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## The Initiating Effect of Vinyl Aromatic and Diene Monomers on the Polymerization of Isobutylene with $VCl_4$

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### ABSTRACT

The polymerization of isobutylene with  $VCl_4$  in n-heptane or in the bulk does not proceed in the dark at temperatures lower than  $-20^\circ C$ , yet it may be induced by the addition of styrene,  $\alpha$ -methylstyrene, p-divinylbenzene, 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene. In these cases the polymerizations proceed with variously long induction periods depending on the type of comonomer used. The shortest induction period was observed after the addition of p-divinylbenzene and 2,3-dimethyl-1,3-butadiene. In a nonpolar medium the copolymerization of isobutylene with isoprene or butadiene in the dark gives rise to copolymers insoluble in heptane, benzene, and  $CCl_4$ , while copolymers formed with the effect of light are soluble. Unlike polymerizations carried out in a nonpolar solution, the polymerization of isobutylene with  $VCl_4$  in methyl chloride proceeds spontaneously in the absence of protonic cointiators. Also, soluble copolymers of isobutylene with isoprene or butadiene arise in the copolymerization in methylchloride solution irrespective of the procedure used when the copolymerization is carried out (in the dark or with the effect of light). Polymerizations and copolymerizations carried out both in nonpolar and in polar solutions are inhibited by the presence of oxygen.

## INTRODUCTION

Numerous papers and comprehensive reports which concern the polymerization of isobutylene with the Lewis acids [1-12] show that very little attention has been devoted to the study of initiation in the presence of vanadium tetrachloride. Vanadium tetrachloride either did not initiate [10] the polymerization of isobutylene, or its catalytic activity was low, and it was included in a group of initiators, along with  $\text{SnCl}_4$ ,  $\text{ZrCl}_4$ , and  $\text{FeCl}_3$ , which, when used in the polymerization, yield polyisobutylenes having a lower molecular weight than that reached under the same conditions with such initiators as  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{AlEtCl}_2$ , and  $\text{TiCl}_4$  [13].

The results originally obtained in our laboratory [9, 10] seemed to confirm the weak activity of  $\text{VCl}_4$ , but further investigation revealed that  $\text{VCl}_4$  is an effective initiator of the polymerization of isobutylene if initiation occurs with the cooperation of UV [14] or visible [15, 16] light. The problem was examined further, and it was found that  $\text{VCl}_4$  under suitable polymerization conditions exceeds the known initiation systems used in the preparation of polymers with high molecular weight, thus occupying the first rank before  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{EtAlCl}_2$ , and  $\text{TiCl}_4$ .

We also found [17] that  $\text{VCl}_4$  initiated the polymerization of isobutylene in bulk or in heptane solution both in the dark and with the effect of light. However, polymerization in the dark proceeds only at higher temperatures,  $t \geq 10^\circ\text{C}$ . At lower temperatures [17, 18],  $t \leq -20^\circ\text{C}$ , polymerization does not occur in the dark but is induced with light. The effect of light also initiates copolymerization of isobutylene and butadiene [19] or isoprene [20] with  $\text{VCl}_4$  in bulk or in heptane solution.

The molecular weights of these copolymers [21] are considerably higher than those of copolymers which under similar conditions were prepared with  $\text{AlCl}_3$  or  $\text{BF}_3$ . Hence, by using vanadium tetrachloride and light it is possible to prepare isobutylene-isoprene copolymers at relatively high temperatures,  $-40$  to  $-30^\circ\text{C}$ . Thus far, these copolymers have usually been obtained with  $\text{AlCl}_3$  or  $\text{BF}_3$  at temperatures about  $-100^\circ\text{C}$ .

For photoinitiated polymerizations of isobutylene and for copolymerizations of isobutylene with butadiene or isoprene in the presence of  $\text{VCl}_4$ , we proved there was inhibition with oxygen [19, 20, 22].

In this study we continue the investigation of the polymerization of isobutylene and of the copolymerization of isobutylene with isoprene in the presence of  $\text{VCl}_4$ . We examine the activation effect of styrene,  $\alpha$ -methylstyrene, *p*-divinylbenzene, 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene on the polymerization of isobutylene carried out in the dark in the absence of an auxiliary solvent. The influence of methylchloride on the polymerization of isobutylene is also investigated in the dark. In the case of the copolymerization of isobutylene with isoprene, carried out in bulk or in heptane, the properties of

copolymers are examined as a function of the copolymerization being performed in the dark or with visible light. For the copolymerization of isobutylene with isoprene in the dark, we investigated the effect of an auxiliary solvent (heptane and methyl chloride) on the polymerization process and on the properties of the copolymer. For the polymerizations of isobutylene and copolymerizations of isobutylene with vinyl aromatic and diene monomers in the presence of  $VCl_4$  performed in the dark, we also investigated the effect of oxygen on the processes.

