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A new family of telechelic copolymers

I. Initiation system activated-PVC/BCl_3

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Summary

A new initiation system is described, allowing bulk polymerizations of isobutylene to be carried out at about -78°C, in the absence of a polar chlorinated solvent. The initiation system consists of two components, the first of which is boron trichloride (BCl_3) used as co-initiator, and the other component is a polymer insoluble in the monomer and containing chloroallyl structures or structures with a chlorine atom bound at the tertiary carbon atom in their chains. Bulk polymerizations of isobutylene proceed at the boundary between the solid and the liquid phase for many hours, and the polymeric initiator used is grafted by isobutylene. Dichloromethane raises reactivity of the initiation system.

Introduction

An extensive study of initiation systems of the polymerization of isobutylene/BCl_3 was carried out by Kennedy and coll. (1-9). Initiators of the polymerizations were chlorides of the allyl type (such as 3-chloro-1-butene, 1-chloro-3-methyl-2-butene, methallylchloride) (1,2), aralkylhalides (3-6), aromatic or aliphatic ethers (7-9) and PVC enriched in chloroallyl structures (10). Only a few papers report, however, that also the system $R\text{-}Cl^t/BCl_3$, where $R\text{-}Cl^t$ is an aliphatic alkylchloride with the chlorine atom bound at the tertiary carbon atom, e.g. tert-butylchloride (11), 2-chloro-2,4,4-trimethylpentane (12), 2,5-dichloro-2,5-dimethylhexane (13,14), is reactive and initiates the polymerization of isobutylene with formation of PIB-Cl or Cl-PIB-Cl. The results obtained suggest that the polymerizations take place only in a polar chlorinated solvent, e.g., dichloromethane; also, this view is generally accepted. So far, no polymerizations have been reported which proceed in the monomer itself, i.e. bulk polymerizations of isobutylene/BCl_3 initiated with initiators mentioned above or with a protogenic compound (H_2O, HCl) (15-18).

Contrary to the view postulated up to now, we have recently found that the bulk polymerization of isobutylene/BCl_3 may be successfully carried out at a temperature about -78°C, if a polymer containing chloroallyl structures or structures having the chlorine atom bound at the tertiary carbon atom in its chains is used as the initiator. This study deals with

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*To whom offprint requests should be sent systems polymerizing in this way, and an attempt is made to elucidate and suggest the possible polymerization mechanism.

Experimental

Polyvinylchloride PVC-A, molecular weight $\bar{M}_w$ about 160 000, with a relatively high content (0.15 mol.%) of chloroallyl structures was obtained by a controlled chemical dehydrochlorination of suspension PVC prepared on a laboratory scale with potassium tert-butoxide (19,20). The copolymer vinylchloride/2-chloropropene (VC/2CP), molecular weight $\bar{M}_w \sim 60\ 000$ and $\bar{M}_n \sim 32\ 000$ containing 5.1 mol.% 2-chloropropene structural units was obtained by suspension copolymerization.

Purification and drying of isobutylene, dichloromethane, BCl_3 and nitrogen have been reported earlier (11). PVC-A and VC/2CP were dried in an ampoule provided with a three-way teflon closure; the ampoule was alternately evacuated and pressurized with dry nitrogen for 24 h. 4-Chloro-2-nonene was dried over molecular sieves.

The polymerizations took place in glass ampoules and was followed dilatometrically by employing techniques described in our earlier paper (11).

Molecular weights of the polymers (weight or number average weights $\bar{M}_w$, $\bar{M}_n$) were determined by gel permeation chromatography (GPC) in a tetrahydrofurane solution (THF) using an HP 1084 B chromatograph (USA). The instrument was calibrated with polystyrene standards. Hence, molecular weights of the polymers are apparent values related to polystyrene.

