

Effect of PVC on low-polar isobutylene polymerization in the presence of BCl_3

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Summary

The isobutylene polymerizations in the presence of BCl_3 were carried out in dichloromethane ($[\text{M}] = 7 \text{ mol/l}$) at -20°C in the presence and absence of PVC. The products of polymerizations in the absence of PVC are oligoisobutylenes with a narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n \approx 1.3$, $\overline{M}_n \approx 2700$); their structure was analyzed by $^1\text{H-NMR}$ spectroscopy. In addition to the signals assigned to known unsaturated terminal structures [δ 4.62 and 4.82 $-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$, 5.12 $-\text{CH}=\text{C}(\text{CH}_3)_2$], a new intense signal was found at δ 5.09 ppm and assigned to the structure $-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$. A mixture of isobutylene homopolymers ($\overline{M}_n \approx 2700, 15000$) and PVC grafted with isobutylene (approx. 9.5% wt. isobutylene grafted) is formed in the presence of PVC.

Introduction

The products of the polymerization of isobutylene, initiated with the $\text{H}_2\text{O}/\text{BCl}_3$ system in a polar chlorinated solvent at temperatures below -40°C , consist of α -tert. butyl- ω -chloropolyisobutylenes (PIB-Cl) with relatively high molecular weights (1). When these polymerizations are carried out in dichloromethane at a temperature of about -20°C and at low monomer concentrations, $[\text{M}] \leq 1.3 \text{ mol/l}$, the products have been identified as low-molecular-weight telechelic PIB-Cl with $\overline{M}_n \approx 1000$ (2,3). So far, it has been generally assumed that the polymerization of isobutylene does not occur with BCl_3 in nonpolar medium in the presence of a protogenic substance such as H_2O or HCl (1,4). Thus, it was surprising to discover that the presence of powdered PVC or of a vinyl chloride/2-chloropropene (VC/2CP) copolymer leads to isobutylene polymers and that the polymerization can be carried out by this method in bulk, i.e. in isobutylene alone, without the presence of a polar solvent (4,5). It can reasonably be expected on the basis of this new finding that the initiation activity of PVC or the VC/2CP copolymer will also affect the polymerization of isobutylene in the presence of polar solvent, such as CH_2Cl_2 , which is a good solvent for PVC resins. Thus, this work is concerned with the study of the polymerization of isobutylene at a temperature of -20°C in low-polar medium in the presence and absence of PVC.

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Experimental

The purification and drying of isobutylene (IB) with a purity of 99.8% (Hüls), BCl_3 (Merck), CH_2Cl_2 and nitrogen, as well as the polymerization technique employed and polymer drying, have already been described (6).

Commercial PVC S-581 (Spolana Neratovice, Czech Republic), $\overline{M}_n = 50000$ was dried before use (4,5).

The $^1\text{H-NMR}$ spectra of our isobutylene oligomers and a commercial sample of Oppanol B3 (BASF), $\overline{M}_n \approx 800$, were measured as 20% w/w solutions in CDCl_3 using a Bruker AC-300 instrument at a frequency of 300.1 MHz at room temperature. The internal standard was hexamethyldisiloxane (HDMS). The chemical shifts δ are related to TMS (δ HDMS = 0.05).

The molecular parameters of the oligomer and polymer samples were determined using GPC with RI detection and a 600×7.5 mm separation column filled with PL gel 10 μm Mixed-B sorbent working in the $5 \times 10^2 - 1 \times 10^7$ molecular weight range (Polymer Laboratories, UK) and THF elution. The chromatographic data were processed using the Data Monitor integration system (Watrex Prague) and calibration with polystyrene standards (Polymer Laboratories, UK) (6).

