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SPECTROSCOPIC RESEARCH OF POLYIZOBUTYLENE DESTROYED BY DESTRUCTION

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Abstract

The temperature dependence of specific heat of poly(isobutene) degraded under the action of strong Lewis acids has been investigated. From the calculated thermodynamic parameters have been drawn conclusions on the structural conversions of the macromolecules in the process of catalytic degradation. By means of 13C NMR the formation of branched macro- molecules was shown. On the basis of the results a degradation mechanism for poly (isobutene) is suggested.

Keywords:
^{13}C nuclear magnetic resonance spectra;
Catalyst;
Polyisobutylene;
Lewis acids;
Polyolefin; Cationic;
Ion-coordination;
Free radical;
Carbocation.

Introduction

Previously in [1] we found out that catalytic degradation of poly(isobutene) (PIB) under the action of strong Lewis acids (LA) ($AlBr_3$, $A1C1_3$, $AlEtCl_2$) under mild conditions of 20 to 60 °C takes place according to the radical-chain mechanism. Itisknown that in radical-chain polymerization, together with the primary reaction, secondary reactions of chain branching take place, which result in substantial structural'conversions [5-7]. To identify the peculiarities of structure formation in the process of PIB catalytic degradation under LA action calorimetric and ^{13}C NMR investigations of degradation PIB were carried out.

From calorimetric studies, it is clear that the process of weakening of the catalyst layer with the help of powerfulLewis acids is subjected to a continuous structural change from the line of polyisobutylene structure and branched macromolecules.

The importance of work confirms ^{13}Cnuclear magnetic resonance information, the origin of branched macromolecules and the presence of segregated polyisobutilenes in macromolecules the radical-chain mechanism of macromolecules disintegration with the action of Lyuis acids. [2]

Experimental

Experiments were conducted at 20-60 °C in a vacuum. Pressure is ($\approx 10^{-3}$ mmHg). The solvents are hexane and decane. Catalysts ($AlEtCl_2$, $AlBr_3$, $AlCl_3$) were used. For 20 °C solvent n-hexane was taken, but for 40 °C solvent decane was taken. [PIB] is – 0.8 g, total volume is 34 ml τ - 1, 3, 5 hours. Density of the catalyst was equal to 0.013 mol/l and $2 \cdot 10^{-2}$ mol/l and $2.7 \cdot 10^{-2}$ mol/l. Deactivation of the reaction system was carried out with methanol. Precipitated polymer was separated from substrate in a glass filter. Then rubber-like polymer was filtered using water pump, dissolved in normal hexane. Such precipitation process was repeated 3-4 times. Separated polymer was dried in a furnace at 40 °C in $\approx 10^{-3}$ mmHg. After separation of a substrate polymer it was analyzed to check the formation of oligomer products. This was conducted by evaporation of a solvent and NMR method.

Calorimetric and (NMR) studies have been conducted to investigate the changes of the stucture of product.The temperature dependence of C_p was studied in a low temperature vacuum adiabatic calorimeter

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with automatic control of adiabatic conditions within the temperature range of 55 to 300 K. The procedure for C_p measurement and the apparatus were described in [6]. The mass of the copper cell was equal to ≈ $6{\cdot}10^{-3}$ kg; the batches of studied PIB samples were about 10^{-3} kg. The error of C_p determination was less than 1%. By means of graphic integration of C_p =f(T) and

C_p=/(lnT) the functions *H(T))-H(O)* and *S(T)-S*(0) were calculated.Tg was calculated from the relation *S(T)—S*(0)=*f*(*T*).

^{13}C NMR spectra were recorded with the spectrometer «Bruker» WP3-200 SU (200.13 MHz). Tetramethylsilaneand deuterobenzene were used as internal standard and solvent, respectively.

Results and discussion

The thermodynamic properties of the studied PIB, which were different from each other only in their treatmentconditions, were correlated with $AlEtCl_2$ concentration and degradation duration. Temperature dependence of C_p for the studied PIB samples and calculated thermodynamic parameters are presented in figure 1 and table 1.

