Polymer Bulletin 29, 15–20 (1992)

Polymer Bulletin

Living carbocationic polymerization

LIII. Common ion effect mediated by a crown ether*

T. Pernecker and J. P. Kennedy*****

Institute of Polymer Science, University of Akron, Akron, OH 44325-3909, USA

Summary

Living carbocationic polymerization (LC$^{\oplus}$Pzn) of isobutylene (IB) has been achieved by the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating systems in the presence of KCl in conjunction with the 18-crown-6 ether in CH_2Cl_2/hexanes solvent mixture at -80°C. The rate of initiation is relatively slow and the molecular weight distribution (MWD) of the polyisobutylene (PIB) becomes narrower ($\bar{M}w/\bar{M}n$ decreases from ~1.8 to ~1.2) in the course of incremental monomer addition (IMA). In the presence of the crown ether, and depending on its concentration, the charges become highly viscous rendering stirring difficult and preventing the synthesis of $\bar{M}n$'s in excess of 15,000 g/mole.

Introduction

We have reported [4] that a conventional carbocationic polymerization of IB can be converted to a living one by the juditious addition of a common ion salt, e.g., nBu_4NCl, to the charge. We became interested to extend these investigations to common anions generated by the use of simple inorganic salts, e.g. KCl, in conjunction with crown ethers. Crown ethers and cryptates have been used to advantage as powerful alkali metal cation solvating agents in anionic polymerization research [1,2,3]. We theorized that LC$^{\oplus}$Pzn could be achieved by adding to a conventional cationic polymerization system KCl plus a suitable crown ether to effect the solubilization of this salt in the relatively low polarity polymerization charges usually employed [4,5,6]. Specifically, we postulated that KCl in the presence of 18-crown-6 will dissolve in CH_2Cl_2/hexanes 60/40 v/v:

$$\mathrm{KCl} + \text{18-crown-6} \rightleftharpoons \textcircled{\scriptsize K$^{\oplus}$}\ \mathrm{Cl}^{\ominus} \qquad (1)$$

where the circle around the K$^{\oplus}$ stands for the crown ether, and that the Cl$^{\ominus}$ in conjunction with the excess $TiCl_4$ commonly present in cationic polymerization charges will increase the concentration of the $TiCl^{\ominus}_5$, the counteranion of the growing cation, by:

$$\textcircled{\scriptsize K$^{\oplus}$}\ \mathrm{Cl}^{\ominus} + \mathrm{TiCl}_4 \rightleftharpoons \textcircled{\scriptsize K$^{\oplus}$}\ \mathrm{TiCl}^{\ominus}_5 \rightleftharpoons \textcircled{\scriptsize K$^{\oplus}$} + \mathrm{TiCl}^{\ominus}_5 \qquad (2)$$

---

*For paper LII in this series see Y. Ysunogae, J. P. Kennedy in J. Macromol. Sci. – Pure and Applied Chemistry, in press

**Visiting scientist, permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1025 Budapest, Hungary

***Corresponding author

By increasing the concentration of the $TiCl^{\ominus}_5$ in the system, the mobile equilibria in the Winstein spectrum will be pushed toward the left [7] and the $LC^{\oplus}$Pzn will arise.

This paper concerns a demonstration of $LC^{\oplus}$Pzn of IB induced by KCl/18-crown-6 ether complexes.

Experimental

Experiments were carried out in a dry box under dry nitrogen using large (75 mL) test tubes. The 18-crown-6 ether (Aldrich) was used as received. KCl (Aldrich) was dried in vacuum at 100°C for at least 48 hrs. The KCl is essentially insoluble in CH_2Cl_2 at room temperature. Usually 0.16 g ($2.1 \cdot 10^{-3}$ mol) KCl was dissolved under constant agitation using 0.6 g ($2.3 \cdot 10^{-3}$ mol) 18-crown-6 in 50 mL CH_2Cl_2 at -80°C over a period of several hours. The amount of the crown ether used was slightly higher than the KCl/crown ether stoichiometric ratio. The preparation of the KCl/crown ether stock solution takes several hours because of the low solubility of KCl even in presence of the crown ether. Interestingly, dissolution is noticeably slower at room temperature than at -80°C, conceivably because the polarity of CH_2Cl_2 increased by lowering the temperature.

The synthesis of 2-chloro-2,4,4-trimethylpentane (TMPCl) has been described [8]. The source and purification of $TiCl_4$, CH_2Cl_2, Hexanes (hex) and IB have been described [5,6]. Polymerizations were initiated by TMPCl/$TiCl_4$ combinations in CH_2Cl_2/hex (60,40) mixtures in the presence of different concentrations of the KCl/18-crown-6 system. The diagnostic incremental monomer addition (IMA) technique was used [6] throughout these experiments.

