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Living polymerization of isobutylene initiated by *p*-dicumyl chloride/BCl_3/*n*-Bu_4NX systems

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Summary

The 1,4-di-(2-chloro-2-propyl)-benzene (pDCC)/BCl_3/IB system was investigated in the presence and absence of n-Bu_4NX. The presence of n-Bu_4NX (X= Cl or I) changes the mechanism increasing the living character of the polymerization of isobutylene in both cases. When n-Bu_4NCl is added, BCl_4^- is formed and as a common ion in excess it shifts the dissociation equilibrium toward the non-dissociated species. In the case of the addition of n-Bu_4NI, an exchange reaction between the gegenions, i.e., BCl_4^- and BCl_3I^- has been recognised and a possible reaction mechanism is given.

Introduction

The livingness of a cationic polymerization is a very important feature to control the molecular weight ($\bar{M}_n$) and molecular weight distribution (MWD) during the polymerization process. Several living systems have been discovered [1,2] during the last ten years but controversial data can be found in the literature concerning the polymerization mechanism. The latest view suggests that the ionicity of the propagating species is very important [2,3], and the living polymerization takes place with the participation of activated, but not dissociated species (Scheme 1)
To obtain insight into the mechanism we have investigated the pDCC/BCl_3/n-Bu_4NX/IB systems. The pDCC/BCl_3/IB system is a so called binifer system [5,6] and the polymerization is assumed to proceed via ionic species [7]. We hoped that by reducing the ionicity the binifer system may change to a living one. To achieve this we added n-Bu_4NX to the system which, in case X=Cl, produces the same anion as the gegenion present:

$$BCl_3 + \underline{n}\text{-}Bu_4NCl \rightleftharpoons BCl_4^- + \underline{n}\text{-}Bu_4N^+$$

The so formed BCl_4^-, the common ion now in excess, shifts by mass low action the dissociation equilibrium in the Winstein spectrum [4] to the left, producing less ionic species.

Besides the common ion (X=Cl) effect we also investigated the influence of n-Bu_4NI on the livingness of the polymerization.

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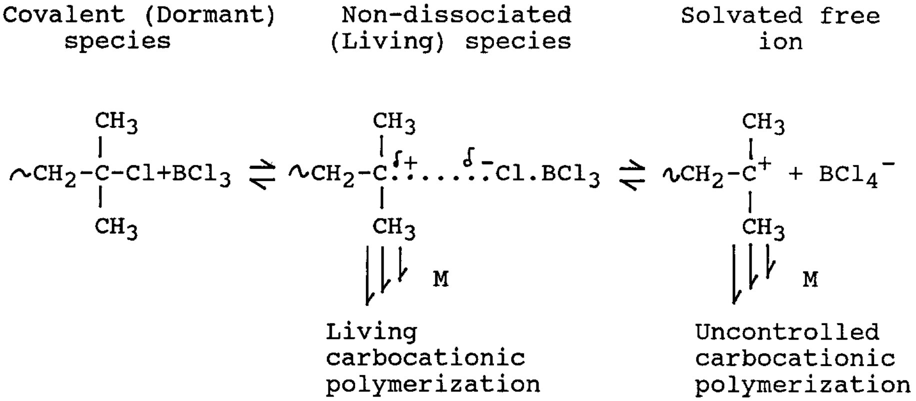
Scheme 1.

Carbocationic polymerization illustrated in the simplified Winstein spectrum



Experimental

p-Dicumyl chloride was synthesized as described [8]. Boron trichloride (Merck) and isobutylene (TIFO, Hungary) were distilled under dry nitrogen atmosphere. Tetrabutylammonium iodide (MERCK) and tetrabutylammonium chloride (ALDRICH) were high quality commercial products and were used without further purification. Methylene chloride was stored over KOH and distilled three times from phosphorous pentoxide right before use. _n_-Hexane was freed from olefinic impurities by a treatment with concentrated sulfuric acid, then washed and distilled.

Polymerizations were carried out under dry nitrogen atmosphere in a dry-box at $-80^{o}C$ and stopped by precooled methanol. After solvent evaporation the products were washed with methanol and dried. The polymer samples were dissolved in _n_-hexane, then the insoluble part was filtered out and after solvent evaporation the polymer was dried to constant weight under vacuum at room temperature.

Molecular weights were determined by using a Waters 501 high pressure GPC instrument, equipped with 410 RI and 440 UV detectors and a series of 500 A, 10^3 A, 10^4 A, 10^5 A ultrastyrogel columns. The polymer samples were dissolved in THF. The calibration curve was prepared by a series of well fractionated PIB samples.

