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A new family of telechelic copolymers

II. Initiation system PVC/BCl$_3$

Rudolf Lukáš and Luděk Toman*

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

Summary

A new initiation system polyvinylchloride (PVC)/boron trichloride (BCl_3) is demonstrated, which makes possible bulk polymerizations of isobutylene at a temperature about -78°C. The bulk polymerizations of isobutylene take place at the boundary between the solid and liquid phase for many hours, and PVC is grafted by isobutylene. Dichloromethane (CH_2Cl_2) raises the reactivity of the initiation system, and a graft copolymer poly (vinylchloride-g-isobutylene) PVC-g-PIB-Cl^t is formed, where --PIB-Cl^t is $+CH_2C(CH_3)_2+_{n}CH_2C(CH_3)_2Cl$. At -20°C the polymerization of isobutylene/BCl_3/CH_2Cl_2 proceeds in the presence of secondary alkylchlorides, such as 2,4-dichloropentane or 2,4,6-trichloroheptane, up to a 100% conversion, with formation of polyisobutylene oil ($\bar{M}_n \sim 3\times10^3$).

Introduction

In our preceding paper (1) we reported a new system (2,3) which initiates the polymerizations of cationically polymerizing monomers. The initiation system consists of two components, the first being BCl_3 (as co-initiator) and the second one being the polymer (as initiator) containing reactive chlorine atoms present in chloroallyl structures (C-Cl^a bonds) or bound on tertiary carbon atoms (C-Cl^t bonds). When using polyvinylchloride having a higher content of C-Cl^a bonds (PVC-A) or the copolymer of vinylchloride and 2-chloropropene (VC/2CP) as initiator, we were surprised to see that the polymerization of isobutylene/BCl_3 successfully proceeds also in the absence of a polar chlorinated solvent, i.e. in bulk, and the initiators are grafted by isobutylene. The bulk polymerization of isobutylene/BCl_3 has not been described yet. Within a suitable time interval the bulk polymerizations can be transferred into the commonly used slurry process by adding CH_2Cl_2 which considerably accelerates the polymerizations. The polymerizations can of course be successfully conducted from the beginning in the presence of CH_2Cl_2, as for the chemically dehydrochlorinated PVC has been proved by Kennedy et coll. (4,5). Since the radically prepared PVC contains both the C-Cl^a and the C-Cl^t bonds in small concentrations, we also tried to find polymerization conditions under which the usual commercial types of PVC could become suitable polymeric initiators, without the necessity of increasing their reactivity by chemical dehydrochlorination. Such conditions were indeed found (6); hence, this study is

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*To whom offprint requests should be sent a description of such initiation systems, including sec. alkyl chloride/BCl_3 systems which, surprisingly enough, are also reactive in the polymerization of isobutylene.

Experimental

As a sample of commercially available PVC we used a suspension type of PVC S-682 (Spolana Neratovice, CS), molecular weight $\bar{M}_w \sim 160\ 000$, sample PVC 1. Sample PVC-2, $\bar{M}_w \sim 155\ 000$, was prepared on a laboratory scale by the usual suspension polymerization of vinyl chloride. Acetone and benzene extracts obtained from the commercial sample PVC-1 are denoted PVC-1AE and PVC-1BE respectively, with the respective molecular weights ($\bar{M}_w$) 30 200 and 27 600. The synthesis of 2,4-dichloropentane (2,4-DCP) and 2,4,6-trichloroheptane (2,4,6-TCH) has been reported earlier (7).

Purification and drying of reaction components and the techniques employed in the polymerization procedures have been reported in papers (1,8). 2,4-DCP and 2,4,6-TCH were dried over molecular sieves.