The polymerizations of IB were carried out at -20°C in 25 ml glass ampoules; the concentration of isobutylene in dichloromethane was 7 mol/l and of BCl_3 , 0.07, 0.09 and 0.11 mol/l. The solutions of PVC in CH_2Cl_2 (40 g/l), prepared by dissolving PVC at room temperature 48 h, were cooled and BCl_3 was condensed. The PVC/ CH_2Cl_2 / BCl_3 mixtures were first left to stand for 4 h at a room temperature ("ageing" of the catalytic system) and then, again after cooling to a temperature of -20°C , isobutylene was condensed into the reaction mixture (Table 1). Polymerization was terminated by the addition of 1 ml of methanol.

The products of the IB polymerizations in the presence of PVC were extracted with hexane for 10 h in a Soxhlet apparatus and analyzed by elemental analysis and determination of chlorine by the Schöniger method (7) (Table 1).

Results and Discussion

The polymerization results obtained are summarized in Table 1, from which it follows that the polymerizations of IB carried out in the absence of PVC proceed much more slowly than the polymerizations under the same conditions but in the presence of PVC. The polymerizations of IB in the absence of PVC yield oligomers with surprisingly narrow molecular weight distributions, polydispersity index $I = \overline{M}_w/\overline{M}_n \approx 1.3$ and \overline{M}_n between 2600 and 2700; no effect of variation of the BCl_3 concentration was observed. The characteristic unimodal GPC record is given in Figure 1.

The polymerizations of IB in the presence of PVC yield more complex products, which were extracted with hexane. Hexane-soluble products contained 0.23–0.26% chlorine and apparently consist of PIB only. However, GPC analysis of these products indicated that they always contain two types of PIB, low (PIB-L) and high-molecular-weight (PIB-H) fractions, Table 1. The characteristic bimodal GPC record is given in Figure 1, from which it follows that the product contains about 12% wt. of the low-molecular-weight fraction ($\overline{M}_n \approx 2600$). It also follows from the GPC record and from Table 1 that the low-molecular-weight fraction corresponds to the products of polymerization in the absence of PVC.

Table 1: Effect of PVC on the low-polar isobutylene polymerization^a in CH₂Cl₂ at -20°C

Run	BCl ₃ [mol/l]	Conversion, %			PIB ^c		PVC- <i>g</i> -PIB		
		12 h	24 h	168 h	$\overline{M}_n \times 10^{-3}$	<i>I</i> ^d	$\overline{M}_n \times 10^{-3}$	<i>I</i> ^d	PIB in graft [wt.%]
1	0.07	0	trace	96.3	2.68	1.3	0	0	0
2	0.07 ^b	98.3	-	-	2.64 (L)	1.4	58.40	3.3	9.4
					15.22 (H)	4.7			
3	0.09	0	trace	97.1	2.68	1.3	0	0	0
4	0.09 ^b	98.9	-	-	2.65 (L)	1.4	57.90	3.2	9.5
					15.30 (H)	4.6			
5	0.11	0	trace	97.3	2.63	1.3	0	0	0
6	0.11 ^b	99.7	-	-	2.65 (L)	1.4	59.10	3.3	9.5
					15.30 (H)	4.6			

^a[isobutylene] = 7 mol/l; ^bin the presence of PVC 40 g/l; ^cL and H are lower- and higher-molecular-weight fractions, respectively; weight ratio H/L ~ 7; ^d $I = \overline{M}_w/\overline{M}_n$

It is apparent from experiments that the hexane-insoluble products should contain PVC or the grafted PVC-*g*-PIB copolymer. The results of carbon analysis have shown that these products contain approx. 9.5% wt. PIB grafted onto PVC (see the GPC records, Figure 2, Table 1).

