Polymer Bulletin 19, 427–433 (1988)

Polymer Bulletin

Living carbocationic polymerization

XXII. Effect of polymer precipitation on molecular weight*

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

[1] Institute of Polymer Science, University of Akron, Akron, OH 44325, USA
[2] Institute of Applied Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary

Summary

The effect of polymer precipitation that occurs during polymerization on the number average molecular weight $\overline{M}_n$ has been investigated in conjunction with the recently described trans-2,5-diacetoxy-2,5-dimethyl-3-hexene ($DiAcODMH_6$)/BCl_3/isobutylene(IB)/CH_3Cl/-35° system using both the IMA and AMI techniques. All the experimental data could be described by a common rectilinear $1/\overline{M}_n$ versus $1/W_p$ (W_p = weight of polymer) plot exhibiting an intercept $1/\overline{M}_{n,max}$. A simple equation has been derived that explains quantitatively the results and suggests that product molecular weights obtained in heterogeneous polymerizations are determined by polymer precipitation which in turn leads to chain transfer. An Arrhenius analysis of $\overline{M}_{n,max}$ values obtained at various temperatures corroborates this proposition and suggests polymer precipitation to control $\overline{M}_n$. That precipitation conditions determine $\overline{M}_n$ seem also to hold true for conventional $AlCl_3$-induced IB polymerizations.

Introduction

In the course of our studies on living polymerization of IB we have encountered numerous heterogeneous polymerization systems, i.e., systems in which polymer precipitation occurs during polymerization. The industrially most important polymerizations and copolymerizations of IB (e.g., butyl rubber) carried out in CH_3Cl at ∿ -100°C, are also heterogeneous "slurry" systems (1). The scientific literature is also replete with heterophase IB polymerization systems (1). Polymer precipitation often leads to undesirable phenomena, e.g., reactor fouling, catalyst occlusion, and may also render

---

* Papers XXI of this series will appear in Polymer Preprints, R. Faust and J. P. Kennedy, 29(2), 1988

** Visiting scientist: Permanent address: Institute of Applied Chemistry, Kossuth Lajos University, Debrecen, H-4010 Debrecen, Hungary

*** Author to whom inquiries should be directed kinetic investigations questionable. It is therefore remarkable that the effect of polyisobutylene (PIB) precipitation on molecular weight has not yet been investigated systematically and no attempts have been published to quantitate this phenomenon.

Recently we have investigated the DiOAcDMH$_6$/BCl$_3$/IB/CH$_3$Cl/-35° system under homogeneous conditions and demonstrated its living nature (2). These investigations included both the "incremental monomer addition" (IMA) and the "all monomer in" (AMI) techniques. We noted that the diagnostic $\overline{M}_n$ versus W_p plots obtained by the IMA and AMI techniques gave somewhat different curves, particularly in the higher $\overline{M}_n$ regime ($\overline{M}_n$ > 5000). Thus efforts have been made to linearize these data. In the course of this work, we have discovered that the results obtained by both the IMA and AMI techniques gave virtually identical straight lines by plotting $1/\overline{M}_n$ versus $1/W_p$.

This paper concerns investigations focusing on the quantitative interpretation of this finding and a proposition that the maximum PIB molecular weight $\overline{M}_{n,max}$ obtainable in a slurry polymerization is determined by the heterogeneity of the system.

Experimental

The synthesis of DiOAcDMH$_6$ has been described (3,4). The source and purification of BCl$_3$, isobutylene and methyl chloride have been published (5). Molecular weights were determined by a Waters high pressure GPC instrument as reported (5). Polymerization details have also been published (5). The reactors were large (75 mL) test tubes. The charges were thoroughly mixed (for ∿10 sec by turbomix) during BCl$_3$ addition and incremental monomer addition (IMA technique), and several times during the polymerizations.

Results and Discussion

IB polymerizations have been carried out by the DiOAcDMH$_6$/BCl$_3$ living initiating system using CH$_3$Cl diluent at -35°C by both the IMA and AMI techniques under the conditions detailed in Table I. The data represent averages of 5 experiments. By the IMA technique, polymerizations became heterogeneous (milky) after the introduction of the third monomer increment (with $\Delta M < 0.2$ mL IB the systems remained homogeneous clear under the same conditions (2)). By the AMI technique the charges became milky when the [M] reached the same level at which heterogeneity appeared by the IMA technique.