Bulk polymerizations of isobutylene were carried out in a dilatometer 10 ml in volume at -78°C. At this temperature the powdered initiator was mixed with BCl_3 and the monomer was dosed as the last component. The syntheses of PVC-g-PIB-Cl^t in CH_2Cl_2 were carried out in a stirred reactor, 300 ml in volume. The mixture PVC-1/CH_2Cl_2/48 h/20°C prepared in advance was cooled and mixed with BCl_3 and the monomer at -78°C. Isobutylene was polymerized in the presence of secondary alkylchlorides, such as 2,4-DCP and 2,4,6-TCH, in glass ampoules 25 ml in volume. The mixture sec.alkylchloride/BCl_3/CH_2Cl_2/48 h/20°C prepared in advance was cooled and then dosed into the monomer at -20°C or -70°C. The reactions were terminated with methanol. The molecular weights of the polymers (weight and number average weights $\bar{M}_w$, $\bar{M}_n$) were determined by gel permeation chromatography (GPC) in a tetrahydrofuran (THF) solution using a HP 1084 B (1, 8) Chromatograph (USA). The instrument was calibrated with polystyrene standards on the basis of the well-known universal calibration principle using the Mark-Houwink equations which in THF hold for polystyrene (PS) $[\eta] = 1.17 \times 10^{-2} M^{0.717}$ and polyisobutylene (PIB) $[\eta] = 5 \times 10^{-2} M^{0.60}$ (with $[\eta]$ expressed in cm^3/g) (8). The $\bar{M}_w$,$\bar{M}_n$ values of the samples PVC and PVC-g-PIB-Cl^t are apparent, related to PS standards.

Results and Discussion

An important finding of the preceding study (1) was that in the presence of BCl_3 the C-Cl^t bonds present in the copolymer VC/2CP initiate the polymerization of isobutylene in both the polar and nonpolar medium, i.e. if the polymerization proceeds in bulk. The radically prepared PVC contains approximately 10^{-2} mol.% of chloroallyl structures and a concentration of the C-Cl^t bonds higher by approximately one order of magnitude. To enable also commercially types of PVC to be used as polymeric initiators without preceding chemical dehydrochlorination, we first concentrated on the possibility of using the activity of the already existing C-Cl^t bonds in these polymers, under polymerization conditions found for the C-Cl^t bonds in the preceding paper (1). A commercial or laboratory PVC sample (PVC-1

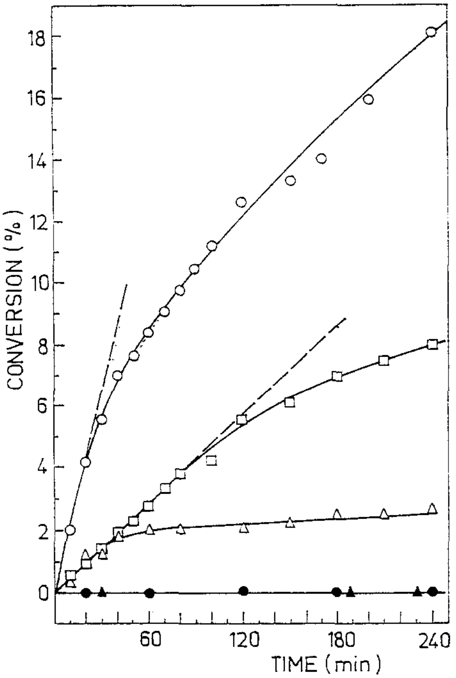


Fig. 1 Dilatometric records of bulk polymerizations of isobutylene/BCl_3 at -78°C in the presence of initiators PVC-1AE in the amounts 60g/l (○), 12g/l (□), PVC-1 60g/l (△) and of compounds 2,4-DCP (●) or 2,4,6-TCH (▲); detailed polymerization conditions are given in Table I

TABLE I

Bulk polymerization of isobutylene in the presence of BCl_3

Initiator		Conversion of PIB % in time						$r_o \times 10^5$	$r_{24} \times 10^6$
(g/l)		20 min	4h	22h	24h	27h	48h	mol/(l.s)	mol/(l.s)
PVC-1BE	60	4.3	18.5	40.9	42.3	43.8	49.7	41.3	16.0
PVC-1AE	60	4.2	18.2	40.6	42.0	43.4	49.0	40.0	14.9
PVC-1AE	12	1.0	8.0	17.8	18.0	18.8	22.6	9.6	8.5
PVC-1BE	12	1.0	7.8	18.3	18.6	19.3	23.1	9.6	7.4
PVC-1	60	1.0	2.6	4.1	4.1	4.1	4.2	9.6	0
PVC-2	60	1.0	3.1	4.8	4.8	4.8	5.0	9.6	0
2,4-DCP	14	0			0		0	0	0
2,4,6-TCH	23	0			0		0	0	0
H_2O, resp.	HCl	0			0		0	0	0

