

Effect of Reaction Conditions on Isoprene Polymerizations Initiated from Ethyl 2-Bromoisobutyrate

Alexandru D. Asandei and Hyun Seok

Institute of Materials Science, Polymer Program, and Department of Chemistry, University of Connecticut, Storrs, CT 06269

Living radical polymerization (LRP) enables control over molecular weight and polydispersity has been widely applied in the synthesis of complex macromolecular structures.¹ While catalytic systems based on late transition metals were successful in LRP mediated by atom transfer radical polymerization (ATRP)^{1,2} dissociation-combination (DC) and degenerative transfer (DT) and initiated from activated halides or thermal initiators, a broader selection of initiators and catalysts is still needed for the controlled polymerization of certain monomers.

The paramagnetic Cp_2TiCl_2 ,³ available in situ by the Zn reduction of Cp_2TiCl_2 ⁴ is a mild one electron transfer agent which catalyzes a variety of radical reactions⁵ including epoxide radical ring opening (RRO)⁶, aldehyde SET reduction and halide abstraction. We have demonstrated the Cp_2TiCl_2 -catalyzed LRP of styrene⁷ initiated by epoxides, aldehydes,⁸ halides⁹ and peroxides.¹⁰ The effect of ligands, reducing agents, solvents, additives, reagent ratios and temperature was also investigated.⁷ This methodology was also applied in the synthesis of branched and graft copolymers.¹¹ Ti alkoxides generated in-situ from epoxides and aldehydes also catalyze the living ring opening polymerization of cyclic esters,¹² epoxides and anhydrides.¹²

1,3-Dienes such as isoprene and butadiene are industrially important¹³ but their controlled polymerization is typically accomplished by anionic¹⁴ or coordination¹⁵ methods requiring stringent synthetic conditions. While ATRP works very well with styrene and (meth)acrylates, extension to dienes,¹⁶ has proven troublesome and with the notable exception of nitroxides¹⁷ and RAFT reagents,¹⁸ metal catalyzed LRP methods have generally failed to control diene polymerizations. Since preliminary experiments on Cp_2TiCl_2 -catalyzed isoprene¹⁹ and butadiene LRP initiated from halides,^{20e,f,i} (as well as epoxides,^{20a,b,g} and aldehydes^{20c,d,h}) and were encouraging, we decided to compare the initiation ability of activated halides for both Cu and Ti.²¹ We are presenting below preliminary experiments of the Cu-catalyzed initiation of isoprene polymerization from activated bromoesters.

EXPERIMENTAL

Materials. Tin (II) 2-ethylhexanoate ($\text{Sn}(\text{EH})_2$, 95 %), tris(2-aminoethyl)amin (TREN, 96 %), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA, 99 %), CuBr, (99+%), all from Aldrich, CuCl (99+ %), ethyl 2-bromoisobutyrate (EBIB, 98 %) all from Acros, and 2,2-bipyridyl (bpy, Alfa Aesar), were used as received. Isoprene (Iso, 99+%, Acros) was dried over CaH_2 and passes through a short Al_2O_3 column. Dioxane (99.7%, Acros) and toluene (J.T. Baker) were distilled over Na/benzophenone.

Techniques. $^1\text{H-NMR}$ (400 MHz) spectra were recorded on a Bruker DRX-400 at 24 °C in CDCl_3 . GPC analyses were performed on a Waters 150-C Plus gel permeation chromatograph equipped with a Waters 410 differential refractometer, a Waters 2487 dual wavelength absorbance UV-VIS detector set at 254 nm, a Polymer Laboratories PL-ELS 1000 evaporative light scattering (ELS) detector and with a Jordi Flash Gel ($1 \times 10^5 \text{ \AA}$, $2 \times 10^4 \text{ \AA}$, $1 \times 10^3 \text{ \AA}$) column setup. THF (Fisher; 99.9 %) was used as eluent at 2 mL/min at 34 °C. Number- (M_n) and weight-average molecular weights were determined from calibration vs. polystyrene standards.

Polymerizations. A 35-mL Ace Glass 8648 # 15 Ace-Thread pressure tube equipped with bushing and a plunger valve containing a mixture of CuBr (28.6 mg, 0.2 mmol), 2,2-bipyridyl (93.6 mg, 0.6 mmol), and toluene (2 mL) was degassed under Ar and stirred for 10

minutes at rt. The tube was opened under Ar and charged with EBIB (0.029 mL, 0.2 mmol) and isoprene (2 mL, 20 mmol), re-degassed and heated at 110 °C for 24h. Conversions were determined by NMR, by integrating the polymer vs. a reference solvent peak.