Results and Discussion

On mixing of powdery PVC-A or of the copolymer VC/2CP with isobutylene and BCl_3, solid polyisobutylene gradually grows at about -78°C on particles of PVC-A or VC/2CP. Approximately 10 min after the components have been mixed the polymerization can be both followed visually and detected dilatometrically from volume contraction with the low initial rate r_o, without any change in the viscosity of the monomeric phase. The polymerization of isobutylene is very interesting because in a nonpolar medium, i.e. in the monomer alone it proceeds at the boundary between the solid and liquid phase without kinetic termination for many hours. For instance, with the copolymer VC/2CP the polymerization of isobutylene proceeds for more than 20 h, and only after some two days it stops spontaneously. With powdery PVC-A used as the initiator the bulk polymerization proceeds slowly for more than 50 h. Control tests performed under the same experimental conditions in the absence of PVC-A or VC/2CP, but in the presence of a protogenic compound (H_2O, HCl) confirmed the nonreactive character of the system isobutylene/BCl_3 reported earlier (17,18). Also, there was no initiation of the polymerization of isobutylene with tert-butylchloride or chloride of the allyl type (4-chloro-2-nonene), even after seven days of observation. The results are summarized in Table 1, the dilatometric measurement is illustrated in Fig.1.

The polymerization of isobutylene/BCl_3 at the boundary between a solid polymeric initiator and a liquid monomeric phase has not been described yet. We believe that the local occurrence of a relatively high concentration of chlorine atoms

Table 1 Reactivity of isobutylene in the presence of BCl_3 in bulk and with various initiators

Initiator	Concentration [mol/1×10^2]	BCl_3 concentration [mol/1 × 10^2]	Time (h)	Conversion (%)	Reference
-	-	35.8	168	polymer traces	Kennedy(17)
H_2O	47.8	12.4	48	0	Kennedy(17)
the residual moisture of the system		22.0	48	0	
the residual moisture of the system		28.4	168	polymer traces	
HCl	28.4	28.4	72	0	
t-BuCl	28.4	28.4	48	0	
$CH_3CH{=}CHCH(Cl)C_5H_{11}$	10	28.4	168	polymer traces	
PVC-A	41^a	28.4	10	8	
PVC-A¨	41^a	28.4	48	30	
PVC-A	41^a	28.4	150	52	
VC/2CP	33^a	24.0	10	5	
VC/2CP	33^a	24.0	20	12	
VC/2CP	33^a	24.0	48	25	

T = ~-78°C, ^{a} in g/l.

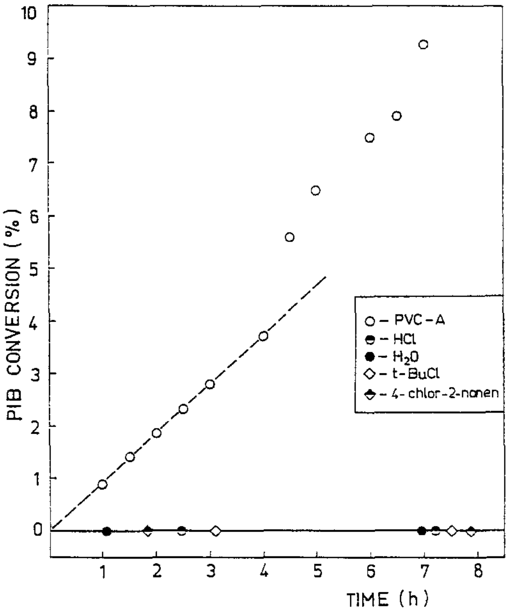
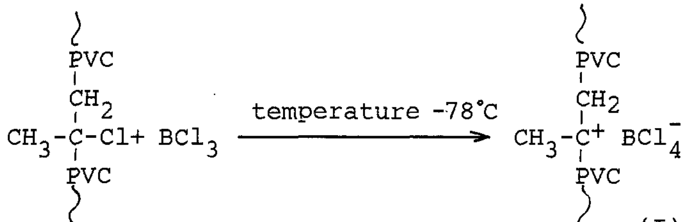