The analysis of the C_p curves for initial and degraded PIB shows their sharp distinctions, in particular in the viscoelastic state (≈ 200 to 300 K). C_p of degraded PIB (2 to 5) have low values in comparison with C_p of the initial PIB (O), while Cp of the degraded PIB (1, 6 to 9) have high values in comparison with C_p of samples 2 to 5 and initial PIB. Such sharp distinctionin C_p of the degraded and initial samples apparently indicate that in the degradation process the PIB structure undergoes substantial changes. It may be supposed that in the degradation process the production of branched macromolecules takes place, as well as decomposition of longer linear macromolecules into some smaller linear macromolecules, which can also differ by the bond type of repeated monomer segments. The origin ofsuch morphological structures is likely to determine the thermodynamic parameters of the studied PIB samples (tabl.1). The production of crosslinking (gels) in the degradation process under the investigated conditions has not been observed [9-10].

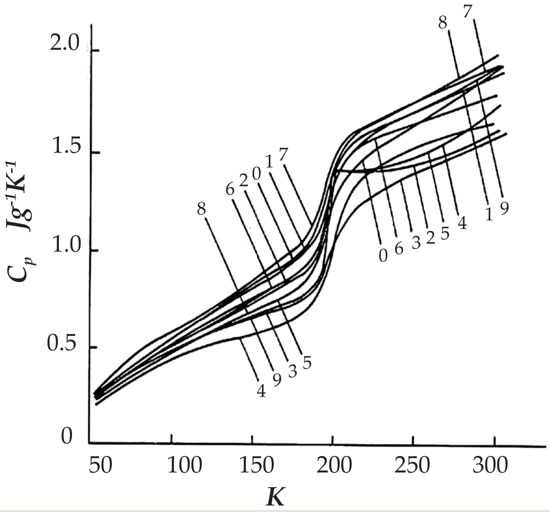


Fig.1. Temperature dependences of C_p for initial and degraded PIB samples. Numbers on the curves correspond to the numbers in table 1

The well-known fact that the thermodynamic parameters of macromolecules are directly connected with

Table 1

Experimental data and thermodynamic parameters of initial degraded PIB [PIB] = 3.8 wt %; *T* = 20 °C Initial PIB: C_p(300) = 1.823 J/g.K; H(300) - H(55) = 263.8 J/g; S(300) - S(55) = 1.430 J/g.K;T = 200 K

№	$[AlEtCl_2]\times$ $\times 10^2$ mol/l	Reaction time, in h	*T* = 60 KJ/g .K	C_p *T* = 150 KJ/g .K	*T* = 250 KJ/g .K	S(300) - S(55) J/g .K	H(300) - H(55) J/g	T_s K
1	0.05	1	0.275	0.731	1.643	1.382	256.7	201
2	0.27	1	0.195	0.842	1.707	1.510	276.2	200
3	1.3	1	0.254	0.558	1.545	1.206	225.0	202
4	0.5	3	0.285	0.794	1.756	1.469	273.7	200
5	0.27	3	0.233	0.749	1.445	1.297	237.6	202
6	1.3	3	0.275	0.734	1.478	1.335	242.5	200
7	0.05	10	0.251	0.730	1.709	1.375	260.4	201
8	0.27	10	0.205	0.644	1.377	1.182	218.6	203
9	1.3	10	0.283	0.835	1.725	1.487	273.8	201

