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Living cationic polymerizations initiated by phosgene

M. Zsuga[1] and T. Kelen[1, 2*]

[1]Institute of Applied Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary
[2]Central Research Institute for Chemistry, Hungarian Academy of Sciences, P.O. Box 17,
H-1525 Budapest, Hungary

ABSTRACT

Living cationic polymerization of isobutylene and styrene was performed by using phosgene as initiator and solvent, $AlCl_3$ as coinitiator in homogeneous phase. Polymerization of isobutylene by using phosgene and $TiCl_4$ also proved to be a living process, however, initiation in this case was performed by "H_2O" impurities, and the system was heterogeneous. In case of the $COCl_2/AlCl_3$ initiating system, ketonic carbonyl functionality was built-in into the polymer. The living character of the process, both in case of $AlCl_3$ and of $TiCl_4$ was demonstrated by the linear increase of $\overline{M}_n$ with the cumulative amount of the monomer successively added, and by the conversion and temperature jump at every monomer additon. Observations on the permanence of the color (intensive yellow with IB and deep red with St) also support that the propagating cations are long living. An explanation of the observed phenomena is suggested on the base of Pearson's theory of "hard" and "soft" acids and bases.

INTRODUCTION

Interest in living cation systems is continuously increasing. A few years ago, Kennedy and coworkers [1] demonstrated conditions which favored quasi-living olefin polymerizations. Higashimura et al. [2] performed living-like and living polymerizations of vinyl ether monomers.

Recently, Faust and Kennedy [3] discovered a new family of initiating systems based on organic tertiary esters.

Working in this line, we were looking for a solvent which is able to dissolve both the Lewis-acids and the formed polymer, in order to insure homogeneous polymerization conditions. We found that phosgene not only fulfils the above requirements, but it is also able to initiate living cationic polymerizations.

EXPERIMENTAL

Polymerizations were carried out in 100 ml three-neck-round-bottom flasks. The reaction vessels were equipped with two burettes, cooled with liquid N_2 or with cold N_2 vapor. The inlet and outlet for dry N_2 gas rinsing were equipped with a rubber septum for sampling, and with a thermometer, respectively. Magnetic stirrer was applied. Condensers located above

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[*] To whom offprint requests should be sent

the burettes were chilled with a slurry of dry ice and isopropanol. Outlets were equipped with $CaCl_2$ towers. The reaction vessel was heated by a flame immediately before use, to remove the rest of moisture.

Materials were purified as follows:

Isobutylene was prepared by dehydration of t-butyl alcohol at 300 °C over alumina catalyst just before use [4]. Liquid IB was dried over KOH pellets (50 cm column) and was fed in liquid or gaseous form.

Styrene, synth. grade, Merck product, was destabilized with 10% NaOH, washed with water, dried with anhydrous Na_2SO_4, and, just before use, distilled under N_2 atmosphere at 5 kPascal.

Methyl chloride was evaporated and dried and freed from HCl over KOH pellets (50 cm column).

Phosgene, 99.9%, free of chlorine, BVK (Hungary) product, obtained in steel pressure flask, was distilled into and fed from a chilled burette.

Aluminum chloride, synth. grade, Merck product, was sublimed at 4 kPascal immediately before use.

Titanium chloride, pract. grade, Fluka product, was used as received.

For the polymerization experiments, first the Lewis acid then the solvent was measured into the reaction vessel. After dissolution (or saturation of the solvent) the temperature was set to the desired value. Monomer was fed in successive steps, the first charge was less than the later charges. After feeding the individual charges, the reaction mixture was stirred for 15 minutes. Then 1 ml sample was taken by a syringe through the septum and was added to 15 ml prechilled CH_3OH. At the end of the experiment, the polymerization was stopped by adding the reaction mixture into 300 ml prechilled CH_3OH. The polymer product was dissolved in 40 ml $CHCl_3$ and precipitated with 120 ml CH_3OH. The purification was repeated three times, then the polymer was dried at room themperature under N_2 atmosphere at reduced pressure.

Characterization of the products was carried out using Perkin-Elmer IR, Nicolet FT-IR and Waters GPC instruments.