T = -78°C, $[BCl_3] = 5.7 \times 10^{-1}$mol/l, H_2O is the residual moisture of the system, $[HCl] = 3 \times 10^{-1}$mol/l

or PVC-2) was used as the polymeric initiator. The results summarized in Table I and Figure 1 indicate that both these types of PVC are also able to initiate the bulk polymerization of isobutylene and that the polymeric initiators PVC-1, PVC-2 are grafted by isobutylene (the products are not soluble in heptane).

In a study of the heat dehydrochlorination of PVC (9,10) it has been demonstrated that structural defects with labile chlorine are more often present in polymer fractions of lower molecular weights. This is why an acetone and benzene extract of PVC were used as polymeric initiators (PVC-1AE and PVC-1BE samples). As expected, the results obtained (Table I and Figure 1) clearly demonstrate the increased initiation activity of those polymeric initiators. With the same amount of PVC-1AE or PVC-1BE in the polymerization mixture the initial rate of polymerization r_o is approximately four times higher than r_o of the polymerization proceeding in the presence of PVC-1 or PVC-2 (cf. Table I, Fig.1). Bulk polymerizations of isobutylene initiated from PVC-1AE or PVC-1BE proceed within times longer than 24 h (rate $r = \sim 1.5 \times 10^{-5}$ mol/(l.s)) and stop spontaneously only after 48 h. The polymerization process can be seen in Fig. 2, where also two polymer layers are indicated. The lower layer shows the polymer formed approximately within 5 h after mixing of the components. The upper layer was formed within ~ 40 h. An analysis of samples of the separated layers (after breaking the dilatometer) revealed that molecular weights in the upper layer are somewhat higher than in the lower layer (upper layer: $\bar{M}_n = 1 \times 10^5$, $\bar{M}_w = 4.8 \times 10^5$ and 9.1 wt. % Cl; lower layer: $\bar{M}_n = 5.6 \times 10^4$, $\bar{M}_w = 4.7 \times 10^5$ and 12.9 wt.% Cl).

Since bulk polymerizations proceed without kinetic termination in the presence of PVC-1AE or PVC-1BE at the boundary between the solid and liquid phase for many hours also when all solid particles of the initiators have already been enveloped by polyisobutylene insoluble in the monomer, we believe that also in the monomer alone ionization of the chain end of the arising telechelic polyisobutylene ~PIB-Cl^t ($\sim CH_2C(CH_3)_2Cl + BCl_3 \rightleftharpoons \sim CH_2C(CH_3)_2\ BCl_4^-$) cannot be rejected. Comparative tests carried out in the absence of initiators based on PVC, but in the presence of a protogenic compound H_2O or HCl (cf. Table I) confirmed the nonreactivity of the system isobutylene/BCl_3 in the absence of a polar chlorinated solvent

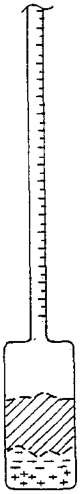


Fig. 2 Bulk polymerization of isobutylene/BCl_3 in the presence of 60 g/l of PVC-1BE as initiator (reaction conditions described in detail in Table I). PVC-1BE ⊞ i-C_4H_8/BCl_3 ☐ , Polymeric layer (lower) formed after ~5h ▤ and within ~ 40 h (upper layer) ▨ .