## EXPERIMENTAL

### Chemicals

The purification and drying of isobutylene (IB), isoprene (IP), butadiene (B),  $VCl_4$ , heptane, argon, and oxygen have been described earlier [17-20, 22]. 2,3-Dimethyl-1,3-butadiene (DMB), produced by Fluka AG, Buchs SG, was redistilled in a stream of argon and dried by standing over molecular sieves (Potasit 3, CSSR). Styrene (ST), a Czechoslovak product, p-divinylbenzene (DVB) produced by Fluka AG, Buchs SG, and  $\alpha$ -methylstyrene ( $\alpha$ MST) from the Koch-Light Laboratories were purified from inhibitor by shaking with 20% aqueous NaOH and then with distilled water to neutral reaction. After drying with  $CaCl_2$ , the monomers were redistilled at reduced pressure in an argon atmosphere and dried with  $CaH_2$ . After another distillation at reduced pressure (0.5 Pa) in an argon atmosphere, the monomers were kept cold at  $-18^\circ C$  in glass ampules, similarly to the monomers isoprene and 2,3-dimethyl-1,3-butadiene. Methyl chloride, a Czechoslovak product, was purified with concentrated sulfuric acid and dried by standing over molecular sieves in a pressure bottle. The moisture of monomers, solvents, and of the inert measured with a Shaw hygrometer varied between 1 and 3 ppm.

### Polymerization

The polymerizations and copolymerizations were carried out in a reactor [23] in which they could be performed both in the dark and in visible light. In the latter case the reaction mixture was irradiated only until the onset of polymerization (induction period); after that, light was switched off and the polymerization proceeded in the dark. The polymerization reactor was provided with a Duralumin head containing the irradiating device (halogen bulb, 12 V, 55 W), the bearing of an anchor stirrer, and the capsule of the thermocouple. The reactor vessel, working volume 100 mL, was made of glass. In polymerizations performed in the presence of oxygen, the latter was introduced into the reactor under the level of the reaction mixture using a capillary made of stainless steel.

In the investigation of the effectiveness of comonomers as cointiators, the induction period ( $i$  = time interval between the injection of the comonomer and the moment of the detection of polymerization by means of a thermocouple) and the polymerization time ( $t$  = time interval within which the polymerization took place) were also recorded.

The polymer samples were obtained after removal of volatile fractions (at 0,5 Pa and 40°C) after polymerizations which were always terminated by adding 1 mL of ethanol.

The molecular masses of the polymers were determined by the viscometric method in heptane at 20°C and calculated using the Flory [24] equation,  $[\eta]/(\text{dL/g}) = 3.6 \times 10^{-4} M_{\eta}^{0.64}$ . The unsaturation of the copolymers of isobutylene and isoprene, and of butadiene and 2,3-dimethyl-1,3-butadiene in mol% was assessed by employing the ozonometric method, with a double bond analyzer ADS-3 (manufactured at the Academy of Sciences of the USSR), using squalene as the calibration standard.

## RESULTS

### The Cointiating Effect of Vinyl Aromatic and Diene Monomers on the Polymerization of Isobutylene

The polymerizations of isobutylene with  $\text{VCl}_4$  were investigated in bulk at temperatures  $\leq -20^\circ\text{C}$ . These polymerizations do not proceed in the dark in the absence of a protonic cointiator of the polymerization, but they are induced by the addition of divinylbenzene,  $\alpha$ -methylstyrene, 2,3-dimethyl-1,3-butadiene, isoprene, 1,3-butadiene, and styrene.

Of the vinyl aromatic monomers examined, the highest activity was observed for divinylbenzene in the presence of which the polymerization (copolymerization) of isobutylene proceeds with the shortest induction period and to the highest conversion. In the presence of dienes the polymerization proceeds best after the addition of 2,3-dimethyl-1,3-butadiene. The decrease in the cointiating activity of vinyl aromatic and diene monomers is in agreement with their order in Table 1. Light reduces the induction period or the polymerizations proceed without it, as also illustrated by Table 1.

In the copolymerizations of isobutylene and divinylbenzene both in the dark and with light, copolymers are formed which are insoluble in heptane, benzene, and  $\text{CCl}_4$ . In the copolymerization of isobutylene with butadiene (10 wt% per mixture) or isoprene (1-3 wt% per mixture) in the dark, the copolymers formed are also insoluble, while those arising in the copolymerization with light are soluble. The copolymer formed in the copolymerization of isobutylene with 2,3-dimethyl-1,3-butadiene, both in the dark and with light, is a soluble one.