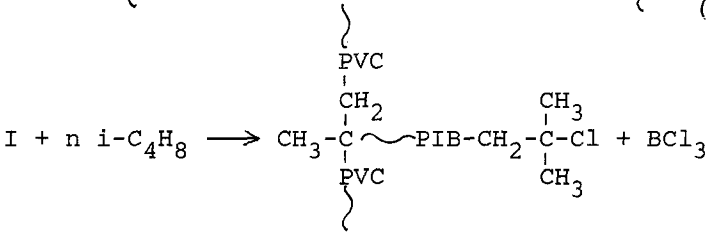
Fig.1 A dilatometric record of the mixture isobutylene/BCl_3 at -78°C in the presence of various initiators and in the absence of a polar chlorinated solvent; [HCl] = [t-BuCl]= 0.284 mol/l, [4-chloro-2-nonene] = 0.10 mol/l, solid PVC-A = 41 g/l, H_2O is the residual moisture in the system; [BCl_3] = const. = 0.284 mol/l; the initial rate $r_0 = 2.9 \times 10^{-5}$ mol/(l.s)

of the initiator which contains reactive units having the chloroallyl structure or the chlorine atom bound at the tertiary carbon atom in the polymer chains is due to the formation of a fixed initiation centre in which the polymerization originates. With the initiator VC/2CP, the polymerization can be illustrated by schemes (1) and (2):



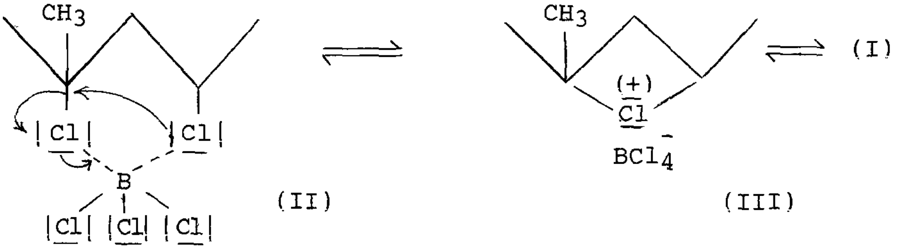
$$\mathrm{CH_3{-}\underset{\underset{\wr}{PVC}}{\overset{\overset{\overset{\wr}{PVC}}{CH_2}}{C}}{-}Cl + BCl_3 \xrightarrow{\text{temperature } -78^\circ C} CH_3{-}\underset{\underset{\wr}{PVC}}{\overset{\overset{\overset{\wr}{PVC}}{CH_2}}{C^+}}\ BCl_4^-} \qquad (1)$$

(I)



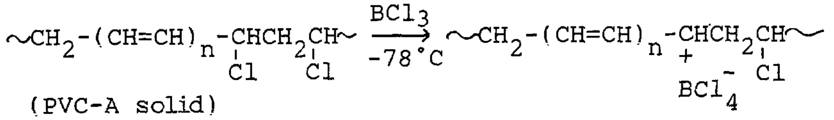
$$\mathrm{I + n\ i{-}C_4H_8 \longrightarrow CH_3{-}\underset{\underset{\wr}{PVC}}{\overset{\overset{\overset{\wr}{PVC}}{CH_2}}{C}}{\sim}PIB{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Cl + BCl_3} \qquad (2)$$

Since low-molecular weight compounds modelling the chloroallyl function or structure with the chlorine atom at the tertiary carbon atom are nonreactive and do not initiate the bulk polymerization of isobutylene (Table 1), it may be assumed that close surroundings of the reacting C-Cl bond, and particularly another C-Cl bond may participate in the formation of the growth centre. The possible transition state of reaction (1) with the formation of a fixed initiation centre (I) is illustrated by structures II and III. The formation of such complex is supported by a theoretical investigation of the PVC chain (21), in which the mutual interaction between chlorine atoms in the 1,3-position is regarded as possibly leading to the formation of an unstable cyclochloronium cation.



