0 mass % relative to the unsaturated compound content.

Our investigations demonstrated that copolymerisation in the presence of PH proceeds at a slow rate and have a small product yield. The best results were obtained with a high

Table 1. Influence of styrene and pinane hydroperoxide content introduced into the batch and duration of the process on the product yield of low-molecular coplymers

	Copolymers yield, mass % at the duration, h:					
Styrene content, %	5 h	10 h	15 h	20 h	30 h	50 h
PH content – 5.0 mass %.						
0	6.5	9.6	12.1	14.0	18.0	21.1
10	7.8	11.6	13.5	17.0	19.8	23.5
25	8.9	12.2	16.0	20.3	24.1	26.8
50	14.5	18.3	23.6	28.0	31.1	35.0
75	20.3	26.5	32.1	37.3	40.4	45.3
90	31.4	36.0	47.0	52.2	59.1	67.1
PH content – 7.0 mass %.						
0	7.5	11.4	15.1	18.5	21.6	25.4
10	9.0	14.0	17.1	20.2	24.1	27.3
25	11.3	17.2	20.8	23.4	27.7	30.0
50	17.5	21.4	26.8	29.8	33.6	38.4
75	22.0	28.7	35.8	40.6	45.0	50.3
90	39.0	44.2	52.1	59.7	66.8	74.1
PH content – 9.0 mass %.						
0	9.2	13.3	17.0	20.3	24.0	27.2
10	10.7	17.2	20.8	23.6	27.0	30.5
25	12.5	20.8	24.2	28.1	31.9	34.8
50	19.8	24.6	27.3	32.4	36.8	41.0
75	25.1	31.0	37.5	41.6	48.5	53.0
90	42.2	47.6	60.6	66.5	74.6	79.4

Notes:- content of styrene and PH in mass % hereafter was calculated relative to the unsaturated compounds involved in the batch.

- PH was introduced once in the beginning of the process.

styrene content in the base mixture of monomers (90 mass %) and extended PH dosage (7–9 mass % relative to the unsaturated hydrocarbons).

The introduction of additional styrene into the oligomerised batch made it possible to increase the total product yield of low-molecular copolymers. This was attained mainly due to the styrene component of the reaction mixture. Conversion of VCH as a low-reactive monomer increased from 15–17 mass % to 30–35 mass %, while the styrene content increased from 0 to 90 mass %. Nevertheless, an increase in the total yield related to low-molecular copolymers was not achieved – the yield did not exceed 80 mass %. A temperature increase of up to 120°C did not result in a notable increase in the copolymer yield. A small increase (of 1.5–5.0 mass %) in the copolymer yield was observed at the start of the copolymerisation process (up to 20 h). However, this advantage would be lost due to the cost of the radical initiator at the beginning of the process. The poor efficiency of the increased dosage of the radical initiator is probably due to the fact there are some impurities that break the growth of the polymer chain in the by-products of the butadiene rubber production investigated. For example, one of these impurities is an antioxidant used in butadiene rubber production with a melting temperature of $T_{melt.} \geq 128°C$. Ingress of antioxidant into the solvent occurred during the extraction of rubber from the solution by the aqueous degassing method. Antioxidant distilled with the vapour of hydrocarbon solvent after condensation flowed into the refinement compartment. During refinement of the return solvent (toluene) by the recovery technique, antioxidant as a higher boiling component was concentrated in a stilling fluid of distillation columns, and it further inhibited the process of radical copolymerisation. One should also note the presence of quite high compound contents of undefined structure in stillage bottoms–their influence on the process of radical copolymerisation of the components investigated is not known either.

After mathematical processing of the experimental results by computer, equations were obtained that describe the effect of styrene in the reaction mixture and the duration of the process (x) on the product yield of low-molecular copolymers from the by-products of butadiene rubber production (Y, mass %). The process was carried out at 100°C and with varying styrene contents of 0 to 90 mass % in the base reaction mixture. The equations are written as follows:

pH dosage 5 mass %

$$Y_0 = 3.34 + 0.68 \cdot x - 6.39 \cdot 10^{-3} \cdot x^2$$
$$Y_{10} = 4.53 + 0.74 \cdot x - 7.18 \cdot 10^{-3} \cdot x^2$$
$$Y_{25} = 3.69 + 1.02 \cdot x - 1.11 \cdot 10^{-2} \cdot x^2$$
$$Y_{50} = 8.93 + 1.15 \cdot x - 1.26 \cdot 10^{-2} \cdot x^2$$
$$Y_{75} = 14.28 + 1.39 \cdot x - 1.55 \cdot 10^{-2} \cdot x^2$$
$$Y_{90} = 21.99 + 1.84 \cdot x - 1.87 \cdot 10^{-2} \cdot x^2$$