RESULTS AND DISCUSSION

The initiation of isoprene polymerizations by EBIB in the presence of Cu complexes is demonstrated in Figure 1. In all cases, the polymer NMR corresponds to a typical free radical polymerization with the *cis* and *trans*-1,4 units ($-\text{[CH}_2\text{-CCH}_3\text{=CH-CH}_2\text{]-}$, a, $\delta = 1.81\text{-}2.16$ ppm, $-\text{[CH}_2\text{-CCH}_3\text{=CH-CH}_2\text{]-}$, b, $\delta = 5.04\text{-}5.26$ ppm, and $-\text{[CH}_2\text{-CCH}_3\text{=CH-CH}_2\text{]-}$, c, $\delta = 1.4\text{-}1.8$ ppm and $-\text{[CH}_2\text{-CCH}_3\text{=CH-CH}_2\text{]-}$, d, $\delta = 1.81\text{-}2.16$ ppm), the 1,2-units ($-\text{[CH}_2\text{-C(CH}_3\text{)CH=CH}_2\text{]-}$, e, $\delta = 1.4\text{-}1.8$ ppm, $-\text{[CH}_2\text{-C(CH}_3\text{)CH=CH}_2\text{]-}$, c', $\delta = 0.88\text{-}1.05$ ppm, $-\text{[CH}_2\text{-C(CH}_3\text{)CH=CH}_2\text{]-}$, f, $\delta = 5.7\text{-}5.84$ ppm and $-\text{[CH}_2\text{-C(CH}_3\text{)CH=CH}_2\text{]-}$, g, $\delta = 4.80\text{-}5.01$ ppm), the 3,4-units ($-\text{[CH}_2\text{-CH(CCH}_3\text{)=CH}_2\text{]-}$, h, $\delta = 1.4\text{-}1.8$ ppm, $-\text{[CH}_2\text{-CH(CCH}_3\text{)=CH}_2\text{]-}$, i, $\delta = 1.8\text{-}2.16$ ppm, $-\text{[CH}_2\text{-CH(CCH}_3\text{)=CH}_2\text{]-}$, k, $\delta = 1.4\text{-}1.8$ ppm and $-\text{[CH}_2\text{-CH(CCH}_3\text{)=CH}_2\text{]-}$, j, $\delta = 4.6\text{-}4.8$ ppm) in 1,4/1,2/3,4 ratio of about 90/5/5. The EBIB connectivity with the polymer is further substantiated by the ester resonance o ($\delta = 4.1\text{-}4.2$ ppm) and the allylic a', a'' ($\delta = 2.2, 2.75$ ppm) resonances. The chain end presents a very poor (about ~16 %) allyl bromide chain end functionality (m, $\delta = 3.9$ ppm).

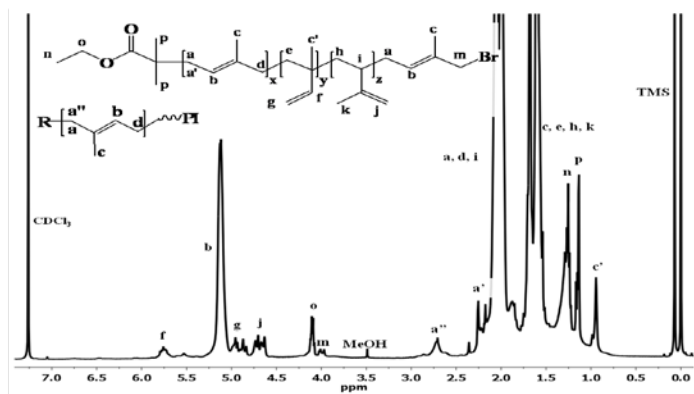


Figure 1. 500 MHz $^1\text{H-NMR}$ spectrum of PI initiated by EBIB. $[\text{IP}]/[\text{EtBriB}]/[\text{CuBr}]/[\text{Bpy}] = 100/1/1/3$ at 110 °C. (R = EBIB fragment).