TABLE 1. The Co-initiating Effect of Vinyl Aromatic and Diene Monomers on the Polymerization of Isobutylene with  $\text{VCl}_4$ <sup>a</sup>

Wt% of comonomers in monomeric mixture	T (°C)	i (min)	t (min)	C (%)	$M_\eta \times 10^{-3}$	u (mol%)
IB without comonomers (dark)	-20	-	(80)	0		
	-40	-	(80)	0		
	-78	-	(80)	0		
0.2 DVB (dark)	-40	10	7	20	ins	
5.0 DVB (dark)	-40	0	1	30	ins	
5.0 DVB (dark)	-20	0	1	28	ins	
0.2 DVB (light)	-40	0	1	28	ins	
0.2 MST (dark)	-40	-	(80)	0		
5.0 MST (dark)	-40	2	10	23	8	
5.0 MST (light)	-40	0	10	30	8	
5.0 ST (dark)	-40	38	10	19	193	
5.0 ST (light)	-40	1	10	26	190	
3.0 DMB (dark)	-40	6	10	28	220	2.10
3.0 DMB (light)	-40	0.3	10	30	220	2.20
3.0 IP (dark)	-40	17	10	53	ins	
1.0 <sup>b</sup> IP (dark)	-40	11	10	53	ins	
1.0 IP (light)	-25	0.5	5	33	300	0.97
3.0 B (dark)	-40	60	50	10	500	0.21
10.0 B (dark)	-40	45	30	46	ins	
10.0 B (light)	-40	21	20	58	470	1.0

<sup>a</sup>The polymerizations were performed in bulk at  $[\text{VCl}_4] = 2 \times 10^{-3}$  mol/L; DVB, divinylbenzene; MST,  $\alpha$ -methylstyrene; ST, styrene; DMB, 2,3-dimethyl-1,3-butadiene; IP, isoprene; B, butadiene; T, polymerization temperature; i, induction period; t, polymerization time; C, concentration; u, unsaturation; ins, insoluble polymer.

<sup>b</sup>IP was added to the mixture of isobutylene with  $\text{VCl}_4$  only 80 min after the injection of  $\text{VCl}_4$ .

TABLE 2. The Effect of Light on the Copolymerization of Isobutylene with Isoprene;  $[VCl_4] = 2 \times 10^{-3}$  mol/L; Meaning of the Other Symbols as in Table 1

Wt% of isoprene in monomeric mixture	T (°C)	C (%)	Copolymerization			
			In the dark, $\bar{M}_\eta \times 10^{-3}$ u (mol%)		With light, $\bar{M}_\eta \times 10^{-3}$ u (mol%)	
2 <sup>a</sup>	-78	30	ins		1100	2.00
		25	ins		1160	1.98
2 <sup>a</sup>	-35	26	ins		390	2.00
		28	ins		391	2.10
1 <sup>b</sup>	-25	27	ins		319	0.92
		25	ins		320	0.96
0,5 <sup>b</sup>	-25	27	ins		322	0.48
		26	ins		322	0.50
1,5 <sup>b</sup>	-9	50	34	1.17	34	1.18
		48	34	1.30	34	1.20

<sup>a</sup>The copolymerizations were carried out in 40% (wt%) of monomeric solution in heptane.

<sup>b</sup>In bulk.

### The Effect of Light on the Copolymerization of Isobutylene with Isoprene

The polymers formed in the copolymerization of isobutylene with isoprene occurring in the dark in bulk or in heptane solution at temperatures of  $-25^\circ\text{C}$  and lower are insoluble in heptane, benzene, and  $\text{CCl}_4$ , as documented by Tables 1 and 2. On the other hand, copolymers formed with light are also soluble at the polymerization temperature  $-78^\circ\text{C}$  (Table 2), when copolymers of a very high molecular mass are obtained (up to  $1 \times 10^6 \bar{M}_\eta$ ). At higher temperatures ( $-9^\circ\text{C}$ , Table 2) soluble copolymers are formed independent of the copolymerization proceeding in the dark or with light.