The data in Table I are plotted in Figure 1. According to this figure (correlation coeff. $r > 0.99$) the $\overline{M}_n$'s obtained at the same W_p's by both the IMA and AMI techniques are virtually identical. Interestingly, the plot shows a significant intercept, whereas a similar plot constructed with data obtained by the IMA technique in homogeneous systems exhibits no intercept (2). The question immediately arises: How come that the $1/\overline{M}_n$ versus $1/W_p$ plot shows no intercept for the homogeneous system but exhibits a sizable intercept for the heterogeneous system? And: Can the intercept be used to quantitate the effect of precipitation on molecular weight? These questions were analyzed by the following train of thought:

TABLE I

Polymerization of Isobutylene by the trans-2,5-diacetoxy-2,5-dimethyl-3-hexene/BCl_3 Initiating System (MeCl, $[BCl_3]$ = 0.11 mole/L, $[I_o] = 3.71 \cdot 10^{-3}$ mole/L, total volume 25 mL, -35°C)

j**	Yield %	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	I^j_{eff} %	Observation
IMA Method (monomer increment ΔM = 0.4 mL = 0.19 mole/L/ every 10 mins.)					
1	100	4590	1.19	62	homog. system
2	97	5820	1.52	94	probably homog.
3	94	8160	1.45	98	milky
4	77	8970	1.43	98	"
5	76	9780	1.45	101	milky, precipitate on wall
6	74	10600	1.43	119	" "
7	72	11500	1.41	124	" "
8	63	11600	1.41	125	" "
9	52	11650	1.42	126	" "
AMI Method (BCl_3 added to charges)					
[M] (mole/L)					
0.15	100	4590	1.19	62	homog. system
0.38	102	7370	1.35	79	probably homog.
0.57	103	8990	1.38	97	milky
0.76	100	9220	1.41	126	"
0.95	100	9620	1.40	151	milky, precipitate on wall
0.19*	2,5	--	--		homog. system

*Control, $[I_o] = 0$. **Number of increments added.

The similarity of the $1/\overline{M}_n$ versus $1/W_p$ plot with the Mayo plot (6) is immediately apparent, and can be described by:

$$1/\overline{M}_n = A/W_p + B \qquad (1a)$$

(or

$$N = A + W_p B \qquad (1b))$$

where A and B are the slope and intercept, respectively, and $\overline{M}_n$ and N are the number average molecular weight and number of polymer molecules formed. Intercept B is the reciprocal maximum $\overline{M}_n$ obtainable in a given system, i.e., $\overline{M}_{n,max}$.

The polymer chemical significance of A and B becomes apparent from eq 2

$$\overline{DP}_n = \frac{{}_0\int^{\infty} R_p\ dt}{{}_0\int^{\infty} R_i\ dt + {}_0\int^{\infty} R_{tr}\ dt} \tag{2}$$

according to which $\overline{DP}_n$ (the number average degree of polymerization) in a heterogeneous system is controlled by the rates of propagation R_p, initiation R_i and various kinds of chain transfer processes R_{tr}, i.e., first and second order and other chain transfer processes.
By integration of the terms in eq 2 and by introducing the number average molecular weight ($\overline{M}_n = M_1 \cdot \overline{DP}_n$), conversion ($C = ([M_o]-[M])/[M_o]$), initiator efficiency ($I_{eff} = ([I_o]-[I])/[I_o]$), and weight of polymer ($W_p = M_1 \cdot [M_o] \cdot C$) we obtain

$$\overline{M}_n = \frac{W_p}{I_o I_{eff} + {}_0\int^{\infty} R_{tr}\ dt} \tag{3}$$

where $[M_o]$, $[M]$, $[I_o]$ and $[I]$ are the starting and actual monomer and initiator concentrations, respectively, and M_1 is the molecular weight of the monomer repeat unit. Thus

$$1/\overline{M}_n = I_o I_{eff}/W_p + [{}_0\int^{\infty} R_{tr}\ dt]/W_p \tag{4}$$

and

$$1/\overline{M}_{n,max} = \frac{{}_0\int^{\infty} R_{tr}\ dt}{W_p} \tag{5}$$

In the limiting case when all chain transfer processes are absent except the bimolecular chain transfer to monomer $R_{tr^2,M}$ (5), eq 5 yields

$$1/\overline{M}_{n,max} = \frac{k_{tr^2,M}}{k_p} \tag{6}$$

where $k_{tr^2,M}$ and k_p are the corresponding rate constants.