Results

According to Scheme 1, the proportion of living propagation can be increased by increasing the concentration of the free gegenion, because then the concentration of the propagating free cations decreases and, at the same time, the amount of the less ionic species increases. It means that the proportion of cationic polymerization by the highly ionic species can be reduced and the polymerization, at least partly, can be converted into a living one.

In the absence of n-Bu_4NX (X= Cl or I) the polymerization of IB initiated by pDCC/BCl_3 is very fast and yields a quite broad MWD ($\overline{M}_w/\overline{M}_n$=1.54). However, in the presence of n-Bu_4NX the polymerization slows down and the MWD narrows (Tables 1,2 and Figures 1,2). The linearity of the plots shown in Figs. 1 and 2 indicate that the polymerizations are first order in monomer and no termination occurs.

To illustrate the absence of transfer in the polymerizations, the $\overline{M}_n$ versus weight of polymer (W_p) plots are shown in Figures 3 and 4. As can be seen, the experimental points are close to the theoretical line.

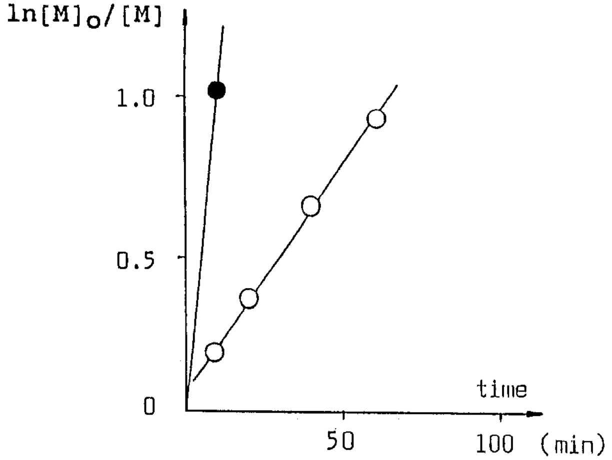


Figure 1. The first order plots of IB polymerization in the presence and absence of n-Bu_4NCl
(Experimental details are in caption of Table 1.)
[n-Bu_4NCl]= (●) 0 mole/L
(o) 0.01 mole/L
$[M]_0$ and [M] are the initial and actual concentrations of the monomer, respectively.

Discussion

As can be seen from the experimental data, in the presence of n-Bu_4NX (both with X=Cl or I) the binifer system changes to a living one. In case of n-Bu_4NCl the possible explanation is similar to that published by Pernecker et al. [3], i.e., the excess common ion (BCl_4^-) formed by the reaction of BCl_3 and n-Bu_4NCl shifts the ionic equilibrium (Winstein spectrum) to the left yielding less ionic species (See equilibrium I in Scheme 2).

On the other hand, in the presence of n-Bu_4NI, with BCl_3 not excess BCl_4^- but BCl_3I^- can only be formed. To obtain less ionic propagating species, i.e., to achieve living polymerization we have to suppose that an exchange reaction between the BCl_4^- and BCl_3I^- ions takes place because the

Table 1. Influence of the n-Bu_4NCl concentration on the rate of polymerization.
([pDCC]=0.0047 mole/L, [IB]=0.2566 mole/L
[BCl_3]=0.1024 mole/L, in CH_2Cl_2 at -80°C;
AMI technique was used)

n-Bu_4NCl (mole/L)	Time (min)	Conv. (%)	$\overline{M}_n$ (g/mole)	$\overline{M}_w/\overline{M}_n$	k_p^A [+] (min^{-1})
0.04	5	18.4	400	1.14	0.0160
(+)	10	25.9	530	1.19	
	20	35.7	860	1.17	
	30	42.3	1090	1.17	
	40	54.2	1420	1.11	
0.02	10	20.1	580	1.19	0.0164
(x)	20	29.9	830	1.23	
	40	51.9	1420	1.19	
	60	63.9	1810	1.10	
	90	68.1	1900	1.08	
0.01	10	18.8	540	1.19	0.0143
(o)	20	31.1	880	1.22	
	40	48.2	1230	1.24	
	60	60.8	1800	1.09	
	90	74.3	2000	1.08	
0.002	10	22.2	650	1.32	0.0150
(△)	20	31.5	910	1.23	
	40	52.5	1350	1.23	
	60	62.1	1520	1.25	
	90	68.5	1970	1.08	
0.001	10	23.0	720	1.30	0.0148
(□)	20	38.9	1040	1.26	
	40	54.5	1480	1.22	
	60	65.3	1680	1.21	
	90	72.6	2020	1.08	
0.00014[++]	5	38.3	950	1.52	
(▽)					
0.0	10	64.0	2850	1.54	> 0.1
(●)					

[+] Obtained from the slope of the first order plots like in Fig.1

[++] Polymer precipitation takes place

BCl_3I^- ions are in much higher concentration than the BCl_4^- ions. With the recombination equilibrium (Equilibrium II in Scheme 2) the free carbonium cation, the concentration of which is much less than the concentration of BCl_3I^-, similarly forms a non-dissociated, less ionic propagating species, allowing the propagation in a living manner.