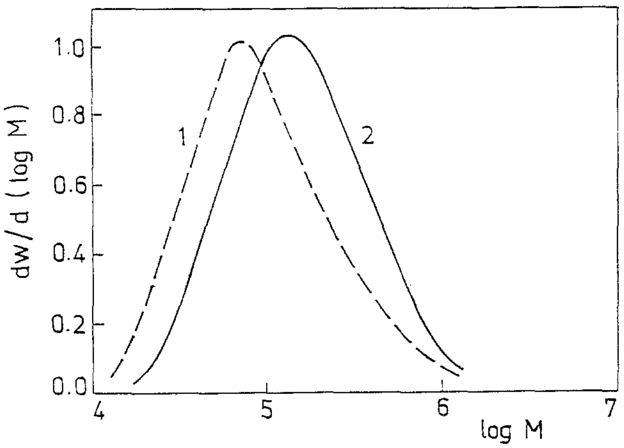


Fig. 3 Molecular weight distribution (MWD) of the initiator PVC-1 (sample 1 containing 54.8 wt.% Cl) and of the product PVC-g-PIB-Cl^t (sample 2 containing 24.7 wt.% Cl, $\bar{M}_n = 8.3 \times 10^4$, $\bar{M}_w = 2\times10^5$). Polymerization conditions: $[i\text{-}C_4H_8] = 1.2$ mol/l, PVC-1 = 51 g/l, $[BCl_3] = 0.1$ mol/l, T = -78°C, synthesis in CH_2Cl_2 conducted to ~100% /4 h.

reported earlier (1,11,12). CH_2Cl_2 raises the reactivity of initiation systems under investigation. At approx. 30 g of initiator in the polymerization mixture ($[i\text{-}C_4H_8] \leq 3$ mol/l, $[BCl_3] > 3\times10^{-2}$ mol/l, T = -78°C) the polymerization proceeds up to a 100% conversion with formation of PVC-g-PIB-Cl^t (~80% conversion is reached within 3-4 h). The GPC analysis of the product is illustrated in Fig. 3. The reaction leading to the formation of PIB-Cl^t or PVC(A)-g-PIB-Cl^t has been proved to occur earlier ($\sim C^+BCl_4^- \rightarrow \sim C\text{-}Cl^t + BCl_4^-$) (4,5,13).

Surprising results were obtained by experiments in which the dimer and trimer of PVC (2,4-DCP/BCl_3 and 2,4,6-TCH/BCl_3) are used as the initiation system. As can be seen in Figure 1 and Table I, these systems do not initiate the bulk polymerizations of isobutylene. The polymerizations proceed in CH_2Cl_2, under conditions where the protonic initiation (11,12) does not occur (i.e. at -20°C). At this temperature isobutylene polymerizes in the presence of the dimer or trimer of PVC, giving rise to the PIB oil ($\bar{M}_n$ ~3×10^3, conversion ~100%/18 h). A GPC analysis of the product is shown in Fig. 4. A ^1H NMR analysis [14] of oils demonstrated the absence of external or internal double bonds. The existence of such bonds (resonances in the region 4.5-4.8 ppm, resp. ~5.1 ppm) (8,15) would suggest that transfer to monomer (M) took place in the system at -20°C:

$$\sim CH_2C(CH_3)_2 + M \rightarrow H\text{-}M^+ + \sim CH_2C(CH_3){=}CH_2 \text{ or } \sim CH{=}C(CH_3)_2.$$

Since the transfer to monomer was not observed, it is obvious that in the reaction system another compound is responsible for the formation of the lower-molecular weight PIB. Suspicion that 2,4-DCP or 2,4,6-TCH in conjunction with BCl_3 may

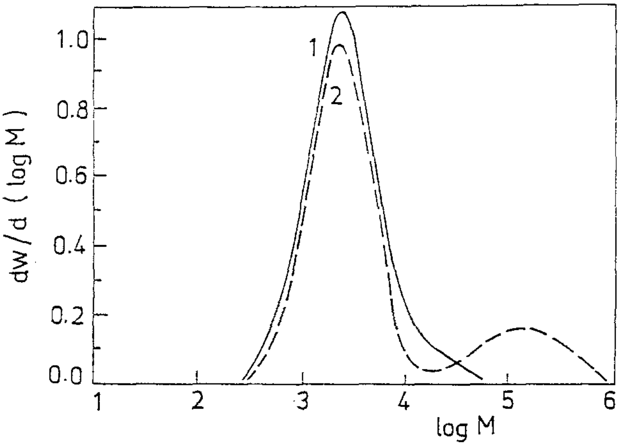
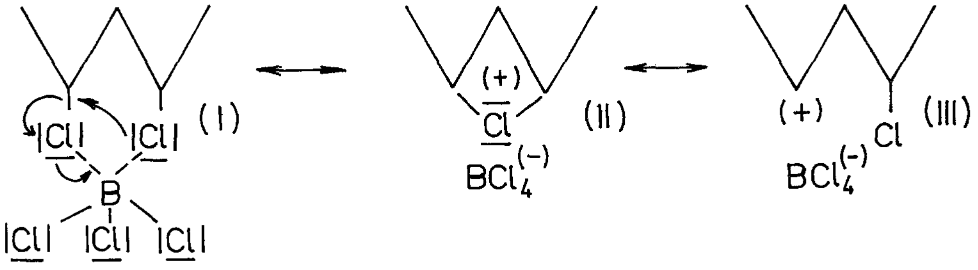