Polymerization in the absence of PVC. It can be seen from Table 1 and Figure 1 that the oligomers are the only product of the polymerization of isobutylene in the absence of PVC. Their molecular parameters basically correspond to oligomers synthesized at temperatures higher than -30°C at monomer concentrations below 1.3 mol/l. The polymerizations are assumed to be initiated protogenically by the H₂O/BCl₃ system (2,3). The test products have only a low chlorine content (0.23–0.26% wt. Cl), indicating that these oligomers are about 90% terminated by unsaturated structures and only about 10% of the

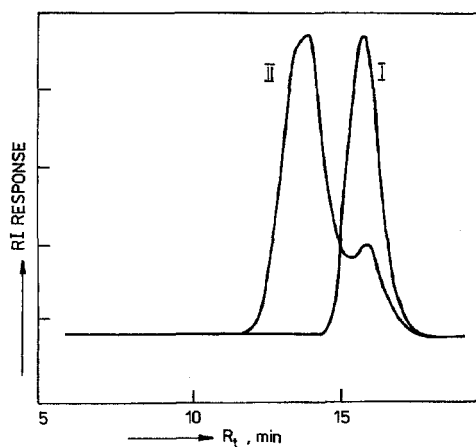


Figure 1: GPC records of PIB prepared by isobutylene polymerization at -20°C in the absence (I) and presence of PVC (II)

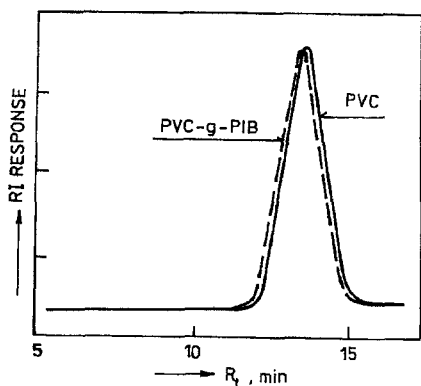


Figure 2: GPC records of PVC and PVC-*g*-PIB copolymer containing ca. 9.5 wt.% of grafted isobutylene

oligomer chains are terminated by a structure containing chlorine (PIB-Cl). It was found by $^1\text{H-NMR}$ analysis that the oligomer typically contains unsaturated end-structures of the $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$ (A) or $-\text{CH}=\text{C}(\text{CH}_3)_2$ (B) type, with signals at δ 4.62 and 4.82 ppm or 5.12 ppm, respectively (8,9). However, a new intensive signal was found in the unsaturated structure region at δ 5.09 ppm (Fig. 3), not found for the commercial oligomer sample, Oppanol B3. In this connection, it is interesting that the polymerization of IB using AlCl_3 yielded a band at 5.10 ppm, which was assigned to the atypical end-structure $-\text{C}(\text{CH}_3)=\text{CHCH}_3$ (9). The formation of this structure was explained in terms of tail-to-tail monomer coupling connected with a 1,2-methide shift (9). An internal double bond $-\text{CH}=\text{C}<$ with the chemical shift > 5.00 ppm could also correspond to the structure $-\text{C}(\text{CH}_3)_2\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$, which would be formed by isomerization across the cyclopropane cation, which is considered to be present in the oligomerization of α -olefins (10). As it would be difficult to assign the unknown band at 5.09 ppm to these

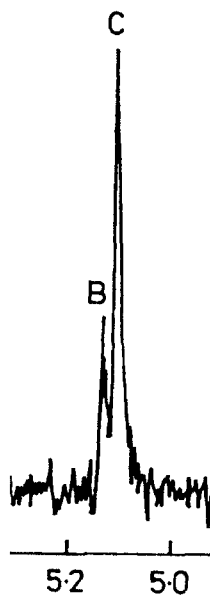
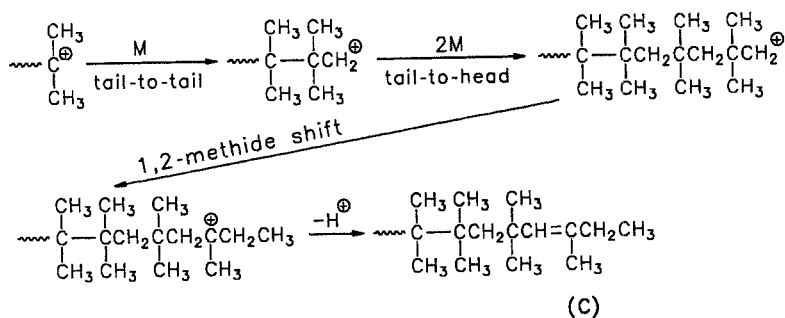