The effect of several reaction variables was further explored as detailed in Table 1. While the table provides the M_n data from both MeOH precipitated and non-precipitated samples, such precipitation does lead to fractionation due to the good PI solubility especially at low M_n . Thus, some of the narrower PDIs may just be due to such fractionation. First, for very low Cu loading (0.1) having stoichiometric or excess bpy still leads only to oligomers and low conversion (exp. 1,2). At medium Cu levels (0.5) and at 130 °C slightly improved initiator efficiency (IE) (exp. 3-5) is observed upon increasing the ligand amount. Doubling the bpy, carrying the polymerization in dioxane vs. toluene or switching from CuBr to CuCl (exp. 6-9) provide very similar conversion but slightly narrower PDI for dioxane and CuBr. At a 1/1/1 EBIB/CuBr/Bpy ratio, increasing the temperature from 110 °C to 150 °C provides only oligomers at 150 °C and an optimum polymerization temperature of 110-130°C. The CuCl/CuBr comparison was further extended while varying the amount of ligand (1/1 to 1/12), temperature and solvent (exp 12-22), providing narrower PDIs (by at least 0.1 units, unprecipitated samples) in all cases. However, large excess of bpy (1/12 exp.22) lead to severe broadening of the PDI.

The ligand effect is illustrated in exp. 14, 23-26. While Me_6TREN and PMDETA give much lower conversion than bpy, TREN also leads to very broad PDI (>5).

Finally, the polymerizations were also attempted in the presence of $\text{Sn}(\text{EH})_2$ ²² (exp. 27-31). As expected, $\text{Sn}(\text{EH})_2$ reduces the in situ

generated Cu(II) halides and thus while conversions are very similar upon increasing the amount of Sn, the PDI values are quite broad.

Table 1. Cu-catalyzed Isoprene Polymerizations Initiated from EBIB in Toluene, t = 24h.

Exp #	Cat./Lig.	[Iso]/[I]/[Cat]/[Co-cat]/[Lig]	T (°C)	Mn	PDI	Conv (%)	IE
1	CuBr/Bpy	100/1/0.1/0.2	130	730	1.09	19	1.77
2	CuBr/Bpy	100/1/0.1/1	130	773	1.18	19	1.67
3	CuBr/Bpy	100/1/0.5/0.25	110	680	1.54	12	1.20
4	CuBr/Bpy	100/1/0.5/0.25	130	1,850	1.12	18	0.66
5	CuBr/Bpy	100/1/0.5/1	130	1,864	1.19	22	0.80
6	CuBr/Bpy	100/1/1/0.5	110	1,360	1.58	17	0.85
7	CuBr/Bpy	100/1/1/1 ^{a)}	110	1,042	1.36	16	1.04
8	CuBr/Bpy	100/1/1/1	110	1,054	1.46	15	0.97
9	CuCl/Bpy	100/1/1/1	110	1,622	1.52	19	0.80
10	CuBr/Bpy	100/1/1/1	130	1,108	1.26	23	1.41
11	CuBr/Bpy	100/1/1/1	150	433	1.20	33	5.18
12	CuBr/Bpy	100/1/1/3 ^{b)}	110	1,448	1.36	18	0.85
13	CuCl/Bpy	100/1/1/3 ^{b)}	110	1,016	1.42	15	1.00
14	CuBr/Bpy	100/1/1/3	110	4,139	1.37	25	0.41
15	CuCl/Bpy	100/1/1/3	130	1,573	1.51	28	1.21
16	CuCl/Bpy	100/1/1/3	110	4,238	1.41	21	0.34
17	CuBr/Bpy	100/1/1/3	130	2,247	1.30	29	0.88
18	CuBr/Bpy	100/1/1/3	110	1,593	1.75	17	0.73
19	CuBr/Bpy	100/1/1/6	90	1,116	1.17	10	0.61
20	CuCl/Bpy	100/1/1/6	110	8,474	1.47	38	0.30
21	CuCl/Bpy	100/1/1/6	130	2,990	1.38	37	0.84
22	CuBr/Bpy	100/1/1/12	110	3,876	2.79	37	0.65
23	CuCl/Me ₆ TREN	100/1/1/2	110	1,574	1.54	12	0.52
24	CuBr/PMDETA	100/1/1/2	110	4,700	1.73	9	0.13
25	CuBr/TREN	100/1/1/2	110	5,600	5.52	17	0.21
26	CuCl/TREN	100/1/1/2	110	6,606	5.98	18	0.19
27	CuBr/Bpy ^{b)}	100/1/0.1/1/1	125	5,158 ^{c)}	1.36	33	0.44
28	CuCl/Bpy ^{b)}	100/1/0.1/1/1	110	4,623	4.30	38	0.56
29	CuCl/Bpy ^{b)}	100/1/0.5/0.5/1.5	110	7,189	2.14	36	0.34
30	CuCl/Bpy ^{b)}	100/1/0.5/1/1.5	110	3,888	4.98	30	0.63
31	CuCl/Bpy ^{b)}	100/1/1/1/3	110	9,307	3.94	38	0.28

