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

II. Vinyl chloride/2-chloropropene copolymer as an initiator

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Summary

The low-polar polymerization of isobutylene (IB) in the presence of BCl_3 was carried out in CH_2Cl_2 ([IB] = 7 mol/l) at -78, -20 and +20°C in the presence of vinyl chloride/2-chloropropene (VC/2CP) copolymer, representing PVC resin enriched in structures with chlorine atoms bonded to the tertiary carbons. The polymerization products consist of mixtures of polyisobutylenes (PIB) and grafted VC/2CP-g-PIB copolymer. Attention was focused on evaluation of the extent of the grafting reaction. VC/2CP-g-PIB was analyzed by GPC, ^{1}H-NMR and ^{13}C-NMR spectroscopies and elemental analysis. The results obtained indicate that the rate of polymerization of IB decreases with increasing temperature but that the grafting efficiency increases. The experiments demonstrated that the VC/2CP copolymer induces strong grafting, compared with PVC, and that it might therefore be assumed that the C-Cl bonds with chlorine atoms bound to tertiary carbons directly initiate the polymerization of IB. The effect of the C-Cl bonds is discussed in terms of their catalytic and initiation activities.

Introduction

Many caationic graft copolymerization attempts failed because of the choice of coinitiator. Conventional Lewis acid coinitiators such as $AlCl_3$, BF_3, $TiCl_4$ or $SnCl_4$ are nonselective, i.e., they combine with traces of electrophilic imputiries (e.g. H_2O, HCl) forming carbenium ions which may initiate undesirable homopolymerization. Controlled carbocationic grafting began with the discovery that certain organoaluminium compounds with trace of protogenic impurities do not initiate polymerization, but need a labile alkyl halide (1-4). This principle was extended to the synthesis of graft copolymers (5-11). It has been proposed that labile chlorines (allylic and/or tertiary) in PVC in conjuntion with suitable organoaluminiums provide initiation sites for grafting (11,12).

It is noteworthy that PVC also catalyzes the IB/BCl_3 system in nonpolar medium and the so-far unknown bulk polymerization of IB was carried out (13,14). Concerning the polymerization of isobutylenes, BCl_3 requires the presence of polar medium (15) and the system IB-BCl_3 is completely non-reactive in nonpolar medium (13-15). In a previous work (16) we demonstrated that in weakly polar medium and with prolonged period of interaction (ageing) of PVC/BCl_3, a significant amount of PVC-g-PIB copolymer is

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formed with PIB content up to 10 wt.% indicating the direct initiation action of PVC.

On the other hand, it should be stressed that in a polar medium, e.g., in CH_2Cl_2 with a low monomer concentration, grafting of PVC failed, because traces of electrophilic impurities in conjunction with BCl_3 formed undesirable polyisobutylene and PVC-g-PIB copolymers have been synthesized only by using PVC backbones containing relatively high concentrations of allylic chlorines obtained by dehydrochlorination with a base prior to use (17-19). It is apparent from the results mentioned above that, when BCl_3 is used, a suitable choice of polymerization conditions and the structure of PVC, i.e. the content of "activated" C–Cl bonds capable of participating in the initiation reaction ($(C–Cl)^{In}$ bonds), can affect the grafting reaction. Thus, this work is concerned with examination of the effect of vinyl chloride/2-chloropropene (VC-2CP) coppolymer, representing PVC enriched in structures with chlorine atoms bonded to tertiary carbons, on the polymerization and grafting of IB in a weakly polar medium, e.g., in CH_2Cl_2 with a high monomer concentration.

Experimental

The purification and drying of IB with a purity of 99.8%, BCl_3, CH_2Cl_2 and nitrogen, and the polymerization technique and treatment of the polymer products by 10 h extraction with hexane, and also the GPC determination of the molecular parameters and determination of the polymer composition by elemental analysis have all been described previously (13,16). Since the Mark-Houwink constants required for the determination of molecular weights are unknown for VC/2CP and VC/2CP-g-PIB copolymers, we used for the comparison of molecular parameters the apparent molecular weights related to PS standards.