### The Effect of Methyl Chloride on the Polymerization of Isobutylene and the Copolymerization of Isobutylene with Isoprene

Isobutylene polymerizes with  $\text{VCl}_4$  in methyl chloride solution after a short induction period in the dark at temperatures lower than  $-20^\circ\text{C}$  (Table 3). The copolymerization of isobutylene with isoprene also

TABLE 3. The Polymerization of Isobutylene and Copolymerization of Isobutylene with Isoprene in Methachloride and Heptane Solution in the Dark;  $[VCl_4] = 6.8 \times 10^{-4}$  mol/L for Copolymerizations in Methyl chloride Solution;  $[VCl_4] = 2 \times 10^{-3}$  mol/L for Copolymerizations in n-Heptane Solution; meaning of the other symbols as in Table 1.

a (%)	T (°C)	b (%)	i (min)		t (min)		Conversion (%)		$\bar{M}_\eta \times 10^{-3}$	
			CH <sub>3</sub> Cl	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> Cl	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> Cl	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> Cl	C <sub>7</sub> H <sub>16</sub>
0	-30	50	1.0	-	15	(120)	80	0	393	-
0	-78	30	0.1	-	10	(120)	32	0	5026	-
1	-40	30	0.1	70	10	60	40	43	560 <sup>c</sup>	ins
2	-35	50	0.5	65	20	60	50	52	230 <sup>d</sup>	ins
			0.5	63	20	60	52	50	230 <sup>d</sup>	ins
2	-35	65	2.0	50	17	50	35	45	240 <sup>d</sup>	ins
			2.5	52	17	50	33	43	240 <sup>d</sup>	ins
2	-35	80	7.0	27	25	30	56	48	ins	ins
2	-20	85	8.0	29	25	30	53	50	ins	ins

<sup>a</sup>Wt% of isoprene in monomeric mixture.

<sup>b</sup>Wt% of monomers in methyl chloride and heptane solution.

<sup>c</sup>Unsaturation of the copolymer 0.5 mol%.

<sup>d</sup>Unsaturation of the copolymer lay within 1 and 1.2 mol%.



proceed in methyl chloride solution in the dark, and the length of the induction period increases with the content of monomers in the initial mixture. The copolymerization of isobutylene with isoprene in monomeric solution (30 to 65 wt%) in methyl chloride gives rise to copolymers soluble in heptane, benzene, and  $\text{CCl}_4$ . On the contrary, in an 80% monomer solution in methyl chloride, insoluble copolymers are formed at temperatures below  $-20^\circ\text{C}$ , similar to copolymerization in bulk or in heptane solution.

### The Inhibitive Effect of Oxygen

The polymerizations of isobutylene or copolymerization of isobutylene with isoprene carried out with  $\text{VCl}_4$  in methyl chloride solution in the dark do not proceed within the observed time (60 min) or are inhibited during polymerization by the addition of oxygen at a 15 or 45% conversion. A similar inhibitive effect of oxygen was observed in the copolymerization of isobutylene with vinyl aromatic and diene monomers in the dark in bulk or in heptane solution.