Figure 3: Part of the 300 MHz ^1H NMR spectra (in CDCl_3 , 20% w/v, 25°C) of PIB (Tab. 1, run 1)

structures, the oligomer was also subjected to ^{13}C -NMR analysis which is described in detail elsewhere (11). It followed from the analysis that this band, similarly to that in the previous case, also corresponds to a trisubstituted olefin, however with the structure $-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (C).

It was also found from thermal depolymerization data (12) that the PIB chain consists predominantly of monomeric units linked head-to-tail, but that about 2% of the PIB in the chain is linked tail-to-tail. If it is accepted that tail-to-tail monomer coupling is possible in the polymerization of IB (9,12), the formation of structure (C) can be considered to result from tail-to-tail monomer coupling (M), followed by tail-to-head addition, accompanied by a 1,2-methide shift and proton expulsion, according to the scheme:



Integration of ^1H -NMR bands A, B, and C yielded the molar ratio of the unsaturated structures A : B : C = 1 : 0.8 : 2.

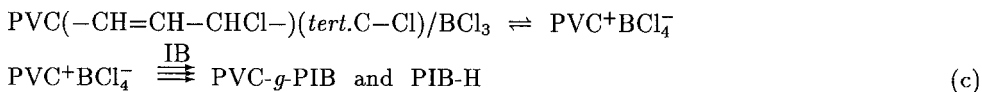
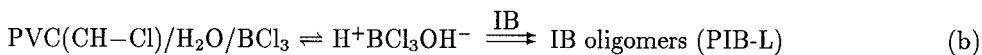
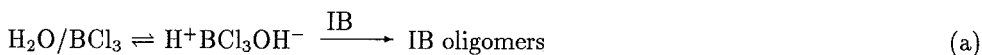
This concept of the possible formation of the unsaturated structure C is supported by the fact that the oligomers are formed in prolonged, slow polymerization of IB (168 h), where isomerization of the oligomers can occur in the reaction system, as has already been demonstrated in a model study with the triisobutylene/ AlBr_3 /deuterium bromide system (13,14). In agreement with this study, structure C was not found by ^1H -NMR and ^{13}C -NMR analyses in the commercial oligomer Oppanol B3.

Polymerization in the presence of PVC. Except for structural defects, chlorine atoms in PVC are bound to secondary carbons $\text{CH}-\text{Cl}$. However, as we found in an earlier work (5), the low-molecular-weight models of PVC containing the $\text{CH}-\text{Cl}$ groups, such as 2,4-dichloropentane and 2,4,6-trichloroheptane, have a catalytic effect on the polymerization of isobutylene in the presence of $\text{BCl}_3/\text{CH}_2\text{Cl}_2$. The conclusion that this effect is only catalytic follows from the experimental finding (5) that PIBs do not contain the structures of these substances bound as the head groups. Analogously, it can be expected that the effect of PVC is only catalytic. Similar properties of PVC were encountered in the polymerization of isobutylene in the presence of SnCl_4 , where the catalytic effect of PVC was explained in terms of pseudoprotogenic initiation consisting of interaction of the $\text{PVC}/\text{SnCl}_4/\text{H}_2\text{O}$ components (15).