their dynamic and morphological structures [4-7] allows to explain the difference of the calculated thermodynamic parameters of the studied PIB samples. High C_p values of degraded samples (1, 6 to 9) in comparison with the initial PIB can evidence that the intermolecular interaction forces in these samples decrease due to the decomposition of long linear macromolecules into linear macromolecules of smaller size.Temperature increase results in the intensification of relaxation processes, which predetermine a labile dynamic structure and rising of C_p both inTg region and in viscoelastic state. Low C_p values of degraded PIB samples (2 to 5) in relation to C_p of the initial (0) and degraded samples (1, 6 to P) can be attributed to the growth of intermolecular interaction. The growth of intermolecular interaction. The growth of intermolecular interaction in saturated polyolefines including PIB can be explained only by the production of branching's leading to the so-called physical crosslinking, which imparts some hardness to the macromolecular structural elements due to the decrease of the frequencies of their oscillating motion. The more branching's there are in the macromolecule and the harder is the macromolecule, the lower is its specific heat [9-10]. Branching's that determine the physical crosslinking result also in the diminishing of the entropy parameter, for example in the samples 2 to 5.

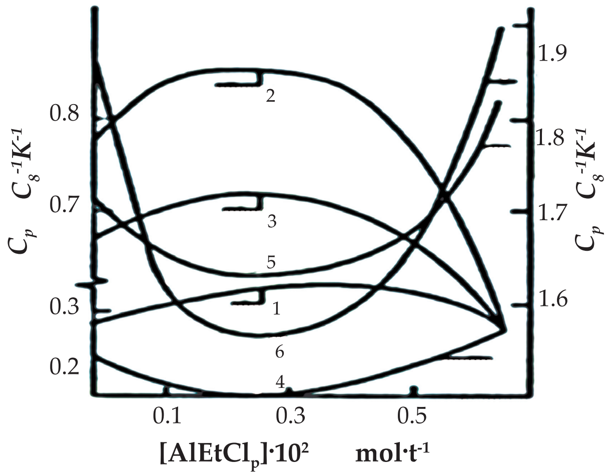


Fig.2. Dependence of C_p of degraded PIB produced at various catalyst concentrations, reaction times, and temperatures.
1 - 60 K, 1 h; 2 - 150 K,lh; 3 - 250 K,1 h;
4 - 60 K, 10 h; 5 - 150 K, 10 h; 6 - 250 K, 10 h

On the contrary, in the samples 1.6 to 9 the entropy value grows, and this can be explained by the fact that in them the atomic-molecular motion of both structural elements and macromolecules on the whole is not hindered due to the labile dynamic structure.

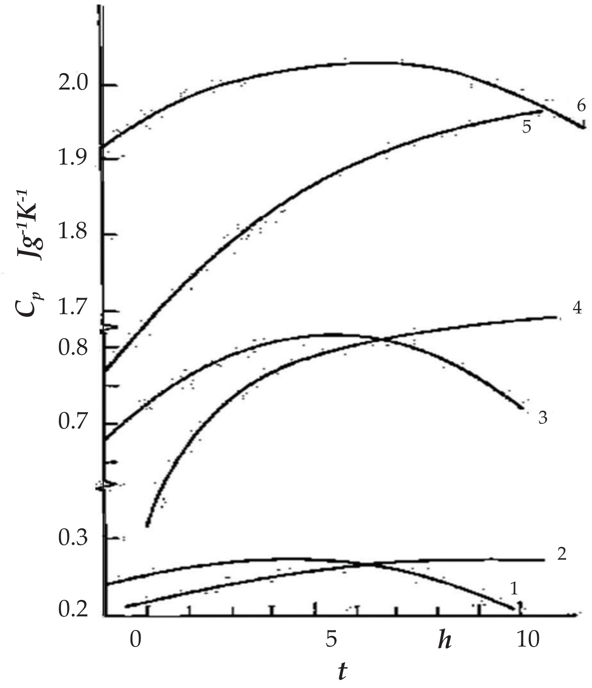


Fig.3. Dependence of C_p of degraded PIB on degradation time.
1, 3, 5 - [AlEtCl$_2$]=9.2 10^{-3} mol/l^{-1},
2, 4, 6 - [AlEtCl$_2$]=2.3 10^{-1} mol/l^{-1}.
1, 2 - *T*=60 K; 3, 4 - *T*=150 K; 5, 6 - *T*=300 K

The structural variations in the PIB macrochain are in direct relation both to the degradation duration and to the catalyst concentration (tabl.1).