Fig. 4 MWD of oil samples synthesized at -20°C (sample 1, $\bar{M}_n = 2.8 \times 10^3$, resp. $\bar{M}_w = 5.6 \times 10^3$) and -70°C (sample 2). Polymerization conditions: $[i\text{-}C_4H_8] = 3.4$ mol/l, $[BCl_3] = 0.2$ mol/l, [2,4-DCP] = 0.2 mol/l, synthesis in CH_2Cl_2 up to ~ 100% conversion/18 h. With 2,4,6-TCH under the same conditions MWD values of samples of PIB oils were similar.

possess the property of transfer agents was confirmed for the polymerization of isobutylene/CH_2Cl_2 also at -70°C. At such low temperature PIB is formed, which contains approx. 80 wt.% of the lower-molecular weight fraction ($\bar{M}_n \sim 3 \times 10^3$, $\bar{M}_w \sim 5.6 \times 10^3$), characteristic of the PIB oil prepared at -20°C, as documented by Fig.4. In the absence of 2,4-DCP or 2,4,6-TCH, PIB-Cl^t is formed by the protogenic initiation at -70°C, $\bar{M}_n$ and $\bar{M}_w$ which are higher by approximately two orders of magnitude, in agreement with the literature (11). 2,4,-DCP and 2,4,6-TCH contain neither C-Cl^a nor C-Cl^t bonds. It is obvious, therefore, that under the polymerization conditions used chlorine atoms bound on secondary carbon atoms, i.e. C-Cl^s bonds, are reactive. Already in our preceding paper (1) we reported that, unlike polymeric initiators of the PVC-A type (higher content of the C-Cl^a bonds) and VC/2CP type (higher content of C-Cl^t bonds) their low-molecular weight models, such as 4-chloro-2-nonene and tert-butylchloride, do not initiate the bulk polymerization of isobutylene. To elucidate the initiation properties of PVC-A and VC/2CP in the bulk polymerization of isobutylene we assumed therefore (1), that also another C-Cl^s bond participates in the formation of the initiation centre on the polymer chain. By analogy with the results of a theoretical study of the dehydrochlorination of regular structural PVC units (14) we suggested (1) the existence of a transition state of the type of the cyclochloronium cation. Hence, in the case of 2,4-DCP and 2,4,6-TCH one may assume the same type of activation of the two adjacent C-Cl^s bonds which may form an activated complex with the structures I-III:



In bulk polymerizations initiated with the systems PVC-A/BCl_3, (VC/2CP)/BCl_3, PVC/BCl_3 activation of the C-Cl^a and C-Cl^t bond by a further C-Cl^s bond is obviously quite sufficient for the formation of a growth centre. Activation of a single C-Cl^s bond by another C-Cl^s bond, however, has to be assisted by a polar medium. It is probable, therefore, that in polymerizations initiated with the system PVC/BCl_3 in a polar medium both the C-Cl^a an d C-Cl^t bonds, on the one hand, and the C-Cl^s bonds, on the other, participate in the reaction.

In a gradual dosage of α-methylstyrene (αMeSt) or styrene (St) into a polymerization mixture containing PVC-1BE (PVC-1AE or PVC-1,2) and CH_2Cl_2/BCl_3, a graft copolymer of the PVC-g-PαMeSt-Cl^t or PVC-g-PSt-Cl^t (6,16) is formed at < -40°C.

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