(II) (III) (I)

In the presence of PVC-A the fixed initiation centre arises probably according to reaction (3), and - similarly to the preceding case - participation of yet another C-Cl bond can be assumed.



$$\sim CH_2-(CH=CH)_n-\underset{Cl}{CH}CH_2\underset{Cl}{CH}\sim \xrightarrow[-78^\circ C]{BCl_3} \sim CH_2-(CH=CH)_n-\underset{BCl_4^-}{\overset{}{C}}\!\!\overset{}{H}^{+}CH_2\underset{Cl}{CH}\sim \qquad (3)$$

(PVC-A solid)

As the grafting of PVC-A or VC/2CP with isobutylene proceeds for many hours, it cannot be ruled out that in the monomer itself ionization of the chain of the arising telechelic polyisobutylene may take place ($\sim C-Cl + BCl_3 \rightleftharpoons \sim C^+ BCl_4^-$). The ionization was assumed for the system Cl-PIB-Cl/BCl_3 already earlier (12), but the medium was CH_2Cl_2.

Grafting of PVC-A with isobutylene in CH_2CH_2 in the presence of BCl_3 giving rise to a grafted copolymer of the PVC(A)-g-PIB-Cl type has been reported earlier (10,22). This is why the effect of the polar chlorinated solvent was investigated in a system in which the copolymer VC/2CP appears as the polymeric initiator. From the results summarized in Table 2 one can see that the conversion of PIB depends on the amount of the copolymer VC/2CP and on the content of dichloromethane in the polymerization mixture. With increasing content of VC/2CP the conversion also increases, and the presence of even a small quantity of the polar chlorinated solvent, i.e. dichloromethane, raises the reactivity of the initiator VC/2CP, as can be seen from a comparison of the results summarized in Tables 1 and 2. At a higher content of dichloromethane in the polymerization mixture, i.e. at the monomer concentration < 7 mol/l, the grafting of VC/2CP by isobutylene proceeds more quickly. The GPC analysis of the product is compared with the initiator in Fig. 2. The reaction leading to the formation of PIB-Cl or PVC(A)-g-PIB-Cl has already been proved earlier ($\sim C^+BCl_4^- \rightleftharpoons \sim C-Cl + BCl_3$) (3,4,7-10,22).

At a concentration of $i-C_4H_8$ about 3 mol/l in CH_2Cl_2/-78°C and with ~35 g/l VC/2CP in the polymerization mixture, products

Table 2 Polymerization of isobutylene/BCl_3 in a mixture monomer - CH_2Cl_2 at a high concentration of isobutylene in the presence of the copolymer VC/2CP (graft copolymer(VC/2CP)-g-PIB-Cl is formed)

Initiator g/l	Isobutylene [mol/l]	Time h	Conversion of PIB %
H_2O^a	8.9	2	0
H_2O^a	8.9	3	0
H_2O^a	8.9	4	0
H_2O^a	7.2	2	polymer traces
VC/2CP 1.0	8.9	2	2.1
VC/2CP 2.5	8.9	2	7.3
VC/2CP 5.0	8.9	2	9.5
VC/2CP 7.5	8.9	2	18.0
VC/2CP 7.5	7.2	2	33.0

T = -78°C, [BCl_3] = const. = 2.8×10^{-2} mol/l, [a] residual water in the system, molecular weight of products $\overline{M}_w$ was below 4.5×10^5. The products were soluble in THF and were swelling in heptane. Initiator, VC/2CP, was dissolved in CH_2Cl_2 at 25°C for 24 h prior to use, cooled and added to the polymerization mixture as the last component.

