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Isobutylene polymerization in the presence of t-BuCl/$SnCl_4$

Luděk Toman*, Rudolf Lukáš, and Jiří Spěváček

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague 6, Czechoslovakia

Summary

The effect of tert-butyl chloride in the polymerizations of isobutylene carried out in the presence of $SnCl_4$ in dichloromethane at temperatures −20°C and −78°C was investigated. Synthesized polyisobutylene samples showed a bimodal molecular weight distribution (MWD) and it was found that the weight content of the lower-molecular weight (LMW) fraction increased with increasing t-BuCl concentration in the polymerization mixture. The effect of ageing of the initiation mixture t-BuCl/$SnCl_4$ in CH_2Cl_2 prepared in advance on MWD of the PIB samples was also studied. Ageing of the initiation system supports the formation of the LMW fraction and this oily PIB is the only product of the polymerization at −20°C, $\overline{M}_n \sim 500$, $\overline{M}_w/\overline{M}_n \leq 1.4$.

Introduction

Basic research concerning the polymerization of isobutylene in the presence of the Lewis acid $SnCl_4$ has been considerably neglected. Generally, it is known that in a nonpolar medium, i.e. under conditions of the bulk polymerization of isobutylene, no initiation of the cationic polymerization takes place, even if protogenic initiators such as water are present (1-3). Only recently we have surprisingly found (4-9) that under certain conditions such polymerizations can be initiated in the presence of both BCl_3 and $SnCl_4$ and that relatively high conversions can be reached. Thus, e.g., bulk polymerizations of isobutylene in the presence of BCl_3 and initiated with low-molecular weight PVC fractions proceed up to a ~ 50% conversion (8). The surprising finding that solid PVC initiates bulk polymerizations of isobutylene can be explained by assuming that the polar matrix of solid PVC combined with a Lewis acid, e.g. BCl_3 (7,8), but also, with $SnCl_4$ (4-6,9) forms initiation polymerization centres. Such view agrees with the observed fact that the polymerizations of isobutylene are initiated from the solid phase and proceed only at a solid and liquid interface (7-9). This analogy between the behaviour of BCl_3 and $SnCl_4$ leads to an assumption that in some respects both these Lewis acids may behave similarly also if isobutylene is polymerized in a polar medium, e.g. in CH_2Cl_2. Since it is known (10,11) that, in particular, aliphatic chlorides with chlorine bound to the tertiary carbon atom strongly affect the cationic polymerization of isobutylene and its molecular weight in the presence of BCl_3, we tried in this study, by using the same conditions, to follow the behaviour of systems co-initiated with $SnCl_4$. The initiation system chosen for this case was t-BuCl/$SnCl_4$; its behaviour has already been investigated (12-16), but only for the cationic polymerization of styrene. In that case t-BuCl raised the polymerization rate in a polar chlorinated solvent 1,2-dichloroethane, but did not influence the molecular weight of the polystyrene product.

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*To whom offprint requests should be sent

Experimental

Materials

The purification and drying of isobutylene, t-BuCl, CH_2Cl_2, and nitrogen have been described earlier (10). $SnCl_4$ (Aldrich) was purified by distillation in vacuo and dosed in a Ch_2Cl_2 solution.

Polymerization Technique

The polymerizations of isobutylene were carried out at −20°C and −78°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 stream of nitrogen. The reaction components were dosed in three ways: mode I — $SnCl_4$ was dosed as the last component into the monomer or a mixture of the monomer and t-BuCl in CH_2Cl_2, mode II — a freshly prepared mixture of t-BuCl and $SnCl_4$ in CH_2Cl_2 was dosed into the monomer, mode III — a mixture of t-BuCl and $SnCl_4$ in CH_2Cl_2, which prior to this had been left to stand at room temperature for 48 h, was dosed into the monomer. The polymerizations were terminated by an addition of methanol. The drying of ampoules, isolation, and drying of samples of the products have been described elsewhere (10).

Analysis

Spectrophotometric measurements of mixtures t-BuCl/CH_2Cl_2, $SnCl_4$/CH_2Cl_2 and t-BuCl/$SnCl_4$/CH_2Cl_2 were carried out in an HP-8451 (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 dosage of the components in a stream of nitrogen. The cell was dried by employing a technique described earlier (10).

Gel permeation chromatography (GPC) was carried out in HP-1084B, with tetrahydrofuran as eluent, MWD's were calculated using the universal calibration. The Mark-Houwink relations for polystyrene and PIB used were reported earlier (10).

