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Polymerization of isobutylene initiated with the system 2,5-dichloro-2,5-dimethylhexane/$SnCl_4$

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Summary

The polymerizations of isobutylene in dichloromethane at -20°C initiated with the system 2,5-dichloro-2,5-dimethylhexane (DDH)/$SnCl_4$ were investigated. The polyisobutylene (PIB) samples obtained were examined by GPC and their molecular weight distribution curves were determined. It was found that PIB products obtained by the conventional procedure have a bimodal MWD and the weight content of the lower-molecular weight fraction increases with increasing concentration of DDH in the polymerization feed. The effect of ageing of DDH/$SnCl_4$ mixtures prepared in advance on MWD of the PIB samples was also proved. The results achieved lead to a conclusion that the ageing of the initiation system consists probably in the formation of the complex DDH-$SnCl_4$-H_2O, which protogenically again initiates the oligomerization of isobutylene, giving rise to oils with a narrow MWD, the polydispersity index $\overline{M}_w/\overline{M}_n \leq 1.3$. The possible role of the coordination polymerization mechanism is discussed.

Introduction

In an earlier paper (1) we investigated the effect of tert-butyl chloride (t-BuCl) on the polymerization of isobutylene in the presence of a Lewis acid $SnCl_4$. We found that the addition of t-BuCl into the polymerization feed gives rise to two polyisobutylene (PIB) products differing in their molecular weight. The isolated PIB samples had a pronounced bimodal MWD and the higher-molecular weight (HMW) fraction was demonstrably a product of the protogenic initiation of cationic polymerization of isobutylene initiated with the system $H_2O/SnCl_4$. The results obtained (1) led to an unequivocal conclusion that the formation of the lower-molecular weight (LMW) fraction is caused by the presence of t-BuCl in the polymerization system.

If isobutylene was polymerized at -20°C with the aged initiation systems t-BuCl/$SnCl_4$, then the only product thus obtained was the LMW fraction of PIB, having the character of PIB oil, $\overline{M}_n < 500$, $\overline{M}_w/\overline{M}_n \leq 1.4$. Since these PIB oils had a very low chlorine content (< 0.4 wt%), it may be assumed that t-BuCl in the reaction system does not act as an initiation-transfer (inifer) agent. A question then arises in what way t-BuCl is operative in the polymerization process, i.e. what polymerization mechanism leads to the formation of the LMW PIB fraction. Since in the case of the initiation system t-BuCl/$SnCl_4$ it cannot be distinguished in what way tert-butyl structures in the heads of PIB chains are formed (protogenic initiation with residual water of the reaction system, initiation with t-BuCl, transfer to monomer), this study has been focussed on a detailed investigation of the polymerization mechanism, using 2,5-dichloro-2,5-dimethylhexane (DDH)/$SnCl_4$ as the initiation system.

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Experimental

The purification and drying of isobutylene, CH_2Cl_2, and nitrogen have been reported earlier (2), along with the preparation of DDH (3). $SnCl_4$ was purified by distillation in vacuo and dosed in a CH_2Cl_2 solution.

Isobutylene was polymerized at -20°C in a CH_2Cl_2 solution in glass ampoules 20 ml in volume, provided with a three-way teflon closure allowing dosage of the reaction components in a flow of nitrogen. The reaction components were dosed by employing three procedures: mode A – $SnCl_4$ was dosed in CH_2Cl_2 as the last component into the monomer, or into a mixture of the monomer and DDH, mode B – a freshly prepared mixture of DDH and $SnCl_4$ in CH_2Cl_2 was dosed into the monomer, mode C – into the monomer was dosed a mixture of DDH and $SnCl_4$ in CH_2Cl_2, which prior to the dosage was left to stand at room temperature for 48 h. The polymerization conditions are summarized in Table 1. Isolation and drying of the products have been reported elsewhere (2).

Spectrophotometric measurements of mixtures DDH/CH_2Cl_2, $SnCl_4/CH_2Cl_2$, and DDH/$SnCl_4/CH_2Cl_2$ were carried out with an HP-8451 A (Hewlett-Packard) apparatus in the wavelength range 200-700 nm, at 25°C in a Hellma 1 mm quartz cell provided with a three-way teflon closure for the dosage of components in a flow of nitrogen. The cell was dried using a procedure reported earlier (2).