PH dosage 7 mass %

$$Y_0 = 3.30 + 0.92 \cdot x - 9.60 \cdot 10^{-3} \cdot x^2$$
$$Y_{10} = 4.87 + 0.97 \bullet x - 1.04 \bullet 10^{-2} \bullet x^2$$
$$Y_{25} = 6.88 + 1.08 \cdot x - 1.25 \cdot 10^{-2} \cdot x^2$$
$$Y_{50} = 12.63 + 1.05 \cdot x - 1.07 \cdot 10^{-2} \cdot x^2$$
$$Y_{75} = 15.08 + 1.57 \cdot x - 1.75 \cdot 10^{-2} \cdot x^2$$
$$Y_{90} = 29.56 + 1.80 \cdot x - 1.82 \cdot 10^{-2} \cdot x^2$$

PH dosage 9 mass %

$$Y_0 = 4.73 + 0.97 \cdot x - 1.04 \cdot 10^{-2} \cdot x^2$$
$$Y_{10} = 6.69 + 1.08 \cdot x - 1.21 \cdot 10^{-2} \cdot x^2$$
$$Y_{25} = 7.68 + 1.31 \cdot x - 1.55 \cdot 10^{-2} \cdot x^2$$
$$Y_{50} = 14.75 + 1.06 \cdot x - 1.07 \cdot 10^{-2} \cdot x^2$$
$$Y_{75} = 17.90 + 1.51 \cdot x - 1.62 \cdot 10^{-2} \cdot x^2$$
$$Y_{90} = 30.34 + 2.29 \cdot x - 2.62 \cdot 10^{-2} \cdot x^2$$

The effect of styrene in the base reaction mixture (z), varying from 0 to 90 mass % at dosages of pH 5, 7 and 9 mass % and a duration of the process of 50 h, can be described by the following equations:

$$Y_5 = 22.82 - 6.73 \cdot 10^{-2} \cdot z + 5.82 \cdot 10^{-3} \cdot z^2$$
$$Y_7 = 27.21 - 0.15 \cdot z + 7.02 \cdot 10^{-3} \cdot z^2$$
$$Y_9 = 29.98 - 0.14 \cdot z + 7.11 \cdot 10^{-3} \cdot z^2$$

Investigations were also carried out into the application of fractional supply of the radical initiator during the synthesis of a low-molecular copolymer based on styrene and the by-products of butadiene rubber production. The introduction of the radical initiator was shown

Table 2. Distribution of oligomer molecules obtained for the styrene content in the batch equal to 80 mass % over the fractions

M_w	More than 7,000	5,000–7,000	3,000–5,000	2,000–3,000	1,000–2,000	500–1,000	Less than 500
Fractions content, %	14.79	4.15	13.00	9.06	22.27	28.96	7.77

to be most efficient when done in four steps (3.0–4.0 mass % at the beginning of the process, 1.0–1.5 mass % at the point of conversion, 35–40, 60–65 mass % and 70–75 mass %). The total yield of polymer products increased up to 84–86 mass %. The total duration of the process was 55–60 h.

From the results of the investigations, it can be concluded that when the radical initiator is applied, it is necessary at the first stage to deactivate the impurities contained in the by-products of butadiene rubber production which inhibit the radical process. The inhibitors can be removed or decreased in several ways:

- By additional water-alkali washing of the raw by-product
- By introducing additional substances to deactivate the antioxidant
- By refining the by-product through distillation

However, all these features complicate the process of oligomerisation and increase the cost, thus reducing the competitiveness of the copolymers obtained. Therefore the most promising method would be a process that would allow a high product yield to be obtained from low-molecular copolymers and a high conversion rate of unsaturated compounds without additional operations.

It should also be noted that the low-active monomer VCH is present in the system, which does not appear to have high reactivity in the radically initiated processes.

Analysis of the molecular masses (Table 2) of the oligomers showed that they are characterised by small magnitudes and high polydispersibility.