The ^{1}H-NMR spectra were recorded with a Bruker AC-300 spectrometer at 300.1 MHz and room temperature. Solutions of t-BuCl and mixtures t-BuCl/$SnCl_4$ in $CDCl_3$ (Merck), concentration c.50% vol. were investigated. Due to the fact that two bands of the hexamethyldisiloxane standard were observed for the t-BuCl/$SnCl_4$ solution, the band of residual $CHCl_3$ situated at 7.29 ppm with respect to TMS was used as the internal reference.

The chlorine content in PIB samples was determined analytically by employing the usual Schöniger method (17).

Results and Discussion

The GPC analysis of PIB samples synthesized in the absence of t-BuCl at −20°C and −78°C showed that these products, as expected, have a typical unimodal molecular weight distribution (Figs 1a, 2, 3). Obviously, the PIB products arising in these polymerizations are a result of the protogenic initiation with residual water of the reaction systen according to the general scheme A,

$$H_2O + SnCl_4 \rightleftharpoons H^{(+)}SnCl_4OH^{(-)} \xrightarrow{nM} H{-}M_{n-1}M^{+}SnCl_4OH^{(-)} \qquad (A)$$

where M is the monomer isobutylene. Figs 1b, 2, 3 reveal the dramatic effect of the presence of t-BuCl in the polymerization mixture. At the temperatures used, the products thus arising have a distinctly bimodal MWD with a characteristic lower-molecular-weight (LMW) and higher-molecular-weight (HMW) fraction. The weight content of LMW and HMW fraction depends on the amount of t-BuCl used; with increasing concentration of

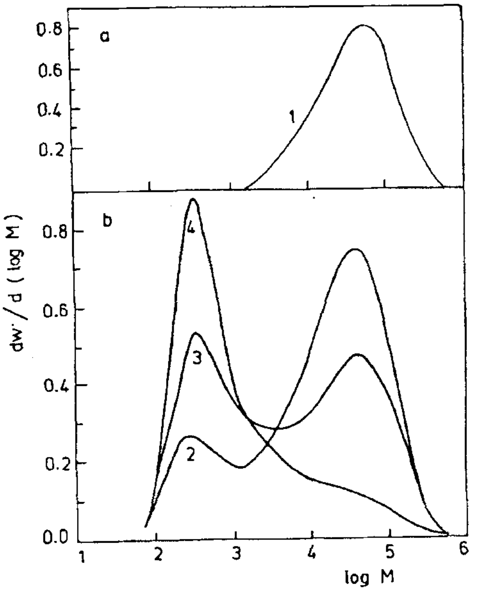

Figure 1: Differential MWD of PIB obtained in the polymerization of isobutylene in CH_2Cl_2 at −20°C (mode I, $[SnCl_4] = 0.077$ M, [isobutylene] = 5 M); 1 - [t-BuCl] = 0, 2 - [t-BuCl] = 0.16 M, 3 - [t-BuCl] = 0.32 M, 4 - [t-BuCl] = 0.64 M

the latter in the polymerization system, the formation of HMW fraction decreases, and consequently, its weight fraction in the final product also decreases. The different dosage of the initiation system, mode I and II, was not reflected within the limits of experimental error in molecular weight values of the PIB samples or in the weight content of both the LMW and HMW fractions. It is obvious, therefore, that during the polymerization of isobutylene in the presence of t-BuCl two different PIB polymers are formed, probably as

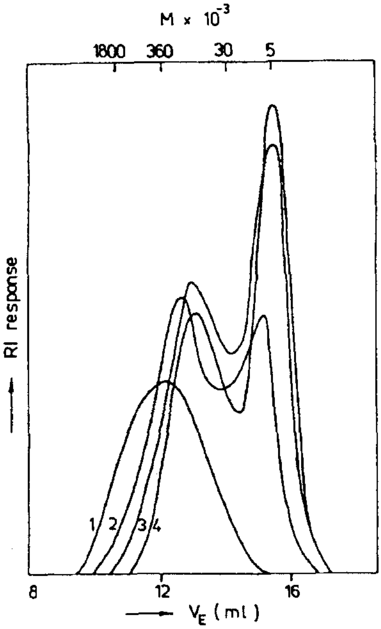

Figure 2: GPC of PIB obtained in the polymerization of isobutylene in CH_2Cl_2 at −78°C (mode I, $[SnCl_4] = 0.077$ M, [isobutylene] = 5 M). 1, 2, 3, 4 — see Fig. 1