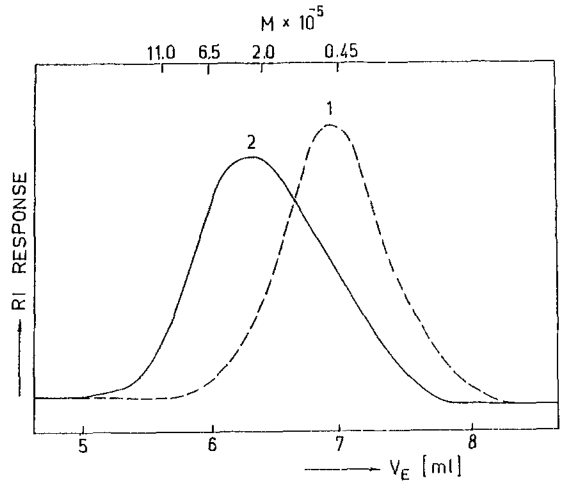
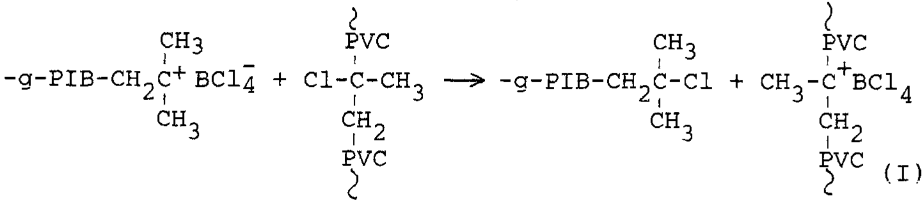


Fig. 2 GPC record: 1 - starting copolymer VC/2CP as initiator ($\overline{M}_w$ = ~6×10^4), 2 - graft copolymer (VC/2CP)-g-PIB-Cl ($\overline{M}_w$ = ~3.4×10^5) as the product of synthesis. Polymerization conditions: [$i\text{-}C_4H_8$] = 3 mol/l, [BCl_3] = 2.8×10^{-2} mol/l, VC/2CP = 30 g/l, T = -78°C, time 3h, conversion ~ 70%, weight composition of the product PIB:VC/2CP = ~4:1, Cl content 12.3 wt%.

arising at a conversion 40-50% are soluble in THF, while in heptane they form swollen gels. Molecular weights ($\overline{M}_w$) of the products are $< 4.0 \times 10^5$. Under the same experimental conditions, but in the absence of VC/2CP in the polymerization mixture and at a conversion of about 45% polyisobutylene is formed $\overline{M}_w \sim 1.1 \times 10^6$, in a good agreement with the molecular weight of PIB-Cl reported by Kennedy [17]. The substantially lower $\overline{M}_w$ values of graft copolymers compared with homopolymers PIB-Cl which arise by protonic initiation (H_2O/BCl_3) suggest that VC/2CP not only has an initiation effect on the polymerization of isobutylene, but that in apolar chlorinated solvent it behaves as an effective transfer agent. The transfer reaction may be illustrated by schemes (5) and (6):



$$\text{-g-PIB-CH}_2\overset{CH_3}{\underset{CH_3}{C^+}}BCl_4^- + Cl\text{-}\overset{\sim PVC}{\underset{\underset{PVC\sim}{CH_2}}{C}}\text{-}CH_3 \longrightarrow \text{-g-PIB-CH}_2\overset{CH_3}{\underset{CH_3}{C}}\text{-}Cl + CH_3\text{-}\overset{\sim PVC}{\underset{\underset{PVC\sim}{CH_2}}{C^+}}BCl_4 \quad (5)$$

(I)

$$I + n\ i\text{-}C_4H_8 \Longrightarrow (VC/2CP)\text{-g-PIB-Cl} + BCl_3 \qquad (6)$$

The polymerizations of $i\text{-}C_4H_8/BCl_3/CH_2Cl_2/-78°C$ initiated with VC/2CP($[i\text{-}C_4H_8] \leq 3$ mol/l, VC/2CP = ~ 30 g/l) always proceed up to a 100% conversion.

By a gradual dosage of styrene (St) or alfa-methylstyrene (αMeSt) into a polymerization mixture containing (VC/2CP)/BCl_3 CH_2Cl_2, graft copolymers of the type (VC/2CP)-g-St-Cl or (VC/2CP)-g- αMeSt-Cl[23,24] are formed at $T < -40°C$. The chlorine end atom could be replaced by some other functional group, e.g. -OH or $-NH_2$, with the purpose of obtaining reactive graft copolymers. The use of VC/2CP as an initiation-transfer agent combined with BCl_3 opens a new route for the preparation of tailor-made functionalized graft copolymers which may be utilized expecially as modifiers of the processing properties of polymer mixtures or as compatibilizers of immiscible polymer mixtures.

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