In the DiOAcDMH$_6$/BCl$_3$/IB system under homogeneous conditions an intercept is absent in the $1/\overline{M}_n$ versus $1/W_p$ plot and end-group studies have directly substantiated the absence of chain transfer (i.e., $\overline{F}_n$ was found to be 2) (2). In contrast, under the present heterogeneous conditions an intercept appears which suggests the presence of chain transfer to monomer. The fact that the apparent I^j_{eff}'s (where j is the number of increments added) far exceed 100% also indicates chain transfer (cf. column 5 of Table I). The conclusion is inescapable: polymer precipitation leads to chain transfer: $R_{tr^2M} = R_{prec}$. We propose that polymer precipitation leads to increasingly encumbered buried active sites, and that the precipitated polymer coil delays or prevents the arrival of the monomer to the growing center. As a consequence of monomer starvation at the active site, proton elimination to a suitable nucleophile (solvent, counter-anion, etc.) will start to compete with propagation. The relatively small protic entity will rapidly diffuse out of the swollen polymer coil and will protonate monomer. At this point chain transfer is complete. The relatively low polymer yields obtained during the later stages of the IMA series corroborate this notion: evidently, the later monomer increments (at j = 8,9 in Table I) are slow to reach the growing sites buried by precipitation.

In line with the above analysis $\overline{M}_{n,max}$ values obtained from $1/\overline{M}_n$ versus $1/W_p$ plots with a given system under homogeneous and heterogeneous conditions could be used to differentiate quantitatively between the effects of chain transfer inherent in homogeneous systems and chain transfer due to precipitation. Specifically, by determining $1/\overline{M}_{n,max}^{het}$ and $1/\overline{M}_{n,max}^{homo}$, where the quantities denote the intercepts of $1/\overline{M}_n$ versus $1/W_p$ plots obtained in hetero- and homogeneous systems, respectively, one could obtain the total (i.e., inherent plus precipitation caused) chain transfer effect on $\overline{M}_n$ and the homogeneous phase chain transfer effect on $\overline{M}_n$. The difference $1/\overline{M}_{n,max}^{het} - 1/\overline{M}_{n,max}^{homo}$ would be an expression of the effect of chain transfer on $\overline{M}_n$ due to precipitation. In the living system under investigation chain transfer is absent in the homophase thus $1/\overline{M}_{n,max}^{het}$ is due only to precipitation.

The effect of precipitation on $\overline{M}_{n,max}^{het}$ was investigated at various temperatures. Thus a series of AMI experiments have been carried out using a series of $[M_0]$'s, as shown in Table II, at -30, -35 and -40°C, and the $\overline{M}_{n,max}$ values have been determined by extrapolation of linear $1/\overline{M}_n$ versus $1/W_p$ plots. (The experimental error is much lower by the AMI than by the IMA technique.) According to the results shown in Table II, $\overline{M}_{n,max}$ decreases with decreasing temperature, i.e., the solubility of PIB decreases with decreasing temperature. Importantly, the sign of the Arrhenius activation energy differences for $\overline{M}_{n,max}$ is positive (i.e., $\Delta E_{\overline{M}_{n,max}} = + 4.6$ kcal/mole (19.2 kjoule/mole)). Had chain transfer or termination been the molecular weight determining event as in conventional systems, the sign of $\Delta E_{\overline{M}_{n,max}}$ would have been negative (7). Thus the molecular weight determining event in the present system cannot be conventional chain transfer or termination but is most likely precipitation. Evidently chain transfer occurs after polymer precipitation, i.e., after the rate of chain growth has declined due to precipitation. In this sense $\overline{M}_{n,max}$ is a quantitative expression of the effect of precipitation on $\overline{M}_n$.