Table 2. Influence of the n-Bu_4NI concentration on the rate of polymerization.
([pDCC]=0.00461 mole/L, [IB]=0.2566 mole/L
[BCl_3]=0.1024 mole/L in CH_2Cl_2 at -80°C;
AMI technique was used)

n-Bu_4NI (mole/L)	Time (min)	Conv. (%)	$\overline{M}_n$ (g/mole)	$\overline{M}_w/\overline{M}_n$	k_p^A[+] (min^{-1})
0.02	10	12.6	450	1.20	0.00688
(x)	20	14.0	680	1.25	
	40	21.6	870	1.26	
	60	39.0	1300	1.25	
	90	50.0	1400	1.27	
0.01	10	12.8	490	1.20	0.0118
(o)	20	24.1	750	1.24	
	40	37.8	1000	1.26	
	60	51.9	1520	1.21	
	90	61.8	1830	1.11	
0.002	10	21.1	560	1.25	0.0121
(Δ)	20	24.8	750	1.27	
	40	40.6	1390	1.13	
	60	54.0	1710	1.16	
	90	65.5	1990	1.08	
0.001	10	28.0	800	1.36	0.0122
(□)	20	33.4	950	1.31	
	40	49.2	1520	1.13	
	60	62.8	1890	1.10	
	90	71.9	2030	1.08	
	90	72.2	2000	1.06	

[+] Obtained from the slopes of the first order plots like in Fig.2

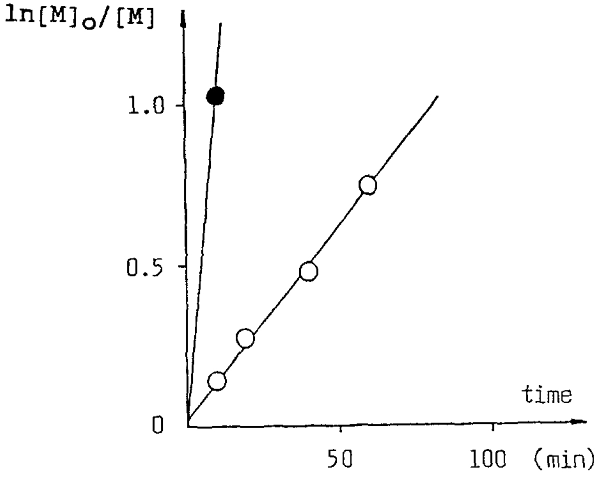


Figure 2. The first order plots of IB polymerization in the presence and absence of n-Bu_4NI
(Experimental details are in caption of Table 2)
[n-Bu_4NI]= (●) 0 mole/L
(o) 0.01 mole/L