^{a)}Dioxane, ^{b)}Sn(EH)₂. (c) Samples precipitated in MeOH. Reaction time: 20 – 25 h.

CONCLUSIONS

The polymerization of isoprene initiated by EBIB was investigated under a variety of reaction conditions such as temperature (90-150 °C), ligand (bpy, PMDETA, TREN, Me₆TREN), catalyst (CuCl, CuBr) and additives (Sn(EH)₂). Thus, while certain trends (130-110 °C > 90 °C, 150 °C, bpy > PMDETA ~ Me₆TREN > TREN; CuBr > CuCl) are observed, the polymerization remained inhomogeneous in all cases, and moreover, the chains retain very poor halide functionality (<20 %), indicating that dienes remain challenging monomers for ATRP.

ACKNOWLEDGEMENTS

The financial support of NSF-CHEM-0518247 and PRF-47274-AC7 is gratefully acknowledged.

REFERENCES

- (1) *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: New York, **2002**, pp 361-462.
- (2) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Progr. Polym. Sci.*, **2001**, *26*, 337.
- (3) Spencer, R. P.; Schwartz, J. *Tetrahedron*, **2000**, *56*, 2103-2112.
- (4) Green, M. H.; Lucas, C. R. *J. Chem. Soc. Dalton Trans.* **1972**, *8*, 1000.
- (5) Barden, M. C.; Schwartz, J. *J. Am. Chem. Soc.* **1996**, *118*, 5484.
- (6) Rajanbabu, T. V.; Nugent, W. *J. Am. Chem. Soc.* **1994**, *116*, 986.
- (7) (a) Asandei, A. D.; Moran, I. W.; Chen, Y.; Saha, G. *J. Organomet. Chem.* **2007**, *692*, 3174-3182. (b) Asandei, A. D.; Moran, I. W.; Saha, G.; Chen, Y. *ACS Symp. Ser.* **2006**, *944*, 125. (c) Asandei, A. D.; Moran, I. W.; Saha, G.; Chen, Y. *J. Polym. Sci.: Part A: Polym. Chem.* **2006**, *44*, 2156. (d) Asandei, A. D.;