It was observed that in the presence of KCl/crown ether systems the viscosity of the charges increased much faster than in the absence of this complex and that the systems became heterogeneous (i.e., blobs of polymer started to precipitate) quite rapidly at $\overline{M}n$~5000. Since PIB is readily soluble in CH_2Cl_2/hex 60/40 v/v charges up to very high molecular weights (at least up to $\overline{M}n$~100,000), heterogeneity in the present system is due to the presence of KCl/18-crown-6 complexes. Due to premature polymer precipitation, controlled polymerizations could not be carried out to $\overline{M}n$'s much beyond 15,000. In efforts to alleviate precipitation experiments were also conducted in 250 mL flasks under vigorous stirring. However, in these instances also, polymer soon precipitated around the stirrer so that incremental monomer addition became ill controlled. Interestingly, the precipitates rapidly dissolved upon quenching the system with a few mL's of MeOH.

Molecular weights were determined by GPC. The equipment and methodology have been described [6].

Results and Discussion

Table 1. shows the data obtained in polymerizations induced by the TMPCl/$TiCl_4$ initiating system in presence of

various amounts of KCl/18-crown-6. In line with previous investigations [4] we expected that the rate of polymerization of IB upon the generation of common ion will be similar to that obtained with nBu_4NCl. Indeed, similarly to polymerizations carried out in the presence of nBu_4NCl, orienting conversion-time studies showed (not reported) the expected rate reduction in the presence of KCl/crown ether systems.

Table 1. Polymerization of IB in presence of KCl/18-Crown-6 ([TMPCL] = 1.35 10^{-2}mol/L, [$TiCl_4$] = 1.75 10^{-1}mol/L, [IB]= 0.64 mol/L/incremental addition in CH_2Cl_2/Hex. (60/40 v/v) -80°C; total volume = 20 mL)

	(KCl/18-crown-6) mol/L	Wp g	$\bar{M}n$ g/mol	$\bar{M}w/\bar{M}n$	N $x\cdot 10^4$
1.	$1.35\cdot 10^{-3*}$	0.7750	3900	1.85	1.98
2.		1.4757	6500	1.67	2.27
3.		2.2052	9200	1.47	2.39
4.		2.8184	10830	1.40	2.59
5.		3.7345	13600	1.22	2.74
6.	$2.70\cdot 10^{-3*}$	0.7194	4500	1.85	1.59
7.		1.5891	6500	1.85	2.44
8.		2.3433	9500	1.45	2.46
9.		2.8326	11000	1.31	2.57
10.		3.7267	13300	1.25	2.80
11.	$1.35\cdot^{-2**}$	0.8770	4000	1.68	2.19
12.		1.3847	5900	1.48	2.34
13.		1.4493	6800	1.54	2.13
14.		2.2762	8800	1.35	2.58
15.		2.0377	8700	1.36	2.34

Conversions close to 100% in every experiment
*IB addition every 4 min.
**IB addition every 8 min.

Figure 1. shows the relationship between the number average molecular weight ($\bar{M}n$) and the weight of polymer (Wp) obtained. The initial $\bar{M}n$ values start somewhat above the theoretical line (constructed by assuming 100% initiator efficiency) but reach it after the 5th incremental IB addition. These facts indicate living polymerization with relatively slow initiation [8].

System heterogeneity due to precipitation was gradually increasing and by the fifth monomer addition agitation became impossible which prevented further monomer additions. The heterogeneity increased with increasing KCl/18-crown-6 concentration. In spite of this precipitation phenomenon monomer conversion in each incremental monomer addition step was close to 100%. Apparently the rate of polymerization was not influenced by the increasing heterogeneity of the system, indicating that monomer diffusion through the precipitated swollen polymer coil did not become rate determining.

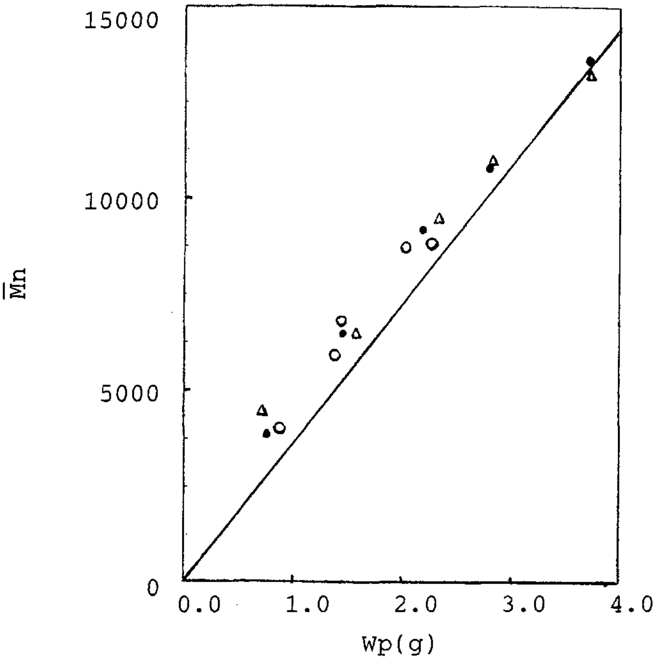

Figure 1. $\bar{M}n$ versus Wp of PIB plot (for experimental conditions see Table 1.). [IB]=0.64 mol/L/4 min (•) and (Δ) 8 min (○), [TMPCl]/[KCl/18-crown-6] 10 : 1 (•); 10 : 2 (Δ); 10 : 10 (○)