Gel permeation chromatography (GPC) was carried out in an HP-1084 B apparatus, with tetrahydrofuran as the eluent. MWD values were calculated using universal calibration; the Mark-Houwink relations used for polystyrene and PIB were reported earlier (2).

The ^{1}H-NMR spectra were recorded with a Bruker AC-300 spectrometer at a frequency 300.1 MHz and room temperature. Solutions of DDH and mixtures DDH/$SnCl_4$ in $CDCl_3$ (Merck) were investigated, the concentration of [DDH] was 0.5 M, the molar ratio of the components $SnCl_4$/DDH was two. Since two bands of hexamethyldisiloxane used as the standard were found for solutions of the DDH/$SnCl_4$ mixtures, the band of residual $CHCl_3$, lying at 7.29 ppm from tetramethylsilane, was used as the internal reference. The ^{1}H-NMR spectra of PIB oils were obtained by measuring 20 wt% PIB solutions in $CDCl_3$.

The chlorine content in the PIB samples was determined analytically by the usual Schöniger method (4).

Results and Discussion

Fig.1 shows GPC records of PIB products obtained in polymerizations differing in the amount of DDH in the polymerization feed, dosage according to mode A. It can be seen in this Figure that also with DDH the isolated PIB is not a uniform product and contains a characteristic lower-molecular weight and higher-molecular weight fraction.

Moreover, from Fig.1 and Table 1, it is obvious that the weight content of the LMW and HMW fraction depends on the amount of DDH used; with increasing concentration of DDH in the polymerization system the formation of the HMW fraction decreases, which in turn reduces its weight fraction in the final product. Another important finding is the fact that within the limits of experimental error the different concentration of DDH does not affect the molecular weights of LMW and HMW PIB. Similarly to the case of t-BuCl(1), the HMW fraction again corresponds by its parameters to the product of protogenic initiation with the system $H_2O/SnCl_4$, having $\overline{M}_n \simeq 20000$ and $\overline{M}_w/\overline{M}_n \simeq 2.5$. Like the case where t-BuCl was used (1), the presence of DDH also slows down the polymerization

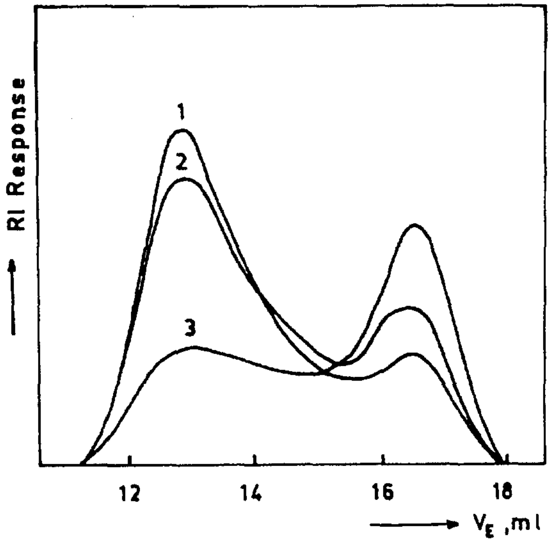


Figure 1: GPC records of PIB prepared at different DDH concentrations in the polymerization feed: 1 - [DDH] = 0.082 M, 2 - [DDH] = 0.17 M, 3 - [DDH] = 0.33 M

of isobutylene. Within the limits of experimental error the different dosage of the initiation system according to mode A and B was not reflected at all, neither in the molecular weights of the PIB samples nor in the weight content of the LMW and HMW fractions. It can be concluded, therefore, that in the presence of DDH, similarly to the case where t-BuCl was used (1), the polymerization of isobutylene leads to the formation of two different PIB polymers, probably as a consequence of two different polymerization mechanisms. Also, it has been shown experimentally that the slowed-down polymerization of isobutylene and the formation of the LMW fraction is caused by the presence of DDH.