The fact that the polymerization of isobutylene in the presence of PVC involves grafting of isobutylene from PVC (Table 1), indicates that carbocations are formed on the PVC chains and thus PVC acts as an initiator of these polymerization reactions. Since $\text{CH}-\text{Cl}$ groups in combination with BCl_3 exhibit only a catalytic effect, it is probable

that structural defects in PVC are responsible for the formation of the carbocations and thus of the growth centres; these defects are primarily allylic chlorine groupings ($-\text{CH}=\text{CHCHCl}-$) and branched structures bearing a chlorine atom on a tertiary carbon (*tert.C-Cl*). The formation of carbocations on PVC can then be generally conceived as either direct interaction of these groups with BCl_3 , as has been proposed for the $\text{CH}-\text{Cl}$ groups on PVC and strong Lewis acids, such as AlCl_3 and TiCl_4 (16), or the utilization of the initiation-transfer behaviour of these groups. However, it is not possible to decide on the basis of experimental results which one of these mechanisms predominates in the formation of carbocations on PVC. Nevertheless, experiments on the ageing of the PVC/BCl_3 initiation system in the absence of the monomer have demonstrated that prolonging the interaction time of PVC with BCl_3 increases the extent of grafting. Thus, if the monomer was added 4 h after mixing PVC with BCl_3 , about 10% of the isobutylene was grafted onto PVC. If the monomer was added immediately after mixing PVC with BCl_3 , then less than 2% of IB was grafted onto PVC. A similar effect was observed in the study of the *t*-BuCl/ BCl_3 system (6). Thus, these results support the concept that carbocations are formed on PVC through the action of BCl_3 as a result of the reaction of allylic (17,18) and "tertiary" chlorines.

It can be expected in low-polar medium that the reaction system will contain only ion pairs and that counter-ions in the immediate vicinity of the growing carbenium ions affect the extent of the transfer reactions. In polymerization in the absence of PVC, it can be expected that the initiation will occur protogenically through the residual water content in the reaction system and that the counter-ion is BCl_3OH^- . When PVC is employed, the reaction system can contain both BCl_3OH^- counter-ions from pseudoprotogenic initiation (interaction of $\text{CH}-\text{Cl}$ with H_2O and BCl_3) as well as BCl_4^- produced by the reaction of allylic and "tertiary" chlorines with BCl_3 . It can be concluded from the similarity of the oligomers in Table 1, run 1, 2 and Figure 1 that the extent of monomer transfer was affected by the same counter-ion, i.e. BCl_3OH^- , while BCl_4^- affected the transfer in the formation of PIB-H and PVC-*g*-PIB. Initiation occurring in low-polar medium in the absence (a) and presence of PVC (b, c) can be depicted by a scheme with indication of relative polymerization rate:



The higher molecular weight of PIB-H compared to PIB-L can also be a result of the fact that relatively long PVC macromolecules are present in the vicinity of the growth centres and that these macromolecules can retard monomer transfer for steric reasons.

It can be concluded from the experimental results obtained that PVC, present in low-polar polymerizations of IB, exhibits both catalytic and initiation behaviour. The regular structure units of PVC facilitate protogenic catalysis of IB polymerizations with

residual water in the reaction system whereas the structural irregularities, such as allylic and "tertiary" chlorines, initiate the polymerizations giving rise to PVC-*g*-PIB products. It is also obvious that the extent of catalytic and initiation behaviour of PVC can be controlled by ageing PVC with BCl_3 and by the content of active structure defects in PVC resins.

The modification of PVC by cationic grafting was described in a number of papers. Except strong Lewis acids (16), such as AlCl_3 , TiCl_4 which instantaneously and efficiently cointiate olefin polymerizations in the presence of moisture, organoaluminium compounds were usually used such as $(\text{C}_2\text{H}_5)_2\text{AlCl}$, $(\text{C}_2\text{H}_5)_3\text{Al}$, $(\text{CH}_3)_3\text{Al}$ (19-26) or PCl_3 (27). When PVC contained relatively high concentrations of allylic chlorines (after controlled dehydrochlorination), BCl_3 was also an efficient cointiator (17, 18, 26, 28). In this paper we have shown that also a commercial PVC can be grafted using BCl_3 .

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