According to the data for C_p changes, the optimization of catalytic degradation becomes possible depending on the above mentioned degradation parameters. That is of great importance for the control of structure formation processes.

Figures 2 and 3 show C_p diagrams for degraded PIB versus catalyst concentration and degradation time, respectively. On the C_p diagram in figure 2, plotted for three temperatures of 60, 150 and 250 K one can see distinctly the extremal dependences of C_p, maximum and minimum of which fall on the average catalyst concentration $0.27\cdot10^{-2}$ mol/l. If one takes into account that the less C_p the stronger is the macromolecule interaction [3], then the conclusion can be drawn from this diagram that to get a stable structure at the degradation time of 1 h a high catalyst concentration of $0.13\cdot10^{-1}$ mol/1 is required. During 10 h more stable PIB is formed at the average catalyst concentration of $0.27\cdot10^{-2}$ mol/1.

Figure 3 shows C_p diagrams for the two extreme catalyst concentrations $0.5 \cdot 10^{-3}$ and $0.13 \cdot 10^{-1}$ mol/1. C_p curves of PIB samples produced at a low catalyst concentration have a maximum at the degradation duration of 5 h, but C_p of PIB samples produced at high catalyst concentration exhibit monotonous C_p rise with degradation duration. The analysis of these curves (fig.3) allows drawing the conclusion that at low catalyst concentration PIB undergoes considerable degradation (i.e. structure conversions) at the degradation duration 5h, but at high catalyst concentration the longer degradation duration, the greater are the structure conversions. Thus, it becomes obvious from the calorimetric investigations that PIB structure in the process of catalytic degradation under the action of strongLAundergoes substantial structural transformations to form both linear and branched macromolecules.

To study the peculiarities of structural transformations, investigations of degraded PIB microstructure have been carried out by means of ^{13}C-NMR. It is known that for polymers with a high stereo regularity interpretation of ^{13}C-NMR spectra can be based on the structure of a single repeating segment. [7] In this case, as the experience shows, the chemical shifts of carbon atoms reflect some averaged segment surrounding conditions over all conformation states. When analyzing monomer sequences the procedure of shift prediction can be successfully applied by calculation of the following *Lindeman-Adams* scheme with the help of the relationship

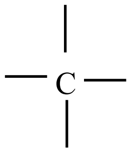
$$\delta(k) = \beta_s + \sum_{M=2}^{4} D_M A_{SM} + \lambda_s N_{kP} + \Delta_s N_{kP}$$

where $\delta(k)$ is the chemical shift of the k-th carbon atom, β_s, A_s, γ_s and Δ_s are constants, D_M is the number of carbon atoms which have M attached carbon atoms and are bonded to the k-th carbon atom; S is the number of carbon atoms, bonded to the k-th atom, N_{kP} is the number of carbon atoms within the distance of P bonds from the k-th carbon atom.

Table 2 shows experimental and calculated values of chemical shifts for the carbon atoms of the PIB elementary segment. The difference between calculated and experimental values of chemical shifts with respect to the data for the carbon atoms $-CH_2-$, >C<, and $-CH_3$ is 5.3, 1.8, and 2.1 ppm, respectively. The experimental chemical shifts are displaced towards weak field, and if one takes into consideration that large shifts towards weak field are typical of α - and β - substitution and that in case of γ - substitution the shift must take place in the opposite direction, then these differences between experimental and calculated chemical shifts can be attributed to the absence of correction both for the polymer chain length and its confirmation in the calculation.