TABLE II

Kinetic Parameters of Polymerization of Isobutylene with the trans-2,5-diacetoxy-2,5-dimethyl-3-hexene/BCl_3 Initiating System Obtained by the Use of Eq 1a (MeCl, $[BCl_3]$ = 0.11 mole/L, $[I_o] = 3.7 \cdot 10^{-3}$ mole/L, $[M_o]$ = 0.19, 0.38, 0.57, 0.76 and 0.95 mole/L, total volume = 25 mL, 10 min, -35°C, AMI method)

t (°C)	$A10^5$ (mole)	$B10^5$ (mole/g)	$\overline{M}_{n,max}10^{-4}$ (g/mole)	r*
-30	4.02	6.25	1.60	0.993
-35	3.73	7.14	1.40	0.996
-40	2.99	9.46	1.05	0.994

*Correlation coefficient

Efforts have been made to apply this analysis to the industrially important heterogeneous "H_2O"/$AlCl_3$-induced polymerization of IB in CH_3Cl diluent. A thorough literature search provided a system, i.e., "H_2O"/$AlCl_3$/IB/CH_3Cl/-35° (8), for which the $1/\overline{M}_n$ versus $1/W_p$ plot could be constructed. Figure 1 shows this plot for the DiOAcDMH$_6$/BCl_3 combination

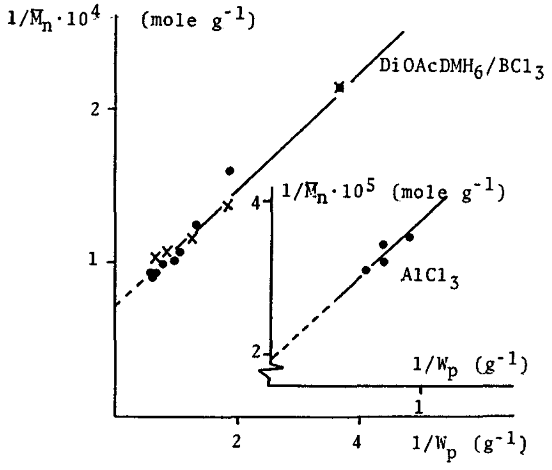

Figure 1. $1/\overline{M}_n$ versus $1/W_p$ plots (see text for explanation. ● = IMA, x = AMI technique. The data points on the $AlCl_3$ plot obtained from ref. 8).

and the inset for the "H_2O"/$AlCl_3$ system. Evidently the plot is linear and shows a sizable intercept. The $\overline{M}_n$'s and the $\overline{M}_{n,max}$ obtained by "H_2O"/$AlCl_3$ are higher than those with the DiOAcDMH$_6$/BCl_3 combination which has been shown to be a slowly initiating living system (2). "H_2O"/$AlCl_3$-induced IB polymerizations carried out in CH_3Cl diluent are known to proceed very rapidly, indeed, the extremely high rates together with system heterogeneity precluded rate determinations to date. Evidently the molecular weights in these IB polymerizations can rapidly grow to remarkably high levels because the rate of polymerization (propagation) far exceeds that of precipitation.

Acknowledgements

This research is based on work supported by the National Science Foundation under Grants DMR 84-18617 and INT-86-07993.

References

1. Carbocationic Polymerization, J. P. Kennedy and E. Marechal, John Wiley-Interscience, New York, 1982

2. M. Zsuga, J. P. Kennedy and T. Kelen: Macromolecules, to be published

3. K. Alder and H. von Brachel: Ann. Chem. 608, 195 (1957)

4. D. R. Paulson, L. S. Gilliam, V. O. Terry, S. M. Farr, E. J. Parker, Y. N. Tang, R. Ullman and G. Ribar, J. Org. Chem. 43(9), 1783 (1978)

5. R. Faust and J. P. Kennedy, J. Polym. Sci., Part A, 25, 1847 (1987)

6. F. A. Mayo, J. Am. Chem. Soc., 65, 2324 (1943)

7. J. P. Kennedy and P. D. Trivedi, Adv. Polym. Sci., 28, 213 (1978)

8. J. P. Kennedy and R. M. Thomas, J. Polym. Sci., 46, 481 (1960)

Accepted February 18, 1988 K