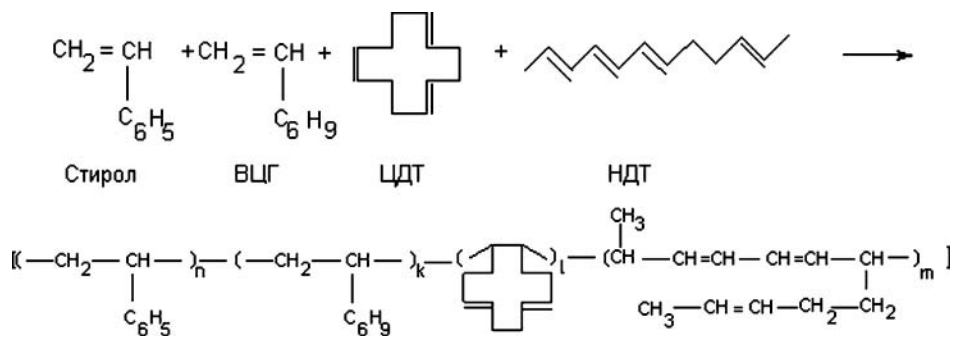
$$M_n = 1202;\ M_w = 6826;\ M_v = 4424;\ M_z = 84173;\ M_w/M_n = 5.68;\ M_z/M_w = 12.33$$

The average molecular weight M_n of all the products obtained was low and did not exceed 2,000. The molecular mass increased with an increase of styrene content in the batch. The low values of the molecular mass M_n of the polymers obtained can be explained by two factors:

- The presence of inhibitors of the radical polymerisation in the system which break the growing polymer chain at an early stage of its formation
- The high synthesis temperature

This could also explain the weak effect of reactive monomers such as styrene on the growth of the polymer chain.

A possible process flow diagram of copolymerisation for unsaturated compounds contained in the stillage bottoms of the return toluene distillation with styrene can be presented in the following form:



The IR spectra of the copolymers obtained show the presence of absorption bands characteristic of the benzene ring at 1660–2000, 1601, 1493, 755 and 700 cm^{-1}; valence vibrations ν (CH) in the groups $CH_2{=}CH{-}$ and $-CH{=}CH-$ at 3080 and 3010 cm^{-1}; ν (C=C) in the group CH=CH at 1690 cm^{-1} and ν (C=C) in the group $CH{=}CH_2$ at 1630 cm^{-1}; valence vibrations ν (CH_2) at 3060–2850 cm^{-1}; and deformation vibrations (δ) of the $-CH_3$ group at 1380 and 1450 cm^{-1}.

The results of PMR spectroscopy confirm the results of the IR spectroscopy investigations of the structure. The spectrum includes signals of aromatic protons in the range of 6.5–7.7 ppm, a broad peak in the range of 0.5–2.7 ppm characteristic of methene and methylene protons in the polymer chain, and a signal in the range of 5.4 ppm characteristic of the protons in the endocyclic double bond.

Synthesised oligomers are characterised by low molecular mass and small macromolecular size, thus making them resemble oils – softeners, in fact. These softeners are widely used in the synthetic rubber industry for the plasticisation of rubbers, in the tyre and mechanical rubber goods industries, in paints and varnishes, as well as in the production of impregnating compositions for treating wood, etc.

Application of Oligomers

A set of properties of the synthesised oligomers made it worth studying them as possible filler for butadiene rubber introduced at the extraction stage from solution.

In accordance with the method used in the industry, during synthetic rubber (SR) synthesis a hydrocarbon solution of butadiene rubber (polymerisate) from the final process vessel of the polymerisation battery was supplied to deactivate the catalytic complex with alkalised water; it was then loaded with antioxidant (bis-(2-oxy-5-methyl-3-tert-butylphenyl) methane) in the form of a toluene solution with a concentration of 4–6 mass %. Thereafter the solution containing the antioxidant was degassed.

In this study, a toluene solution of synthesised oligomer was first stirred with antioxidant with an agitator. The solution obtained was introduced into the polymerisate before degassing. The polymerisate, which contained antioxidant and oligomers, was then degassed. The rubber grit formed in this process, which contained oligomers, was wrung out after it had been separated from the aqueous phase, and then crushed and dried at 80–85°C.