Table 2

Experimental and calculated values of chemical shifts of carbon atoms of the PIB elementary segment

carbon atom	Chemikal shifts		
	experimental$^{(1)}$ ppm	calculated$^{(1)}$ ppm	experimental$^{(2)}$ ppm
$-CH_2-$	59.6	54.3	59.5
	38.2	36.4	38.3
$-CH_3$	31.3	29.2	31.6

Nevertheless, ^{13}C-NMR spectra of PIB are well interpreted within the model of one repeated segment, in which the contributions of monomer units to the chemical shifts are additive. Figure 4 illustrates ^{13}C-NMR spectra of degraded PIB. The spectra of the initial and of the degraded PIB are substantially different. The resonance signals of carbon atoms of the repeating unit display slight shifts towards weak field. The value of this shift changing from sample to sample is not equal for various atoms of one unit. It is 0.8, 0.6 and 0.4 ppm for groups $-CH_2-$, >C<, and $-CH_3$, respectively (table 3). The fact that the value of resonance signal shift does not change from sample to sample seems to demonstrate, first, a single degradation mechanism and, second, this can result from conformation changes in PIB microstructure as well, the occurrence of which is also a consequence of a single mechanism of catalytic polymer conversion.

Taking into account the radical-chain mechanism of PIB macromolecule decomposition under the action of LA as established previously [1-3], one can suppose the realization of probable structures shown in Scheme 1.

Table 4 illustrates the values of chemical shift for carbon atoms of all tree structures, calculated after the *Lindeman-Adams* equation and values of chemical shift corrected with experimental data by the method of graphic

Table 3

Chemical shifts of resonance signals in the ^{13}C-NMR spectra of degraded

Sıgnal №	Chemikal shift			
	İntial PİB ppm	I ppm	II ppm	III ppm
1	$59.9^{(1)}$	60.2	$60.3^{(1)}$	$60.3^{(1)}$
2	$38.3^{(1)}$	60.0	59.8	59.9
3	$31.6^{(1)}$	57.4	51.5	50.0
4		51.7	45.0	43.1
5		48.2	$38.9^{(1)}$	39.7
6		40.8	38.4	39.4
7		39.1	$32.0^{(0)}$	$38.9^{(1)}$
8		$38.9^{(1)}$	31.2	32.9
9		38.6		32.5
10		$32.0^{(1)}$		$32.0^{(1)}$
11		31.6		
12		25.5		