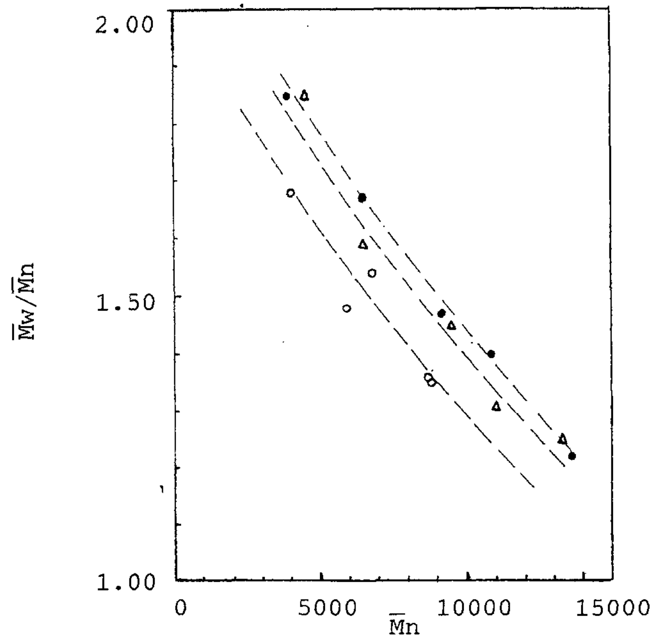

Figure 2. $\bar{M}w/\bar{M}n$ versus $\bar{M}n$ relationship (conditions and concentrations given in Table 1. and Figure 1.)

Figure 2. shows the molecular weight distribution (MWD) expressed by $\overline{M}w/\overline{M}n$ versus $\overline{M}n$'s. Evidently the MWDs become rapidly narrow with increasing $\overline{M}n$'s and increasing amount of common ion. The relatively broad MWD ($\overline{M}w/\overline{M}n$~1.8) obtained upon the first monomer addition is most likely due to slow initiation.

The rapidly declining $\overline{M}w/\overline{M}n$ values also indicate living polymerization. Such a decrease of $\overline{M}w/\overline{M}n$ was not observed in experiments carried out in the presence of nBu_4NCl [4]. We speculate that the observed MWD narrowing is due to the presence of the uncomplexed crown ether (present in the system because of the equilibrium shown by eq.1) which is a functional electron donor (ED). That ED's mediate LC$^{\oplus}$Pzn and cause the narrowing of MWDs been amply demonstrated [7,9,10].

The concentration of the free 18-crown-6 however, cannot be high because in a control run in which $1.35 \cdot 10^{-2}$ mol/L 18-crown-6 was used in the absence of KCl (other conditions identical to those given in Table 1.) the conversion of IB was less than 10% in 8 min.; this is in good agreement with earlier observations [11].

As mentioned in the Experimental, the precipitated material rapidly dissolves upon MeOH addition. We speculate that the precipitates are aggregates of living polymer held together by coordination with the free nucleophilic crown ether; upon the introduction of MeOH the aggregates fall apart. Polymer precipitation during polymerization with nBu_4NCl was not observed [4].

Conclusion

LC$^{\oplus}$Pzn of IB with relatively slow initiation has been achieved with the $TMPCl/TiCl_4$ initiating system in presence of KCl/18-crown-6. The living polymerization is most likely due to the increased concentration of the common anion $TiCl^{\ominus}_5$ which pushes the equilibria operating in the Winstein spectrum toward the left [7]. The results on hand, however, do not allow clearly to separate the common ion effect and possible ED effect caused by the possible presence of uncomplexed crown ether in the charge.

Acknowledgement

Financial support by the NSF (Grant 89-20826) is gratefully acknowledged.

References

1. M. Swarc, Adv. Polym. Sci., 49, 1 (1983)
2. S. Boileau, K. Kaemp, J. M. Lehn and F. Schue, Polym. Lett., 12, 203 (1974)
3. Z. Jedlinski, P. Kurcok and M. Kowalczuk, Macromolecules, 18, 2679 (1985)
4. T. Pernecker, and J. P. Kennedy, Polym. Bull., 26, 305 (1991)

5. G. Kaszas, M. Gyor and J. P. Kennedy, J. Macromol. Sci., A18(9), 1367 (1982-83)
6. R. Faust and J. P. Kennedy, J. Polym. Sci., Part A, 25, 1847 (1987)
7. J. P. Kennedy and B. Ivan, Designed Polymers by Macromolecular Engineering: Theory and Practice, Hanser Pub., (Munich), 1991
8. M. Zsuga, J. P. Kennedy and T. Kelen, J. Macromol. Sci. Chem., A26(9), 1305 (1989)
9. G. Kaszas, J. Puskas, J. P. Kennedy and C.C. Chen, J. Macromol. Sci. Chem. 26, 1099 (1989)
10. G. Kaszas, J. Puskas, C. C. Chen and J. P. Kennedy, Polym. Bull., 20, 413 (1988)
11. L. Sipos, M. Zsuga and T. Kelen, Polym. Bull., 27, 495 (1992)

Accepted June 1, 1992 K