A specific feature of this method is that the toluene solution of the oligomer obtained was used for preparation of the mixture of antioxidant and oligomer without preliminary distillation of non-polymerised monomers. This seems quite reasonable, since low-molecular fractions were later distilled from the oligomer during water degassing, simultaneously with a solvent and unsaturated compounds from the polymerisate of the butadiene rubber. After

Table 3. Properties of butadiene rubber and vulcanisates with different oligomer contents

	Oligomer contents in butadiene rubber, mass %		
Factors	0.3	0.6	1.0
Mooney viscosity MB 1 + 4 (100)	47.0	46.0	45.5
Loss of mass at drying, %	0.16	0.18	0.16
Mass fraction of ashes, %	0.14	0.15	0.16
Mass fraction of antioxidant: Agidol-2, %	0.8	0.8	0.8
Engineering stress at 300 % elongation, MPa	7.5	7.3	7.3
Engineering strength at extension, MPa	19.5	19.0	18.9
Relative elongation at disruption, %	550	540	540
Relative residual deformation after disruption, %	8	8	8

Note: The oligomers were synthesised when styrene was introduced into the batch in an amount of 50 mass %. The vulcanisation temperature was +143°C; the duration of the vulcanisation process was 40 min.

distillation of the return solvent, the low-molecular fraction was once again concentrated, while unsaturated compounds remaining in the stillage bottoms were repeatedly returned for polymerisation.

Rubber compounds were produced from the samples of butadiene rubber obtained according to the standard procedure. These compounds were vulcanised and tested according to the conventional procedures. The results of the tests are presented in Tables 3 and 4.

Table 4. Properties of butadiene rubber containing 1 mass % of oligomers and vulcanisates obtained from this rubber

	Styrene content in the batch, mass %						Reference sample
Factors	0	10	25	50	75	90	
Mooney viscosity MB 1 + 4 (100)	44.0	45.0	45.0	45.5	46.0	47.0	47.0
Loss of mass at drying, %	0.21	0.19	0.18	0.16	0.17	0.14	0.15
Mass fraction of ashes, %	0.15	0.17	0.18	0.16	0.17	0.18	0.18
Mass fraction of antioxidant: Agidol-2, %	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Engineering stress at 300 % elongation (M_{300}), MPa	6.9	6.7	7.0	7.3	7.2	7.3	7.1
Engineering strength at extension (f_p), MPa	18.0	18.2	18.4	18.9	19.2	19.4	19.7
Relative elongation at disruption ($E_{disr.}$), %	560	550	550	540	530	520	510
Relative residual deformation after disruption ($E_{resid.}$), %	10	10	9	8	9	7	8

Note: The vulcanisation temperature was +143°C; the duration of the vulcanisation process was 40 min.

Table 3 shows that the introduction of the oligomer into the butadiene rubber in an amount of 0.3–1.0 mass % (the styrene content in the base batch was 50 %) resulted in a slight decrease in the strength properties and the Mooney viscosity.

The introduction of 1 mass % of the oligomer into the rubber (the styrene content in the base batch was 0–50 %) (Table 4) resulted in a simultaneous decrease in engineering stress at 300 % elongation (M_{300}) for vulcanisates, a decrease of engineering strength at extension (f_p), an increase in relative elongation at the disruption ($E_{disr.}$), and relative residual deformation after disruption ($E_{resid.}$). This can be explained by partial plasticisation of the butadiene rubber with this oligomer. Moreover, the presence of 1 mass % of the oligomer resulted in a decrease of Mooney viscosity of the rubber by 2–3 arbitrary units, which is similar to the effect of introducing a conventional plasticiser, PN-6k oil, into rubbers.

In turn, the introduction of the same amount (1 mass %) of oligomer obtained with a large styrene content in the macromolecule (the base content of the styrene in the batch was 75–90 %) mitigates the effect of plasticisation. The value of f_p is reduced to a lesser extent, while the M_{300} factor increases. The values of $E_{disr.}$, $E_{resid.}$ for vulcanisates with the oligomer do not in fact differ from those of the reference product of butadiene vulcanisation. The plasticising effect of the synthesised oligomer with a high styrene content on butadiene rubber is probably compensated for by its specific influence on vulcanisates, similar to the effect of a resin with a high styrene content used for rubber filling [6].

Conclusions

The presence of small amounts of additives (1.0 mass %) of oligomer synthesised at various styrene contents in the batch equal to 75–90 mass % has a weak plasticising effect on butadiene rubber with little loss of f_p and Mooney viscosity and without deterioration of the factors M_{300}, $E_{disr.}$ and $E_{resid.}$ for vulcanisates.

The advantages of this approach to waste utilisation are the following:

- Decrease in losses of hydrocarbon raw materials – solvent (toluene) and butadiene with insignificant cost of raw styrene
- Purposeful use of stillage bottoms for solvent recovery in polybutadiene production for the fabrication of oligomers
- Partial replacement of the oil plasticiser by synthesised oligomers, which makes it possible to control the Mooney viscosity of polybutadiene

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