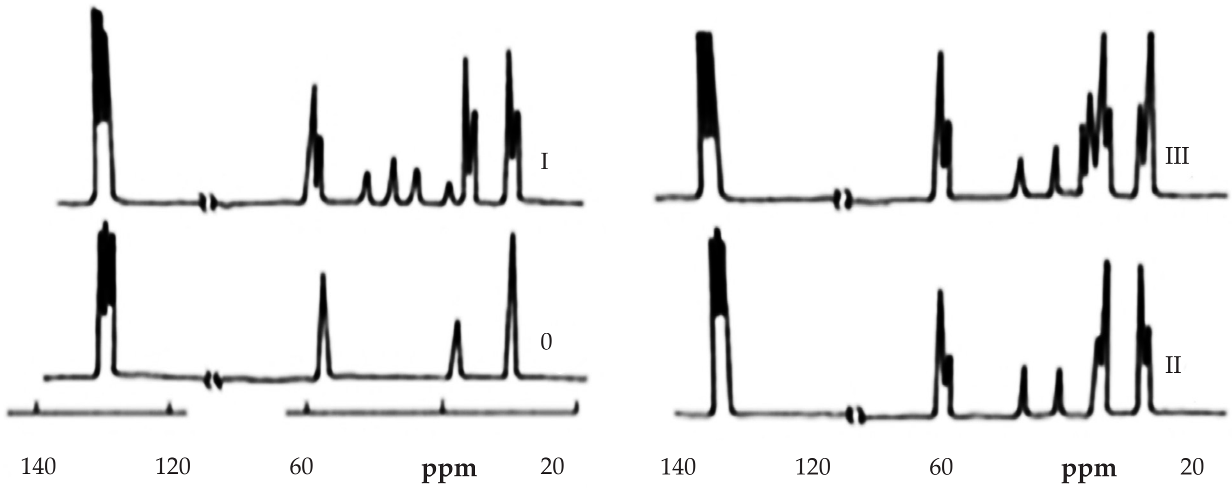


Fig.4. ^{13}C-NMR spectra of the initial PIB (0) and of degraded PIB
Degradation conditions:
I - [PİB] = 1.43 wt %; $[AlEtCl_2] = 0.27 \cdot 10^{-2}$ mol/l; $T = 20$ °C; $t = 1$ h
II - [PİB] = 3.8 wt %; $[AlEtCl_2] = 0.27 \cdot 10^{-2}$ mol/l; $T = 20$ °C; $t = 3$ h
III - [PİB] = 3.8 wt %; $[AlEtCl_2] = 0.27 \cdot 10^{-2}$ mol/l; $T = 60$ °C; $t = 3$ h

extrapolation with respect to the carbon atom signals of a repeated segment [8].

Analyzing the data of tables 3 and 4 one can affirm that in the samples under study the structure (2) is mainly realized It is particularly distinctly confirmed for the PIB1 sample.

For the PIBIII sample realization of structure (3) can beprobably considered. A thorough analysis of ^{13}C-NMR spectra for degraded PIB allows to conclude that in the process of catalytic degradation the PIB structure undergoes considerable changes confirming the results of calorimetric investigations to form branched macromolecules [4].

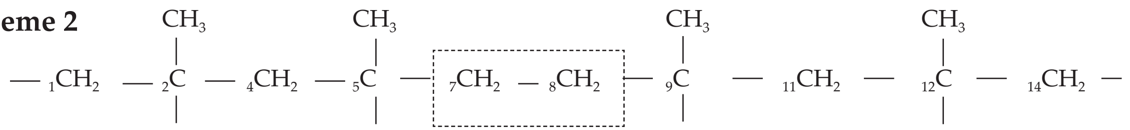
Structures (2) and (3) are derivatives of structure (1) and therefore their production can be shown by the structural conversions of PIB as a result of catalytic decomposition (Scheme 2). Thus, the ^{13}C-NMR data, namely production of branched macromolecules and occurrence of degradative PIB segments in the macromolecules, confirm a radicalchain mechanism of catalytic decomposition of the macromolecule under the action of strong Lewis acids [2] (Scheme 3).

Table 4

Calculated values of chemical shifts of carbon atoms

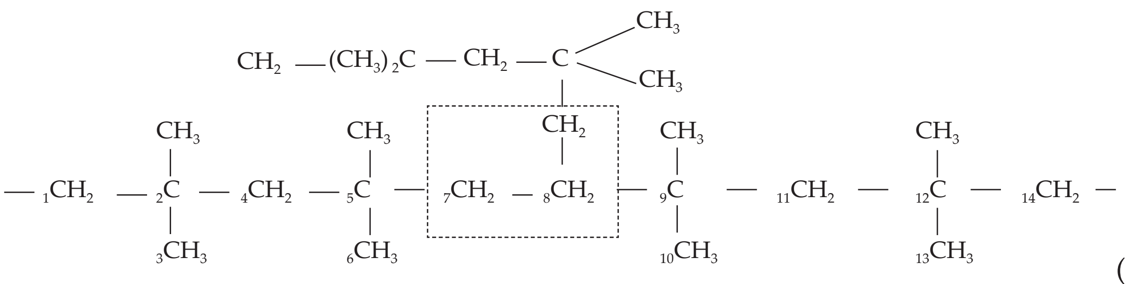
Carbon atom	Fragment	Chemikal shifts					
		Structure (1)		Structure (2)		Structure (3)	
		calculated ppm	graphic extrapol-on ppm	calculated ppm	graphic extrapol-on ppm	calculated ppm	graphic extrapol-on ppm
C_1	$-CH_2-$	54.32	59.3	59.32	59.3	54.32	59.3
C_2	$-\overset{\mid}{\underset{\mid}{C}}-$	36.37	39.4	36.37	39.4	36.37	39.4
C_3	$-CH_3$	29.24	31.2	29.24	31.2	29.24	31.2
C_4	$-CH_2-$	53.82	58.8	54.09	59.2	54.07	59.1
C_5	$-\overset{\mid}{\underset{\mid}{C}}-$	35.01	37.9	35.69	38.6	35.69	38.6
C_6	$-CH_3$	28.26	30.03	28.75	30.8	28.75	30.08
C_7	$-CH_2-$	36.76	40.0	41.77	45.6	35.89	38.9
C_8	$-CH$	–		36.87	40.01	49.11	53.7
C_9	$-\overset{\mid}{\underset{\mid}{C}}-$	–	–	37.39	40.5	38.75	42.2
C_{10}	$-CH_3$	–	–	25.76	27.5	26.74	28.5
C_{11}	$-CH_2-$	–	–	51.38	56.3	51.88	56.8
C_{12}	$-\overset{\mid}{\underset{\mid}{C}}-$	–	–	36.37	39.4	36.37	39.4
C_{13}	$-CH_3$	–	–	29.24	31.2	29.24	31.2
C_{14}	$-CH_2-$	–	–	54.32	59.3	54.32	59.3