In our preceding investigation of the initiation behaviour of the system t-BuCl/$SnCl_4$ we found (1) that the mixture shows the effect of "ageing", similarly to the systems t-BuCl/BCl_3 (2) and DDH/BCl_3 (3,5). The results of these studies (1,2,5) demonstrate that the extended time of interaction between both components of the initiation system

Table 1: Effect of DDH and its dosage mode on the properties of PIB

Dosage mode	[DDH] mol/l	LMW PIB wt.%	HMW PIB wt.%	Mol.weight $\overline{M}_n$
A[a]	0	0	100	20000
A,B	0.082	17	83	bimodal MWD
A,B	0.17	30	70	bimodal MWD
A,B	0.30	50	50	bimodal MWD
C	0.13	100	0	440
C	0.20	100	0	350
C	0.23	100	0	320

Polymerization in CH_2Cl_2 at −20°C: [isobutylene] = 5 M, [$SnCl_4$] = 0.0844 M, polymerization time 24 h, conversion c. 100%.
[a]Ref.(1)

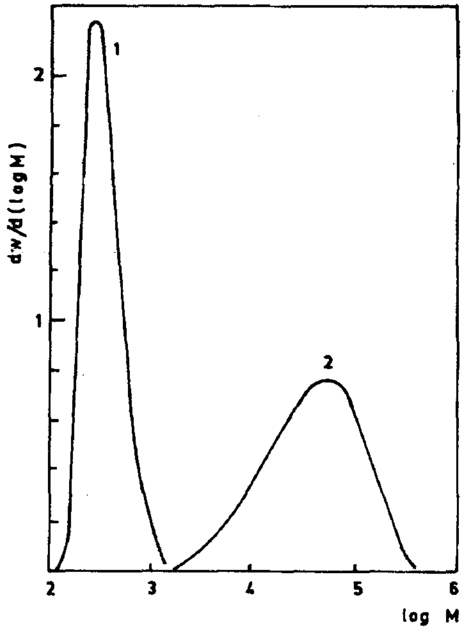


Figure 2: MWD curves of PIB samples obtained in the polymerization of isobutylene (in CH_2Cl_2, −20°C): 1 - [DDH] = 0.13 M, dosage mode C, 2 - in the absence of DDH, dosage mode A

before its addition to the solution of isobutylene in CH_2Cl_2 affects the composition of the PIB product, giving rise to the LMW fraction with a comparatively narrow MWD. Thus, e.g., if isobutylene is polymerized in CH_2Cl_2 at -20°C with the mixture t-BuCl/$SnCl_4$ as the initiator, which before being added to the solution of the monomer was left to stand at room temperature for 48 h, the only isolated product is the LMW fraction, having the character of PIB oil with the polydispersity index $\overline{M}_w/\overline{M}_n \leq 1.4$. This is why we carried out analogous polymerizations of isobutylene at -20°C, initiated with aged initiation systems DDH/$SnCl_4$, dosage of the initiation system according to mode C. The GPC analysis of polymeric products confirmed the anticipated effect of ageing of the initiation system. In these polymerizations, performed at the same concentrations of DDH as those used in the dosage of initiation systems according to mode A and B, no characteristic HMW fraction is formed any more (Table 1). Only the LMW PIB arises and the samples thus obtained have the character of oils, $\overline{M}_n < 500$, $\overline{M}_w/\overline{M}_n \leq 1.3$. The characteristic MWD of the sample of PIB oil is given in Fig.2 (curve 1), where for the sake of comparison the curve 2 demonstrates the MWD of PIB, $\overline{M}_n \simeq 20000$, $\overline{M}_w/\overline{M}_n \simeq 2.5$, synthesized in the absence of DDH. It may be assumed that the latter product is formed by the protogenic initiation with residual water in the reaction system (1).

The initiation system DDH/$SnCl_4$/CH_2Cl_2 changes its colour during ageing and the originally colourless mixture gradually turns to yellow and violet. We therefore investigated the interaction between DDH and $SnCl_4$ spectrophotometrically in the time interval 48 h, wavelength range $\lambda \geq 300$ nm, where the individual solutions of DDH and $SnCl_4$ in CH_2Cl_2 at the concentration 0.5 M did not show any absorption. The measurements showed that immediately on mixing the CH_2Cl_2 solutions of DDH and