- Moran, I. W.; Saha, G.; Chen, Y. *J. Polym. Sci.: Part A: Polym. Chem.* **2006**, *44*, 2015. (e) Asandei, A. D.; Moran, I. W. *J. Polym. Sci.: Part A: Polym. Chem.* **2006**, *44*, 1060. (f) Asandei, A. D.; Moran, I. W. *J. Polym. Sci.: Part A: Polym. Chem.* **2005**, *43*, 6039. (g) Asandei, A. D.; Moran, I. W. *J. Polym. Sci.: Part A: Polym. Chem.* **2005**, *43*, 6028. (h) Asandei, A. D.; Moran, I. W. *J. Am. Chem. Soc.* **2004**, *126*, 15932. (i) Asandei, A. D.; Moran, I. W.; Castro, M. A. *Polym. Prepr.* **2003**, *44(1)*, 829. (j) Asandei, A. D.; Chen, Y.; Saha, G.; Moran, I. W.; *Tetrahedron*, **2008**, *64*, 11831.
- (8) Asandei, A. D.; Chen, Y. *Macromolecules* **2006**, *39*, 7549.
- (9) (a) Asandei, A. D.; Chen, Y. *Polym. Mater.: Sci. Eng.* **2007**, *97*, 450. (b) Asandei, A. D.; Saha, G. *Polym. Prepr.* **2007**, *48*, 272.
- (10) Asandei, A. D.; Saha, G. *J. Polym. Sci.: Part A: Polym. Chem.* **2006**, *44*, 1106.
- (11) Asandei, A. D.; Saha, G. *Macromolecules* **2006**, *39*, 8999.
- (12) (a) Asandei, A. D.; Saha, G. *Macromol. Rapid Commun.* **2005**, *26*, 626. (b) Asandei, A. D.; Chen, Y.; Adebolu, O. I.; Simpson, C. P. *J. Polym. Sci.: Part A: Polym. Chem.* **2008**, *46*, 2869. (c) Asandei, A. D.; Chen, Y.; Adebolu, O. I.; Simpson, C. P. *Polym. Prepr.* **2008**, *49(2)*, 740.
- (13) Schops, M.; Leist, H.; DuChesne, A.; Wiesner, U. *Macromolecules* **1999**, *32*, 2806.
- (14) Hirao, A.; Hayashi, M. *Acta Polym.* **1999**, *50*, 219.
- (15) Evans, W.; Giarikos, D.; Allen, N. *Macromolecules* **2003**, *36*, 4256.
- (16) Wootthikanokkhan, J.; Peesan, M.; Phinyocheep, P. *Eur. Polym. J.* **2001**, *37*, 2063.
- (17) (a) Grubbs, R. B.; Wegrzyn, J. K.; Xia, Q. *Chem. Commun.* **2005**, *1*, 80. (b) Kamachi, M.; Kajiwara, A. *Macromolecules* **1996**, *29*, 2378. (c) Keosherian, B.; Georges M.; Quinlan, M.; Vergin, R.; Goodbrand, B. *Macromolecules* **1998**, *31*, 7559. (d) Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **2000**, *33*, 363. (e) Li, I. Q.; Howell, B. A.; Dineen, M. T.; Kastl, P. E.; Lyons, J. W.; Meunier, D. M.; Smith, P. B.; Priddt, B. B. *Macromolecules* **1997**, *30*, 5195. (f) Gavranovic, G.; Csihony, S.; Bowden, N. B.; Hawker, C. J.; Waymouth, R. M.; Moerner, W.; Fuller, G. *Macromolecules* **2006**, *39*, 8121.
- (18) (a) Germack, D. S.; Wooley, K. L. *J. Polym. Sci.: Part A: Polym. Chem.* **2007**, *45*, 4100. (b) Jitchum, V.; Perrier, S. *Macromolecules* **2007**, *40*, 1408. (c) Skaiff, H.; Emrick, T. *Angew. Chem. Int. Ed.* **2004**, *43*, 5383.
- (19) Asandei, A. D.; Simpson, C. P.; Yu, H. S.; Adebolu, O. I.; Saha, G.; Chen, Y. *ACS Symposium Series*, **2009**, *1024*, 149-166.
- (20) (a) Asandei, A. D.; Saha, G. *Polym. Prepr.* **2005**, *46(2)*, 474. (b) Asandei, A. D.; Simpson, C. P. *Polym. Prepr.* **2008**, *49(1)*, 452. (c) Asandei, A. D.; Simpson, C. P.; Yu, H. S. *Polym. Prepr.* **2008**, *49(2)*, 73. (d) Asandei, A. D.; Adebolu, O.; Yu, H. S.; Simpson, C. P.; Gilbert, M. *Polym. Prepr.* **2009**, *50(1)*, 177. (e) Asandei, A. D.; Simpson, C. P. *Polym. Prepr.* **2008**, *49(2)*, 75. (f) Asandei, A. D.; Yu, H. S.; Adebolu, O.; Simpson, C. P.; Duong, O. *Polym. Mater.: Sci. Eng.* **2009**, *100*, 366. (g) Asandei, A. D.; Yu, H. S. *Polym. Prepr.* **2009**, *50(2)*, 601-602. (h) Asandei, A. D.; Yu, H. S.; Adebolu, A. *Polym. Mater.: Sci. Eng.* **2009**, *101*, 1377-1378. (i) Asandei, A. D.; Yu, H. S.; Simpson, C. P. *Polym. Mater.: Sci. Eng.* **2009**, *101*, 1379-1380.
- (21) Asandei, A. D.; Yu, H. S.; Simpson, C. P. *Polym. Prepr.* **2010**, *51(1)*, 545-546.
- (22) Jakubowski, W.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 4139-4146