Scheme 2

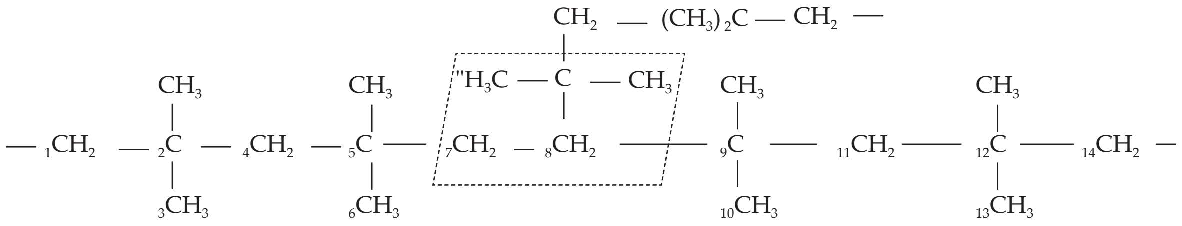


$$-{}_1CH_2-{}_2\overset{CH_3}{\underset{{}_3CH_3}{C}}-{}_4CH_2-{}_5\overset{CH_3}{\underset{{}_6CH_3}{C}}-\boxed{{}_7CH_2-{}_8CH_2}-{}_9\overset{CH_3}{\underset{{}_{10}CH_3}{C}}-{}_{11}CH_2-{}_{12}\overset{CH_3}{\underset{{}_{13}CH_3}{C}}-{}_{14}CH_2-$$

(1)