The VC/2CP copolymer was prepared by suspension copolymerization of vinyl chloride with 2-chloropropene; the content of 2-chloropropene units in the PVC chain was 8% wt. (elemental analysis), $\overline{M}_w$ = 43 000, $\overline{M}_n$ = 15 000 (molecular weight calculated as PVC); apparent molecular weights related to polystyrene standard, $\overline{M}_w$ = 71 000, $\overline{M}_n$ = 23 000. The VC/2CP copolymer was dried by the technique described previously (13).

^1H-NMR and ^{13}C-NMR spectra of the VC/2CP copolymer and grafted products VC/2CP-g-PIB were measured using 10% solutions in $CDCl_3$ at 60°C on a Bruker AC-300 spectrometer at frequencies of 300.1 MHz and 75.5 MHz, resp. The internal standard was hexamethyl disiloxane (HMDS). The chemical shifts given in the work are related to TMS (δHMDS = 0.05 ppm and 2.0 ppm in the ^1H and ^{13}C NMR spectra, respectively).

The grafting of IB from the VC/2CP copolymer (Table 1) was carried out in 25 ml glass ampoules at temperatures of -78°C to 20°C; concentration of IB in CH_2Cl_2 7 mol/l, BCl_3 0.07 and 0.09 mol/l, amount of VC/2CP copolymer 20-38 g/l. BCl_3 was condensed after cooling into a VC/2CP solution in CH_2Cl_2 (dissolved 24 h at room temperature) and this solution was either left to stand for 4 h at 25°C (runs 1, 2, 4, 5, 7, 8,Table 1) or was maintained at -20°C for 10 h (runs 9, 10, Table 1). Then the solution containing VC/2CP

Table 1 Synthesis of the VC/2CP-g-PIB grafted copolymer

Run	T	BCl_3	VC/2CP	IB	GE[a]	VC/2CP-g-PIB		
				Conversion		$\overline{M}_w{}^b \times 10^{-3}$	I[c]	PIB[e]
	°C	mol/l	g/l	%	%			wt.%
1	-78	0.07	20	31.5	6	466	5.2	37
2		0.09	25	30.0	8	467	5.1	38
3		0.09	0	0	0	-	-	-
4	-20	0.07	38	22.0	22	353	3.7	50
5		0.09	38	20.5	24	355	3.6	50
6		0.09	0	0	0	-	-	-
7	+20	0.07	38	7.0	43	108	4.4	31
8		0.09	38	7.1	42	189	4.3	31
9[d]		0.09	38	7.0	47	190	3.8	34
10[d]		0.09	38	7.2	46	-	3.7	34
11		0.09	0	0	0	-	-	-

[a] Definition of the graft efficiency: weight of PIB in grafts x 100/total weight of PIB products; [b] apparent molecular weight related to polystyrene standard, for original VC/2CP copolymer, $\overline{M}_w = 71\ 000$; [c] index of polydispersity $\overline{M}_w/\overline{M}_n$; [d] prolonged interaction of VC/2CP with BCl_3; [e] determined by elemental and ^{1}H-NMR analyses.

and BCl_3 in CH_2Cl_2 was added to the ampoule with the monomer. As a result of the change in the polarity of the medium, VC/2CP was present in the mixture in the form of a swollen precipitate. The ampoules were then placed in baths tempered at 20, -20 and -78°C. The polymerization was terminated after 4 h by addition of methanol to the reaction mixture.