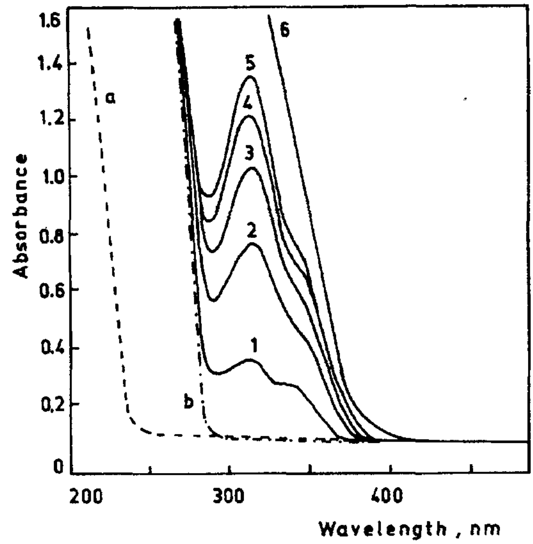


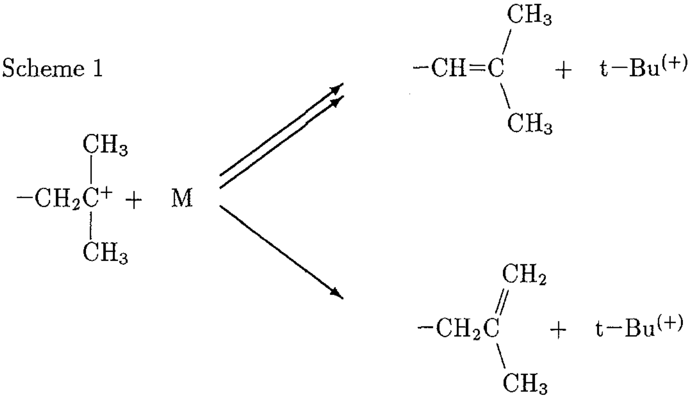
Figure 3: Time development of UV-Visible spectra of the system DDH/$SnCl_4$ in CH_2Cl_2: a - DDH only, [DDH] = 0.5 M, b - $SnCl_4$ only, [$SnCl_4$] = 0.5 M, 1,2,3,4,5 and 6 - spectra of the mixture recorded in 3,8,13,18,20 and 60 min., resp., after mixing 0.5 M solutions of DDH and $SnCl_4$, in the mole ratio 1:2

$SnCl_4$, the molar ratio [$SnCl_4$]/[DDH] = 2, a weak absorption band is formed in the range 300-350 nm. Absorbancy in the maximum of the band at 314 nm increased with time (Fig.3). The results obtained lead to a conclusion that DDH and $SnCl_4$ mutually interact, similarly to DDH and BCl_3 (3). It may be assumed, therefore, that on mixing of these components the complex DDH-$SnCl_4$ is formed in the system and its concentration increases with time. On the other hand, however, the interaction between DDH and $SnCl_4$ might also give rise to a new compound, especially if the possible role of dehydrochlorination products of DDH are taken into account. The system DDH/$SnCl_4$ was therefore subjected to a ^{1}H-NMR analysis. The spectra of DDH alone, of the freshly prepared mixture DDH/$SnCl_4$, and of the mixture DDH/$SnCl_4$ left to stand at room temperature for 48 h prior to measurement were compared with each other. The peaks observed corresponded to methylene and methyl groups and even at high amplification, no other groups, such as $CH_2=$ and $-CH=$, indicating the presence of dehydrochlorination products, could be detected.

In the polymerization of isobutylene it is generally assumed (6) that the transfer to monomer gives rise to polyolefin with the terminal double bond, i.e. that the proton is eliminated from $-CH_3$ groups against Saytzeff's rule. However, we have reported recently (7) that the transfer to monomer in the cationic polymerization of isobutylene carried out in the presence of $AlCl_3$ proceeds preferentially with the participation of the $-CH_2-$ group of the terminal monomeric unit, i.e. that the proton is eliminated according to Saytzeff's rule. In order to find out what terminal unsaturated structures are present in PIB obtained by using the initiation system DDH/$SnCl_4$ we carried out the ^{1}H-NMR analysis of samples of oils synthesized according to mode C. The analysis showed that PIB oils contain the end-unsaturated structures, with both the internal bond $-C\underline{H} = C(CH_3)_2$

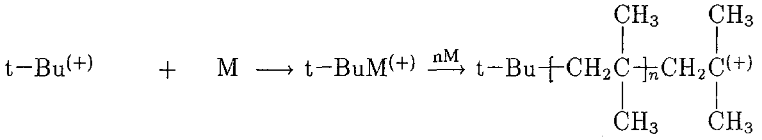
(δ 5.1 ppm) and with the external double bond $-C(CH_3) = CH_2$ (δ 4.58 and 4.78 ppm). The molar ratio of these characteristic unsaturated groups being c. 2.5 shows, however, that also in the case of $SnCl_4$ the transfer to monomer leads preferentially to the formation of PIB oil containing an internal double bond according to Eq.1, scheme 1, where M is the monomeric isobutylene. The signal at 1.00 ppm confirmed the presence of tert-butyl groups in polymer chains, with the molar ratio $t\text{-}Bu/(CH_2{=} + -CH{=})$ being approx. 1.3. The chloroisopropyl group $Cl(CH_3)_2C-$ (δ 1.66 ppm) has also been detected in a low concentration. The chemical shifts of all these groups are in agreement with the reported data (2,8,9). It should be mentioned, however, that the ^{1}H-NMR spectra of the oily LMW fraction are very difficult to interpret. For this reason, the content of chloroisopropyl groups, which is needed for the understanding of the role played by DDH in the polymerization process, was also determined from the analysis of chlorine. The chlorine content in various samples of PIB oils was always lower than 0.5 wt%.