RESULTS AND DISCUSSION

The systems studied are numbered as follows:

I: "H_2O"/$AlCl_3$/Isobutylene/CH_3Cl
II: "H_2O"/$AlCl_3$/Isobutylene/$CH_3Cl:COCl_2 = 15:4$
III: $COCl_2$-"H_2O"/$AlCl_3$/Isobutylene/$COCl_2$
IV: $COCl_2$-"H_2O"/$AlCl_3$/Styrene/$COCl_2$
V: "H_2O"/$TiCl_4$/Isobutylene/$COCl_2$

The first item listed is the initiator whereby "H_2O" denotes the water impurities remaining in the system. Then the applied Lewis-acid is given, followed by the monomer.
The last item is the solvent.

Table 1 summerizes the experimental conditions. The primary observations and results are shown in Table 2. In the control experiments, System I and II, no color development could be observed and the conversion, in spite of the single

Table 1: Experimental conditions

System	Amount of				Total amount of		Number of feeds	Temperature (C^o)
	$AlCl_3$ (g)	$TiCl_4$ (g)	CH_3Cl (cm^3)	$COCl_2$ (cm^3)	IB (g)	St (g)		
I	0.502	-	50.0	-	2.347	-	1	- 70.0
II	1.00	-	15.1	4.0	3.92	-	1	- 70.0
III	0.675	-	-	17.9	7.43	-	5	- 20.0
IV	0.698	-	-	18.0	-	13.65	4	- 20.0
V	-	1.001	-	17.6	8.44	-	4	- 35.0

Table 2: Experimental results

System	Color		Final conversion %	Character of polymerization
	A	B		
I	- [a]	-	33	-
II	- [a]	-	72	-
III	pale yellow [b]	intensive[c] yellow	80	living[e], ketonic carbonyl func. [f]
IV	pale yellow [b]	intensive[c] red	100	living[e], ketonic carbonyl func. [f]
V	- [a]	yellow [d]	100	living[e]

a: heterogeneous system
b: homogeneous system
c: color appeared at the first monomer addition, and remained unchanged till killing
d: intensity of color (appearing at every monomer addition) decreases during the mixing period (15 min)
e: living character demonstrated by color, conversion, temp. jump and linear $\overline{M}_n$ increase
f: built-in carbonyl group demonstrated by IR and FT-IR

feeding, was relatively low. Methyl chloride could not dissolve the total amount of $AlCl_3$ (System I), moreover, it precipitated $AlCl_3$ from its phosgene solution (System II).

On the contrary, in Systems III-V, yields related to the total added amount of monomer are high, i.e., the polymerization was continued when a new monomer charge was added. This indicates living polymerization wich is also shown by the intensive color of the reaction mixture, remaining unchanged till the killing of the process (Systems III and IV). In case of System V, the intensity of the color decreased during the intervals between two feedings, however, it became intensive again at every monomer feeding. The living character of this polymerization is also shown by the temperature jumps observed at every successive feeding.

A typical molecular weight distribution curve is shown in Figure 1 (System III). As can be seen, the distribution is bimodal, and one of the peaks shifts toward the higher molecular weights as a result of successive monomer additions. At the same time, the weight fraction of polymers belonging to this peak increases. $\overline{M}_n$ vs. the weight of polyisobutylene formed (System III and V) is shown in Figure 2. The data plotted in this Figure were obtained by curve resolution for the increasing peak, thus they represent only approximate values.

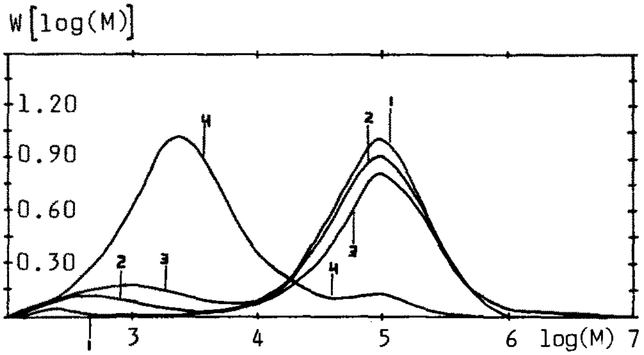


Figure 1: A typical bimodal molecular weight distribution curve obtained in the presence of residual "H_2O" (System III). The curves are numbered according to the successive monomer additions

