



# Mn<sub>2</sub>(CO)<sub>10</sub>-promoted cationic polymerization of isobutylene upon visible light irradiation

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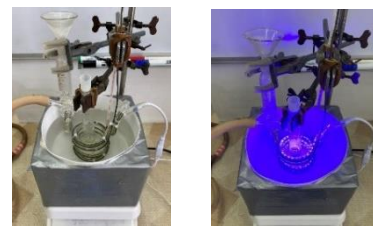
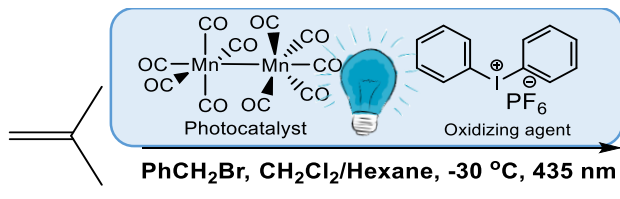
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## Introduction

In the last decade photocatalysis in polymer synthesis has rapidly advanced owing to significant progress in photocontrolled cationic polymerization. The most promising approach to perform photocontrolled cationic polymerization involves using a suitable photoredox catalyst (PC) paired with a chain transfer agent (CTA), capable of mediating the polymerization via reversible-deactivation mechanism. However, despite the wide range of PCs and CTAs reported, this field remains limited to polymerization of highly reactive monomers such as vinyl ethers. Recently, an alternative approach using a benzyl bromide(BB)/Mn<sub>2</sub>(CO)<sub>10</sub>/diphenyliodonium salt catalytic system for visible-light-induced living cationic polymerization of vinyl ethers was developed<sup>1</sup>. The reaction occurs via radical oxidation/addition/deactivation mechanism, which can be potentially applied for the polymerization of less reactive monomers such as isobutylene.

## The visible-light-induced cationic polymerization of isobutylene

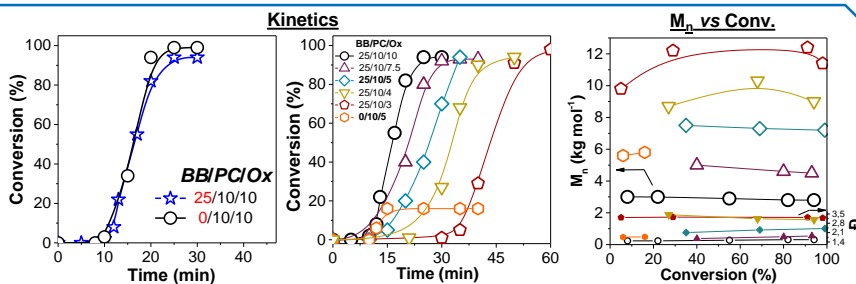


## Control experiments

[IB]/[PhCH <sub>2</sub> Br]/[Mn <sub>2</sub> (CO) <sub>10</sub> ]/[Ph <sup>+</sup> PF <sub>6</sub> <sup>-</sup> ]	Light	Time, min	Conv. (%)	M <sub>n</sub> g mol <sup>-1</sup>	D
2000/25/10/10	+	25	94	3000	1.7
2000/25/10/10	-	90	0	-	-
2000/25/10/0	+	90	0	-	-
2000/25/0/10	+	90	0	-	-
2000/0/10/10	+	25	98	4300	1.8
2000/0/10/10 <sup>1</sup>	+	120	0	-	-
2000/25/10/10 <sup>1</sup>	+	120	0	-	-

Polymerization conditions: T = -30 °C; [IB] = 1 M; CH<sub>2</sub>Cl<sub>2</sub>/Hexane 80:20 v./v.