Scheme 1



(1)

(2)



$$t\text{-}Bu^{(+)} + M \longrightarrow t\text{-}BuM^{(+)} \xrightarrow{nM} t\text{-}Bu\text{-}[CH_2C(CH_3)_2]_n\text{-}CH_2C(CH_3)_2^{(+)} \qquad (3)$$

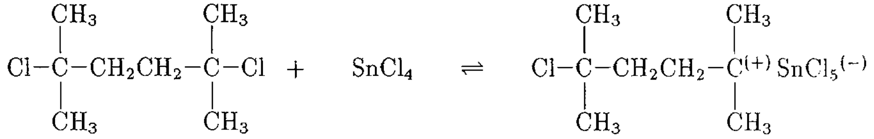
Let us now summarize the results obtained so far and discuss them in relation to the process of the polymerization of isobutylene. First, it is obvious that in the polymerizing system DDH/$SnCl_4$/isobutylene/CH_2Cl_2 two polymerization processes compete with each other, leading to different PIB products. The HMW fraction of PIB is a product of the protogenic initiation with residual water in the reaction system, Equations 4, 5, while the

$$SnCl_4 + H_2O \rightleftharpoons H^+SnCl_4OH^- \qquad (4)$$

$$\text{isobutylene} \xrightarrow{H^{(+)}SnCl_4OH^{(-)}} \text{HMW PIB} \qquad (5)$$

formation of LMW PIB is a consequence of the presence of DDH, which probably acts in the form of the complex DDH-$SnCl_4$. Due to the mutual affinity between H_2O and $SnCl_4$ and by analogy with the system t-BuCl/$SnCl_4$ (1) it may be assumed that the real initiation system giving rise to LMW PIB is the complex DDH-$SnCl_4$-H_2O. The content of the LMW and HMW fraction in the final PIB product is given by the concentration of DDH in the polymerization feed and as shown by experiments with aged initiation systems, by the concentration of the arising complex DDH-$SnCl_4$-H_2O, respectively.. It can be seen that initiation of the polymerization by this complex predominates over the protogenic initiation with the system $H_2O/SnCl_4$ because the increase in the concentration of the complex suppresses the formation of HMW PIB. An extreme case is seen in the fact that with the aged initiation system (mode C) no further HMW fraction is formed, which indicates that the protogenic initiation with the $H_2O/SnCl_4$ system has been completely suppressed. It is surprising, moreover, that with increasing concentration of DDH in the polymerization mixture (mode A,B) only the weight content of the LMW and HMW fraction of PIB varies; their $\overline{M}_n$ values remain similar within the limits of experimental error. Thus, it is probable that, similarly to t-BuCl (1), also DDH does not play any pronounced role in the polymerization system as the initiation-transfer agent (inifer). This assumption is also supported by results of the analytical determination of chlorine, because PIB oils (LMW fraction) have a chlorine content below 0.5 wt %. This means that at the degree of polymerization $\overline{P}_n \simeq 6-8$ only 6% of oligomeric chains at most may contain the chlorine-bearing terminal structural unit. However, the results of polymerizations initiated with aged systems DDH/$SnCl_4$ (Table 1, dosage mode C) suggest a certain drop in $\overline{M}_n$ with increasing concentration of DDH in the polymerization feed.