Infrared spectra of samples of System III and IV show that a C=O group from the phosgene is built-in into the polymers. As an example, Figure 3 shows the spectrum of a polyisobutylene sample (System III). The peak at 1706 cm^{-1} (at 1718 in case of polystyrene) corresponds to a ketonic carbonyl functionality. This peak cannot be found in polyisobutylene samples of System V. These experimental facts can be explained only by assuming that the iongeneration step of initiation is different with $AlCl_3$ than with $TiCl_4$. According to the different complex forming ability of $TiCl_4$ [5], it probably does not form a stable ionic complex with $COCl_2$. Iongeneration with $TiCl_4$ proceeds, correspondingly, on the usual way:

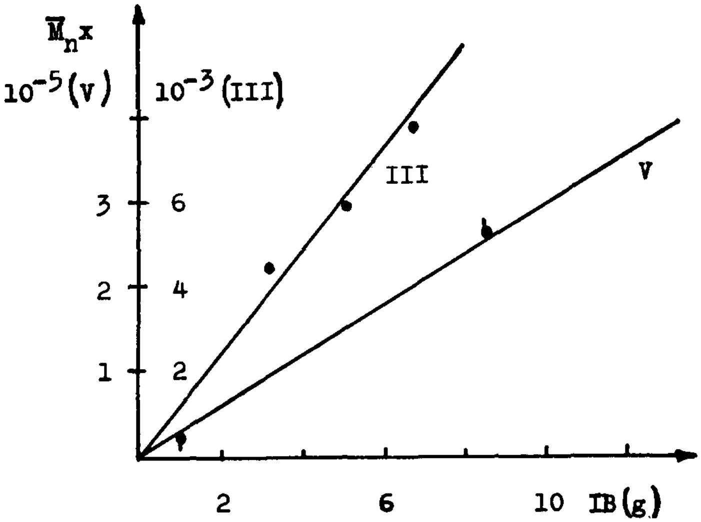


Figure 2: Dependence of $\tilde{M}_n$ on the cumulated amount of the polymer formed during successive addition of monomer (System III and V). Only data belonging sufficiently resolvable GPC curves are represented

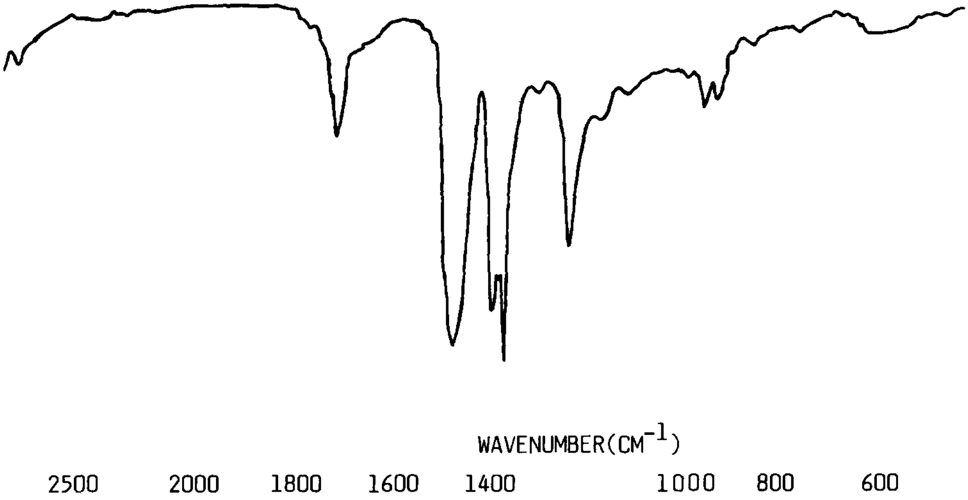
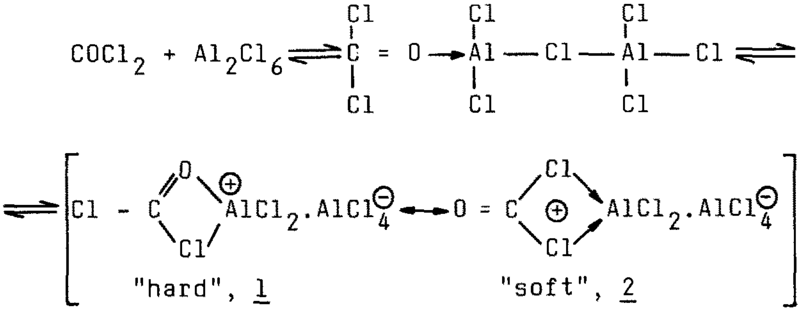