<sup>1</sup> Solvent = dichloroethane



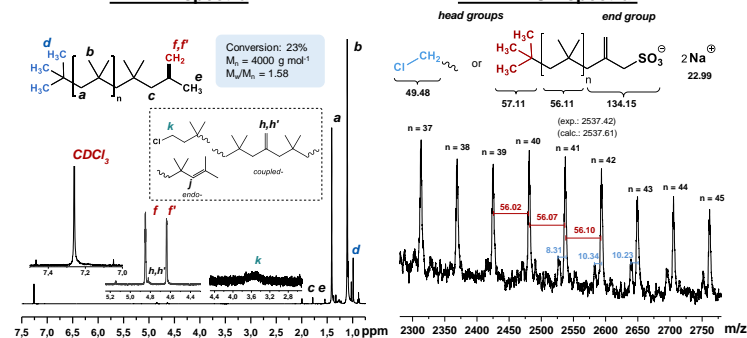
Polymerization conditions: [IB]/[PC] = 2000/10; T = -30 °C; [IB] = 1 M; CH<sub>2</sub>Cl<sub>2</sub>/Hexane 80:20 v./v.

The photoinduced cationic polymerization of IB in CH<sub>2</sub>Cl<sub>2</sub> occurred even without the addition of benzyl bromide affording polymer with slightly higher molecular weight and polydispersity. Kinetic studies shows identical shape for kinetic curves with and without BB. The decrease of diphenyliodonium salt concentration results in the termination of the polymerization at incomplete monomer conversion. However, the monomer conversion can be improved by the addition of benzyl bromide. The duration of the induction period gradually increased, while the molecular weight and polydispersity increased with the decrease of diphenyliodonium salt concentration.

## Structure of polyisobutylene

### <sup>1</sup>H NMR spectra

### MALDI-TOF spectra



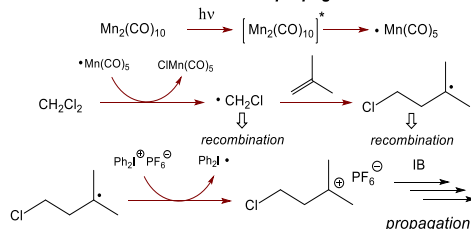
Polymerization conditions: [IB]/[PC]/[Ox] = 2000/10/10; T = -30 °C; [IB] = 1 M; CH<sub>2</sub>Cl<sub>2</sub>/Hexane 80:20 v./v.

The absence of signals of the aromatic protons from benzyl group in <sup>1</sup>H NMR spectrum of the polymer unambiguously suggests that benzyl bromide is not a true initiator of the polymerization. <sup>1</sup>H NMR and MALDI-TOF analyses clearly demonstrate the presence of -CH<sub>2</sub>Cl head group in the polymer chain.

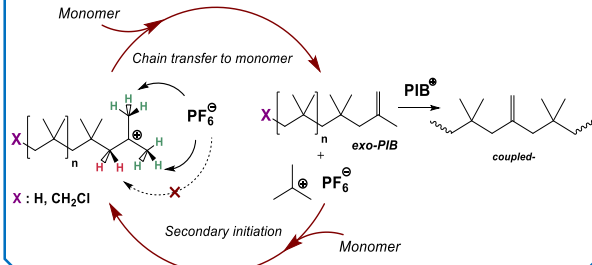
Polyisobutylene contains large amount of exo-olefinic end groups with only minor appearance of endo-olefinic terminal groups, which opens up opportunities for polymer modification and therefore makes the product interesting for industrial application.

## Proposed mechanism

### Initiation and propagation



### Chain transfer reaction



## Conclusion

In this study, the visible-light-induced cationic polymerization of isobutylene using photoinitiating system PhCH<sub>2</sub>Br/Mn<sub>2</sub>(CO)<sub>10</sub>/Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup> was investigated in a mixture of CH<sub>2</sub>Cl<sub>2</sub>/n-hexane at -30°C. Polyisobutylenes with a number-average molecular weight up to 3000 g·mol<sup>-1</sup>, relatively low polydispersity (Đ<1.7), and high content of exo-olefin end groups (>90%) were obtained. It was proven that the true initiator of polymerization is CH<sub>2</sub>Cl<sub>2</sub>, and not PhCH<sub>2</sub>Br.

## Acknowledgement

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