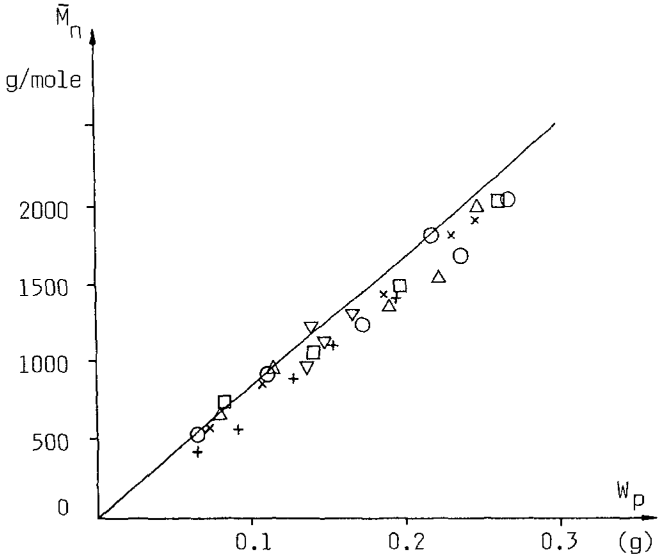


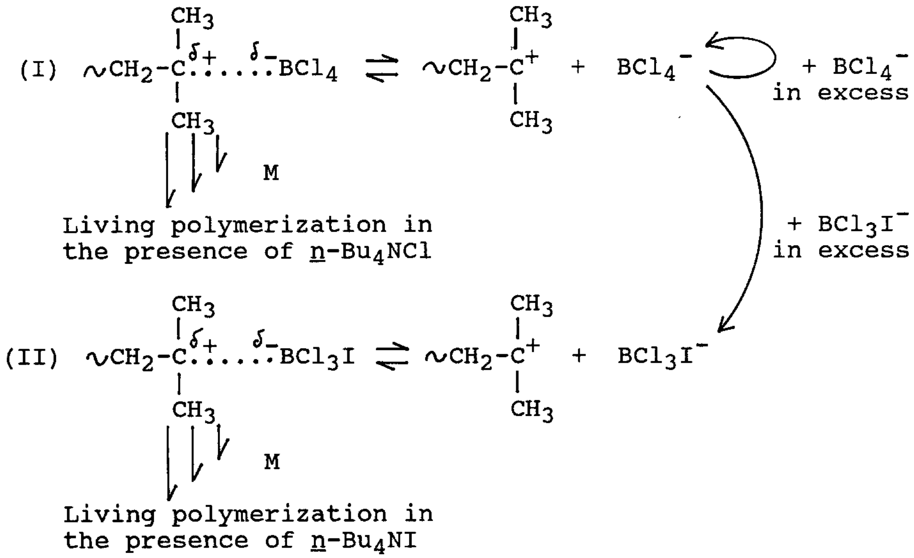
Figure 3. Living polymerization of IB in the presence of n-Bu_4NCl (Conditions are given in Table 1, the solid line is theoretical.)

Scheme 2.

In the presence of n-Bu$_4$NX the following reaction have to be taken into account:

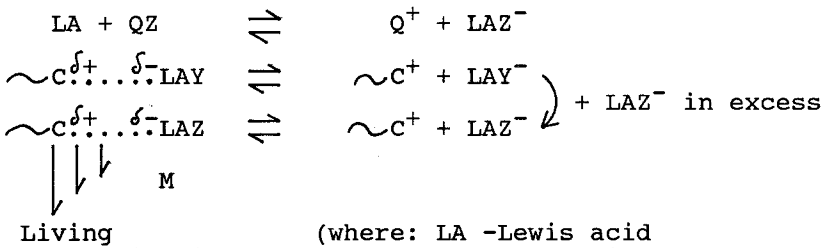
$$n\text{-Bu}_4\text{NCl} + \text{BCl}_3 \rightleftharpoons n\text{-Bu}_4\text{N}^+ + \text{BCl}_4^-$$

$$n\text{-Bu}_4\text{NI} + \text{BCl}_3 \rightleftharpoons n\text{-Bu}_4\text{N}^+ + \text{BCl}_3\text{I}^-$$



In this way, in general, one may probably obtain new living systems using large excess of possible gegenions to form new equilibria and new kind of non-dissociated growing specii as shown in Scheme 3.

Scheme 3.



(where: LA -Lewis acid
QZ -salt which can react with the Lewis acid)

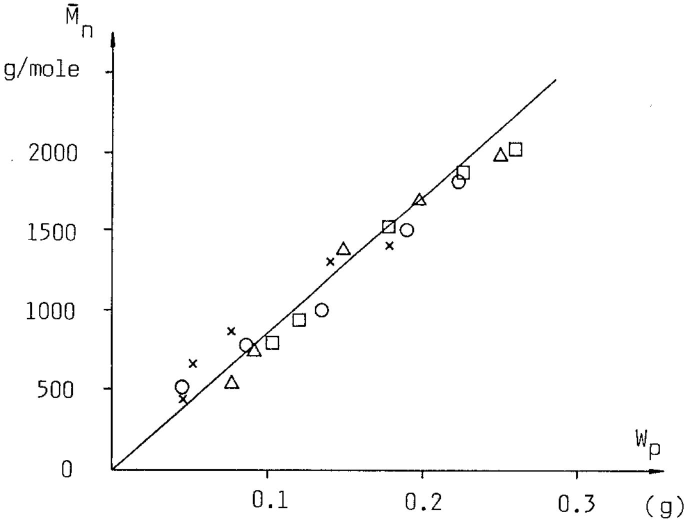


Figure 4. Living polymerization of IB in the presence of n-Bu_4NI (Conditions are given in Table 2, the solid line is theoretical.)

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