Figure 3: IR spectrum of a polyisobutylene film sample on KBr pellet (System III)

$$TiCl_4 + H_2O \rightleftharpoons H^{\oplus}[TiCl_4OH]^{\ominus}$$

On the contrary, $AlCl_3$ forms stable complexes with $COCl_2$ [6,7], thus the initiation with $AlCl_3$ in phosgene can be assumed as follows:

Iongeneration (self-ionization of $AlCl_3$):

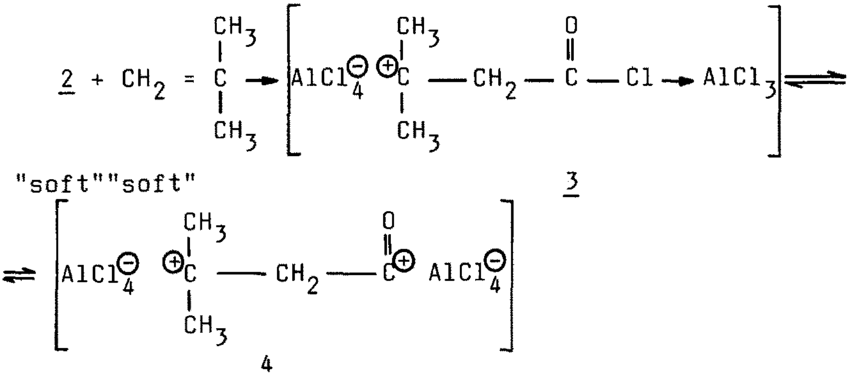


"hard", 1

"soft", 2

i.e., according to Pearson's theory of acids and bases [8], the "hard" type cation 1 transforms into the "soft" type 2. The "soft" form of the cation is more probable than the "hard", because of the more extended delocalization. The "soft" cation 2 enters easily into reaction with a monomer which is a "soft" base.

Cationization:



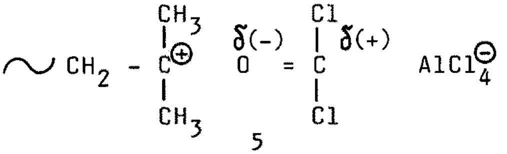
$$2 + CH_2 = \overset{CH_3}{\underset{CH_3}{C}} \rightarrow \left[AlCl_4^{\ominus}\ {}^{\oplus}\overset{CH_3}{\underset{CH_3}{C}} - CH_2 - \overset{O}{\overset{\|}{C}} - Cl \rightarrow AlCl_3\right] \rightleftharpoons \left[AlCl_4^{\ominus}\ {}^{\oplus}\overset{CH_3}{\underset{CH_3}{C}} - CH_2 - \overset{O}{\overset{\|}{C}}{}^{\oplus}\ AlCl_4^{\ominus}\right]$$

"soft""soft" 3

4

The coordinated acyl chloride 3 can be regarded as a substituted acetyl chloride which forms with $AlCl_3$ an acylium complex, 4 [9,10].

The living character of the propagation can be explained by the solvent-separated ion-pair 5:



$$\sim CH_2 - \overset{CH_3}{\underset{CH_3}{C^{\oplus}}} \quad \overset{\delta(-)}{O} = \overset{Cl}{\underset{Cl}{C}}{}^{\delta(+)} \quad AlCl_4^{\ominus}$$

5

Insertion of the phosgene molecule between the growing cation and the gegenion increases the "soft" character of the cation. Thus the reactivity of the propagating cation with "soft" bases (monomer) increases and with "hard" bases (gegenion, impurities etc) decreases, i.e., the probability of transfer and termination decreases.

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