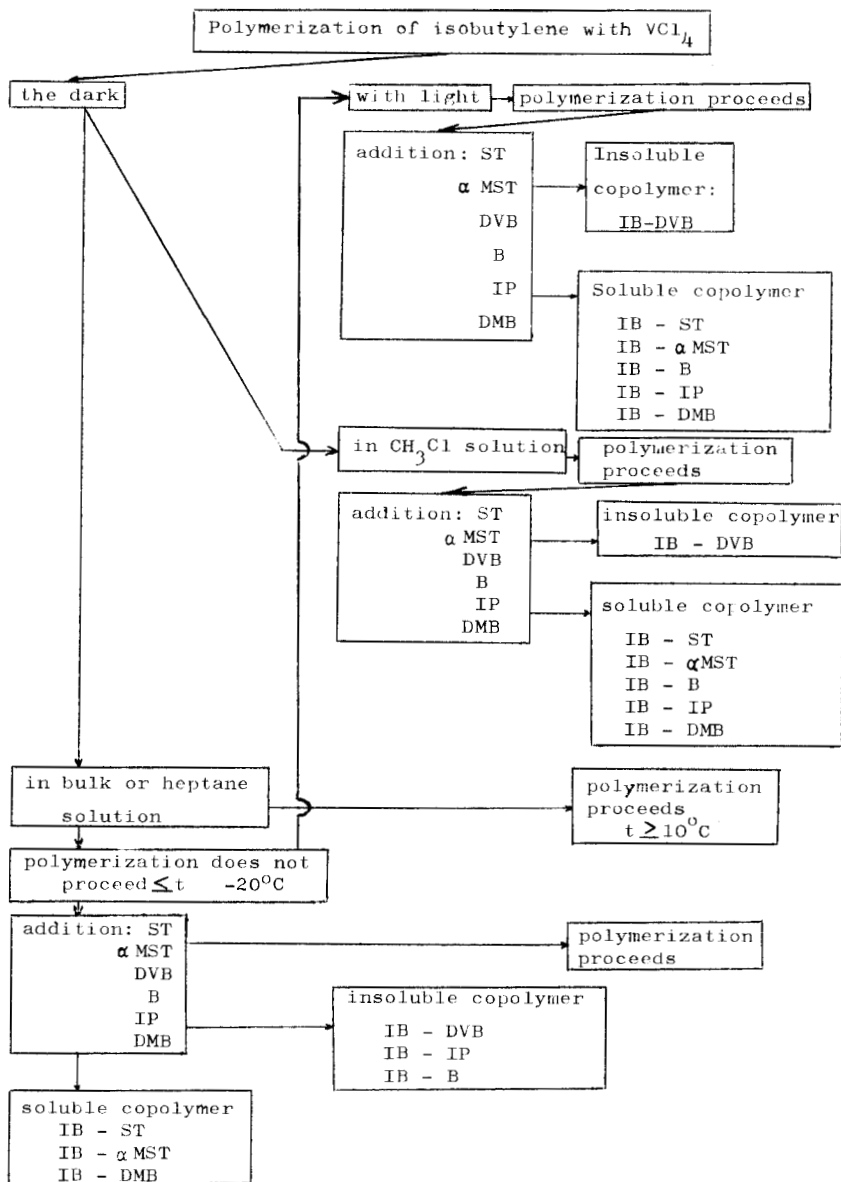
### DISCUSSION

Vanadium tetrachloride differs from the other initiation systems of the cationic polymerization in that its activity in the polymerization of isobutylene strongly depends on the way in which the polymerization is performed, as can be seen in Scheme 1. The properties of the copolymers of isobutylene with butadiene or isoprene also depend on the method of copolymerization.

As has been reported earlier [17], vanadium tetrachloride forms a charge-transfer complex with isobutylene in the molar ratio 1:1. The effect of light induces in the CT complex a one-electron transition from the electron donor (isobutylene) to the electron acceptor ( $\text{VCl}_4$ ), accompanied by the formation of radical ions. Radical cations of isobutylene have been detected in the ESR spectrum [25]. Radical cations in the case of butadiene and isoprene or of their mixture with isobutylene have been similarly detected [19, 20].

The CT complex of isobutylene with  $\text{VCl}_4$  need not be excited only with the energy of light; it may also be excited by thermal energy, and therefore probably at temperatures of  $10^\circ\text{C}$  and above the polymerization of isobutylene in a nonpolar medium in the dark is spontaneous. At temperatures of  $-20^\circ\text{C}$  and below the thermal energy is probably insufficient for exciting the CT complex, and isobutylene does not polymerize in the dark.

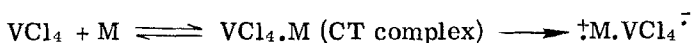
In methyl chloride, on the other hand, radical ions (with the possibility of dissociation) are formed more readily; as a consequence, the polymerizations also proceed more readily, even at a  $\text{VCl}_4$  concentration three times lower (Table 3), than if they take place in heptane.



SCHEME 1. Polymerization of isobutylene with  $VCl_4$  depending on conditions and procedure used.

The inhibitive effect of oxygen in the photoinitiated polymerization of isobutylene with  $\text{VCl}_4$  and the copolymerization of isobutylene with butadiene or isoprene were studied earlier, and organic peroxy radicals were detected in the ESR spectra of the reaction mixture [19, 20, 25]. Since in the dark the polymerization of isobutylene and the copolymerization of isobutylene with vinyl aromatic or diene monomers are also inhibited with oxygen, we are inclined to believe that the polymerization also proceeds via radical-cation intermediates, similar to the polymerization of isobutylene with light.

The formation of radical cations:



The inhibition effect of oxygen:



where M is isobutylene, vinyl aromatic, or diene monomer,  $\text{M}^{\cdot+}$  is a radical cation of monomer, and  $\text{}^{\cdot}\text{M-O-O} \cdot$  is a peroxy radical cation of monomer.

The copolymerization of isobutylene with butadiene (butadiene content in the mixture of monomers is  $\geq 10$  wt%,  $t \leq -40^\circ \text{C}$ ) or isoprene (isoprene content in the mixture of monomers is  $\geq 0.5$  wt%,  $t \leq -25^\circ \text{C}$ ) in the dark in nonpolar medium gives rise to insoluble copolymers. In methyl chloride solution (monomer concentration  $\leq 65$  wt%, Table 3), soluble copolymers are formed, both with light and in the dark. The explanation of the formation of a soluble or insoluble copolymer, depending on the procedure used in the copolymerization, is the subject of a forthcoming paper [26].

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