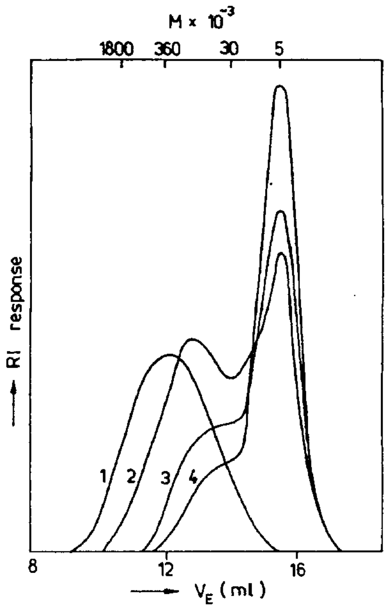

Figure 3: GPC of PIB obtained in the polymerization of isobutylene in CH_2Cl_2 at −78°C (mode III, $[SnCl_4] = 0.077$ M, [isobutylene] = 5 M). 1, 2, 3, 4 — see Fig.1

a consequence of two different polymerization mechanisms. A comparison between Figs 1a and 1b shows that HMW fraction of PIB is a product of the classical protogenic initiation according to the above scheme A. It can be concluded, therefore, that t-BuCl is responsible for the formation of the LMW fraction of PIB. Also, as can be seen from Table 1, the presence of t-BuCl in the polymerizing system diminishes the conversion of isobutylene reached at the same polymerization time. To be able to estimate the role of t-BuCl in the polymerization process, a mixture of t-BuCl and $SnCl_4$ in CH_2Cl_2 was studied photometrically in the time interval of 48 h and in the wavelength range $\lambda > 300$ nm, where the individual solutions of t-BuCl and $SnCl_4$ in CH_2Cl_2 at concentration 1 M do not show any absorption at all. The measurements revealed that immediately after the CH_2Cl_2 solutions of t-BuCl and $SnCl_4$ (molar ratio t-BuCl/$SnCl_4 = 1$) had been mixed, a weak absorption band in the 300–350 nm range was formed. Absorbancy in the maximum of this band at 310 nm increased with time and after 1, 2, 5, and 24 h reached the respective values 0.2, 0.3, 0.45, and 0.9. At the molar ratio t-BuCl/$SnCl_4 = 0.8$ the behaviour was similar. At t-BuCl in excess, i.e. at the molar ratio t-BuCl/$SnCl_4 = 5$, another band with a maximum at 380 nm appeared (Fig. 4). Hence, the results suggest that t-BuCl and $SnCl_4$ interact with each other and with all likelihood form a complex. The concentration of the arising complex t-BuCl-$SnCl_4$ increases with time, which can also be observed visually, because the original colourless mixture gradually turns yellow to brown-orange.

With respect to the initiation of polymerization it is important to know, however, whether the interaction between t-BuCl and $SnCl_4$ does not lead to the formation of

Table 1: Polymerizations of isobutylene in the presence of t-BuCl in CH_2Cl_2 at −20°C.[a]

[t-BuCl](M)	0	0.17	0.34	0.66	0.96	1.23
Conversion (%)	~ 100	48	47	48	30	28

[a] $[SnCl_4] = 0.043$ M, [isobutylene] = 5 M, polymerization time 1.5 h, $SnCl_4$ dosed as the last component according to mode I

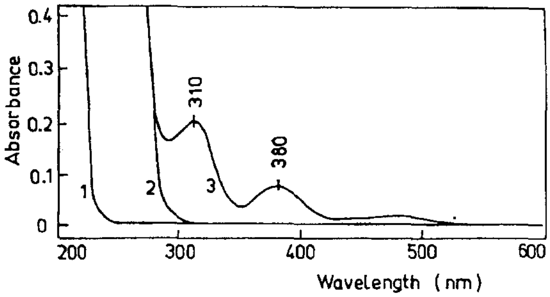

Figure 4: UV and visible spectra of initiation systems in CH_2Cl_2 (25°C, $l = 1$ mm, 48 h after mixing); 1 - t-BuCl (1.27 M), 2 - $SnCl_4$ (0.25 M), 3 - t-BuCl (1.27 M) and $SnCl_4$ (0.25 M)

isobutylene or to oligomers of PIB according to scheme B:

$$\text{t-BuCl} + SnCl_4 \rightarrow (CH_3)_2C{=}CH_2 + H^+SnCl_5^- \rightarrow \text{PIB oligomers} \qquad (B)$$