Results and discussion

The polymerization results obtained are given in Table 1. It is apparent that the blank polymerization tests carried out in the absence of the VC/2CP copolymer at -78, -20 and 20°C (runs 3,6,11) did not yield any polymer products. This finding is in accordance with the observations published by Kennedy et al. (15). This fact indicates that the high concentration of IB in CH_2Cl_2 used (7 mol/l) forms such a weakly polar medium that common protogenic initiation is suppressed similarly as for polymerization carried out in the nonpolar medium of IB monomer alone (13,15). The non-reactivity of IB with BCl_3 observed is also in accordance with a recently suggested initiation mechanism, based on a self-ionization of BCl_3, which does not operate in low-polar medium either (20). However, a completely different situation occurs when the polymer system also contains

VC/2CP. The polymerization occurs in the heterogeneous phase of swollen VC/2CP, in which the PIB formed is precipitated, while the clear IB/CH_2Cl_2 layer does not exhibit any substantial viscosity changes. It is thus obvious that the presence of the VC/2CP copolymer is responsible for producing the polymerization of IB. In accordance with an earlier work (16), we feel that the effect of the VC/2CP copolymer can be explained in the following manner: The polymer chains of the VC/2CP copolymer containing C-Cl polar bonds locally substitute the effect of the polar solvent and their presence thus catalyzes the appearance of protogenic initiation of polymerization by the residual water in the system. It is suggested on the basis of the previous results on evaluation of the PIB products formed (16) that this protogenic initiation is based on interaction of all the components of the VC/2CP-BCl_3-H_2O system and, in contrast to common protogenic initiation, it will be called pseudoprotogenic initiation (16). The polymerization reactions occur relatively rapidly at low temperatures and, e.g. 30% conversion of IB is attained at -78°C over 4 h (Table 1). As the temperature increases, and especially above -20°C, pseudoprotogenic initiation is suppressed and the direct initiation effect of active $(C\text{-}Cl)^{In}$ bonds in the VC/2CP polymer chain begins to become important, leading to the VC/2CP-g-PIB grafted copolymer, e.g. according to the scheme:

$$(C{-}Cl)^{In} + BCl_3 \longleftrightarrow C^{(+)}BCl_4^{(-)} + IB \longrightarrow C{-}IB^{(+)}BCl_4^{(-)} + nIB \longrightarrow C{-}(IB)_nIB^{(+)}BCl_4^{(-)}$$

It can be seen from Table 1 that, as the temperature increases and thus the degree of effectiveness of the individual polymerization mechanisms changes, the conversion of IB decreases and the graft efficiency GE increases. So far, the highest content of PIB in VC/2CP-g-PIB was found for grafted copolymers prepared at a temperature of -20°C, i.e. 50% wt. It also follows from earlier experiments (16) that ageing, i.e. prolonging of the time of interaction of PVC with BCl_3 in the absence of IB, favours the formation of the grafted copolymer. This fact is also apparent from Table 1, where the ageing of VC/2CP with BCl_3 appears as an increase in the grafting efficiency (cf runs 7,8 and 9,10), i.e. there is an increase in the preference for $(C{-}Cl)^{In}$ bonds capable of direct initiation. If the polymerization reactions given in Table 1 are carried out without ageing of VC/2CP with BCl_3, i.e. where the IB is added immediately after the mixing, then the content of PIB in the VC/2CP-g-PIB does not exceed 12% wt. in the range of temperatures studied, in agreement with out previous results (14).

The hexane-extracted PIB products had properties corresponding to PIB polymers isolated in IB polymerization in the presence of PVC and were described previously (16). The grafted VC/2CP-g-PIB copolymer obtained as the insoluble fraction after extraction with hexane was analyzed by GPC (Fig. 1) and by ^1H-NMR and ^{13}C-NMR spectroscopy (Figs 2 and 3) and its composition was also determined by elemental analysis (Table 1). The ^1H-NMR spectrum of the initial VC/2CP polymer is given in Figure 2a. While only the resonances of the methine protons of the consecutive VC units lie in the