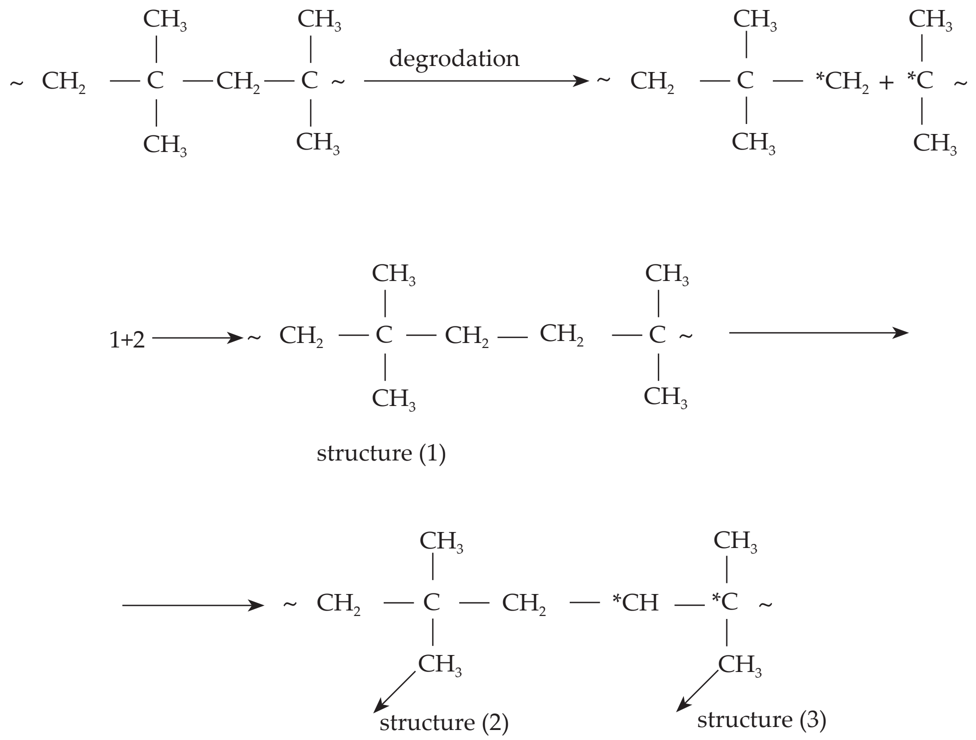


(2)

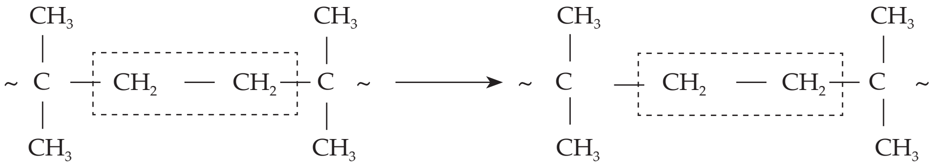


(3)

Scheme 2



Scheme 3



Result

1. It is known that to the initial reaction of polymerization with the radical chain mechanisms, secondary reactions occur resulting in a strong structural change occur.

2. By the effects of Lewis acids calorimetric and ^{13}C-NMRnuclear magnetic resonance studies have been conducted to detect the characteristics of structural formation in the process of catalytic destruction of polyisobutylene

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Спектроскопические исследования полиизобутилена разрушенного деструкцией

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Реферат

Изучены термодинамические функциональные исследования деструктурированного полиизобутилена под действием сильных кислот Льюиса при низкотемпературной и вакуумной адиабатической калориметрии. Структурные изменения макромолекул при низкой плотности катализатора основаны на вычисленных термодинамических результатах. ^{13}C-NMR показана структура разветвленных макромолекул через углерод-ядерный магнитный резонанс. В соответствии с результатами предлагается изменение механизма полиизобутилена.

Ключевые слова: ^{13}C-NMRспектры; катализатор; полиизобутилен; кислоты Льюиса; полиолефины; катион; ионная координация; свободные радикалы; карбокатион.

Desturuksiyaya məruz qalmiş poliizobutilenin spektroskopik tədqiqatlari

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Xülasə

Güclü Lyuis turşularının təsiri ilə desturuksiya olunmuş poliizobutilenin termodinamiki funksional araşdırmaları aşağı temperaturalı vakuum adiobatik kalorimetrdə öyrənilmışdir. Katalizatorun aşağı qatılığında makromolekullardakı struktur dəyişikliyi hesablanmış termodinamik nəticələr əsasında əldə edilir. ^{13}C-NMR karbon-nüvə maqnit rezonansı vasitəsilə şaxələnmiş makromolekulların quruluşu göstərilir. Nəticələrə əsasən poliizobutilenin mexanizmindəki dəyişiklik təklif edilir.

Açar sözlər: ^{13}C-NMR spektri; katalizator; poliizobutilen; Lyuis turşuları; poliolefin; kation; ion-koordinasiya; sərbəst radikal; karbokation.