The ^{1}H-NMR analysis of PIB oils and the fact that these samples contain only small quantities of chlorine give rise to a question in what way DDH participates in the initiation process of polymerization. The classical initiation of the cationic polymerization of isobutylene in the sense of Equation 6 probably does not proceed at all. An objection

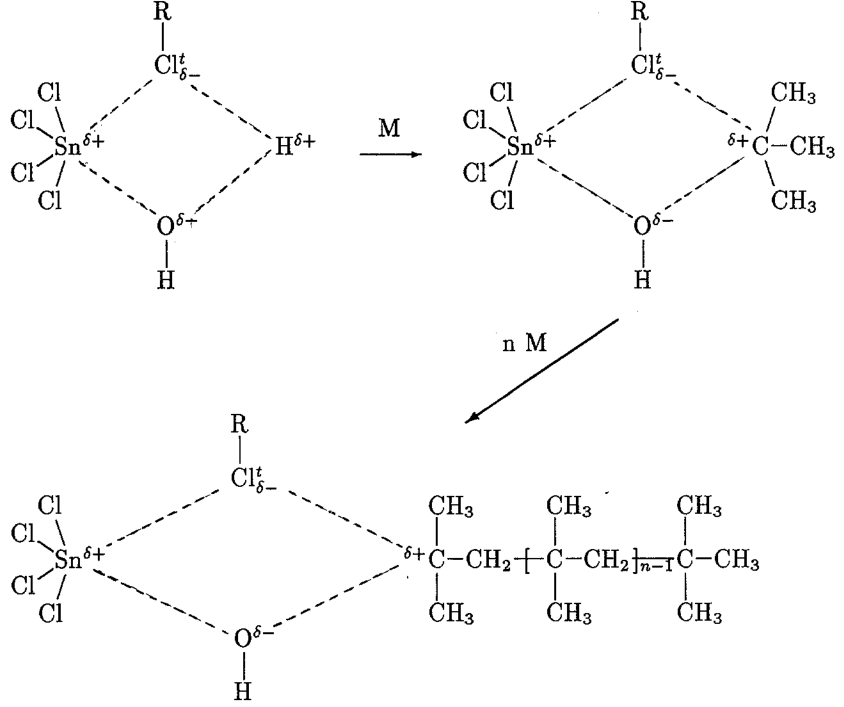


$$\mathrm{Cl{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}Cl} \;+\; \mathrm{SnCl_4} \;\rightleftharpoons\; \mathrm{Cl{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{}^{(+)}\,SnCl_5{}^{(-)}} \qquad (6)$$

that DDH could initiate by both terminal structures and the resulting PIB product would therefore not contain chlorine does not hold, because under the same conditions t-BuCl (1) and DDH give rise to oligomers with approximately the same $\overline{P}_n$. Also, it could be deduced from the ^{1}H-NMR spectra that the LMW fraction contains more tert-butyl groups situated in the heads of oligomeric chains than terminal unsaturated structures. Although tert-butyl groups are predominantly formed by the addition of protons to isobutylene in the transfer to monomer (Scheme 1, Equations 1-3), explanation of their higher concentration requires another possible source of protons - most probably, residual water of the reaction system. The presence of tert-butyl and unsaturated groups suggests that in the polymerizing system a strong transfer to monomer takes place, and it is surprising, therefore, that the oligomeric LMW PIB has such narrow MWD, $\overline{M}_w/\overline{M}_n \leq 1.3$.

On summarizing the discussion and bearing in mind the fact that the presence of both DDH and t-BuCl slows down the polymerization of isobutylene, it may be assumed, tentatively, that the LMW PIB fraction is the product of isobutylene obtained by polymerization proceeding by the coordination mechanism. One of the possible explanations of the facts observed can be seen in the formation of the coordination centre, the assumed structure of which and its role in the polymerization mechanism are indicated in Scheme 2, Equations 7, 8, where Cl^t is the chlorine atom bound onto the tertiary carbon atom, R is the tert-butyl group or $ClC(CH_3)_2CH_2CH_2C(CH_3)_2-$, n is 5-7. According to this scheme, the oligomerization of isobutylene is again initiated with residual water in the reaction system, but in such protogenic initiation the addition of the proton from water to the monomer is controlled by the coordination of components in the complex DDH-$SnCl_4$-H_2O or t-BuCl-$SnCl_4$-H_2O. A theoretical investigation of the possible existence of such coordination centre of the polymerization of isobutylene is underway.

Scheme 2



(7)

(8)

In conclusion, it may be said that the LMW fraction presented here is an alternative procedure for the preparation of unsaturated reactive PIB oils, but in comparison with those known so far it saves advantageously one reaction step. The unsaturation can be easily converted to another function, e.g. to the -OH group. Such telechelic PIB-OH are macromonomers useful for condensation reactions and for the synthesis of polyurethanes.

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