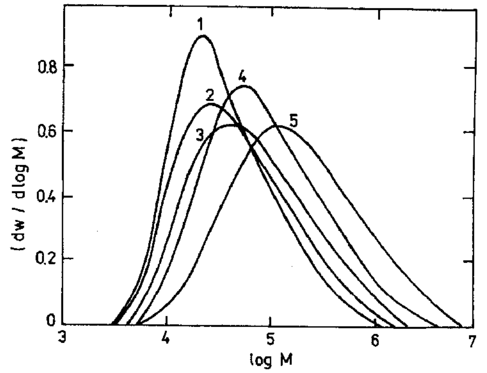

Figure 1 Differential distribution curves of the apparent molecular weights of VC/2CP (1) and VC/2CP-g-PIB samples from Table 1: run 7 (2), run 9 (3), run 4 (4) and run 2 (5)

4.2-4.7 ppm range, the 1.7-2.6 ppm range contains the resonances of both the VC units (CH_2 protons) and the 2CP units (CH_2 and CH_3 protons). The integrated intensities of these bands lead to the conclusion that the VC/2CP copolymer contains 7.9% wt. 2CP structural units, in very good agreement with the results of elemental analysis, yielding the value 8.0% wt. The ^{1}H-NMR spectrum of VC/2CP-g-PIB (run 2, Table 1) is depicted in Figure 2b. The presence of PIB grafts is documented by strong resonance at 1.1 ppm (CH_3) and 1.45 ppm (CH_2). The integrated intensities of the individual bands indicate that the grafted polymer from run 2 contains 38.7% wt. IB, again in agreement with the

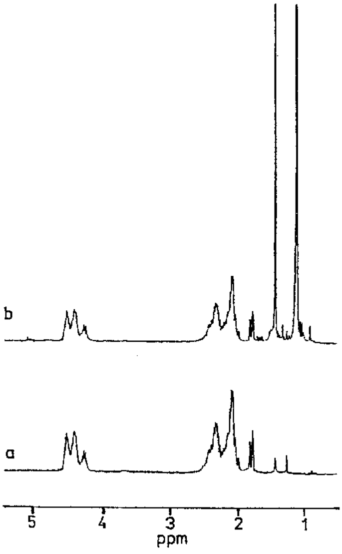

Figure 2 300.1 MHz ^{1}H-NMR spectra in $CDCl_3$ at 60°C (a) VC/2CP and (b) VC/2CP-g-PIB (run 2)

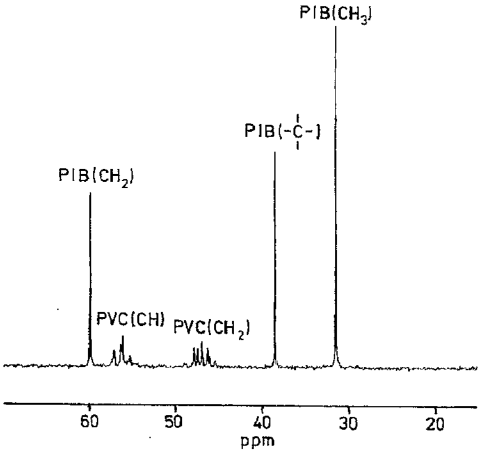

Figure 3 75.5 MHz ^{13}C-NMR spectrum of VC/2CP-g-PIB (run 2) in $CDCl_3$ at 60°C

value 38% wt. obtained by elemental analysis (Table 1). The presence of PIB grafts in the test sample of the grafted copolymer from run 2 is also apparent in Figure 3, which depicts the ^{13}C-NMR spectrum (cf. ref. 20). The resonances of 2CP are not visible in the spectrum because of its low content; these resonances (e.g. CH_3 carbons in the range 29-33 ppm) appear only at great amplification. The content of grafted PIB determined from the integrated band intensities in the ^{13}C-NMR spectrum agrees with the results of ^{1}H-NMR analysis.

The results of this work indicate that effective grafting of PVC by a cation-polymerizing monomer can be also achieved using weaker Lewis acids such as BCl_3, assuming that the PVC contains enhanced concentrations of $(C–Cl)^{In}$ bonds capable of participating in the initiation.

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