For this purpose, the initiation system was subjected to an ^{1}H-NMR analysis. While t-BuCl alone has its resonance band at 1.598 ppm (from TMS), an addition of $SnCl_4$ makes its shift to 1.623 ppm. The observed difference between chemical shifts proves that an interaction takes place in the mixture of t-BuCl and $SnCl_4$, in agreement with the spectrophotometric measurement. Of interest is the finding that the difference between the chemical shifts $\Delta = 0.025$ ppm is the same as that observed with the system 2,5-dichloro-2,5-dimethylhexane (DDH)/BCl_3 investigated earlier (18), where an interaction between the two components was also proved spectroscopically. Only 72 h after t-BuCl and $SnCl_4$ had been mixed with each other could two weak singlet resonances at 4.81 and 1.77 ppm be detected in the ^{1}H-NMR spectrum at great amplification, the intensity ratio being c. 1:3. These resonances were attributed to the protons in the $=CH_2$ and $-CH_3$ groups of isobutylene, respectively. From the integrated intensities of these bands it follows, however, that the content of isobutylene thus formed is very low, being about 0.17 mol.% related to t-BuCl.

In connection with the "ageing" of the initiation system t-BuCl/$SnCl_4$ one should mention a similar phenomenon observed during the investigation of interactions of the initiation systems DDH/BCl_3 (11) and t-BuCl/BCl_3 (10). The results of these studies demonstrate that the extended time of interaction between components of the initiation system prior to its addition to the isobutylene solution in CH_2Cl_2 affects the composition of the PIB product. In these cases too the ageing of the initiation system is reflected in the formation of LMW fraction with a relatively narrow MWD. This is why a series of polymerizations of isobutylene at −20°C and −78°C was carried out, initiated with the systems t-BuCl/$SnCl_4$, left to stand at room temperature for 48 h prior to use, dosage according to mode III. The GPC analysis of polymeric products confirmed the anticipated effect of ageing of the initiation system. Surprisingly enough, however, at −20°C and at the same concentrations of t-BuCl as in the cases of dosage of the initiation systems according to mode I and II, no characteristic HMW fraction is formed in these polymerizations. Only LMW fraction of PIB arises, and the samples thus obtained have the character of oils, molecular weight $\overline{M}_n \leq 500$, polydispersity index $\overline{M}_w/\overline{M}_n \leq 1.4$. Unlike oils formed at −20°C, which do not contain HMW any more, the PIB samples synthesized at −78°C are again bimodal and contain the same LMW and HMW fractions as in the case of synthesis with the dosage according to mode I and II. At the same concentrations of t-BuCl the content of HMW fraction is lower, however (Fig. 3).

Let us now discuss the possible role played by t-BuCl in the polymerizations of isobutylene investigated in this study. Experimental data lead to a conclusion that two polymerization processes compete with each other in the polymerizing system. The protogenic initiation with residual water in the reaction system is responsible for the formation of HMW fraction of PIB, at $-20°C$, $\overline{M}_n \leq 20000$, $\overline{M}_w/\overline{M}_n \leq 2.5$, while LMW PIB is the product of initiation with the t-BuCl–$SnCl_4$ complex. The content of LMW and HMW fraction in the final PIB is given by the concentration of t-BuCl, or – as follows from experiments concerning the agent of the initiation system – it is determined by the concentration of the t-BuCl–$SnCl_4$ complex formed in the reaction. It is obvious, moreover, that initiation of the polymerization of isobutylene with this complex dominates the protogenic initiation because an increase in the concentration of the complex suppresses the formation of HMW fraction. An extreme case is seen in the fact that, if the aged initiation system is used (mode III), no HMW fraction of PIB is formed in the polymerization of isobutylene at $-20°C$ any more, which suggests that the protogenic initiation with the $H_2O/SnCl_4$ system has been fully suppressed. One of the possible explanations of this finding may consist in a view that the actual initiation centre is not the complex t-BuCl-$SnCl_4$, but the mutual interaction among the components in the complex t-BuCl-$SnCl_4$ $-H_2O$. Also, a surprising fact is that with increasing concentration of t-BuCl in the polymerization mixture (dosage according to mode I and II) only the weight content of LMW and HMW fraction in PIB varies, while their $\overline{M}_n$ values remain similar within the limits of experimental error. It is probable, therefore, that t-BuCl does not act in the polymerizing system as an initiation-transfer agent (inifer), as is also documented by the low chlorine content detected analytically in the PIB oil (below 0.4 wt.%).

To elucidate the polymerization mechanism, which is responsible for the formation of LMW PIB, a continuation of this study follows the effect of the initiation system 2,5-dichloro-2,5-dimethylhexane/$SnCl_4$ on the polymerization of isobutylene. The results obtained will be reported in our forthcoming paper.

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