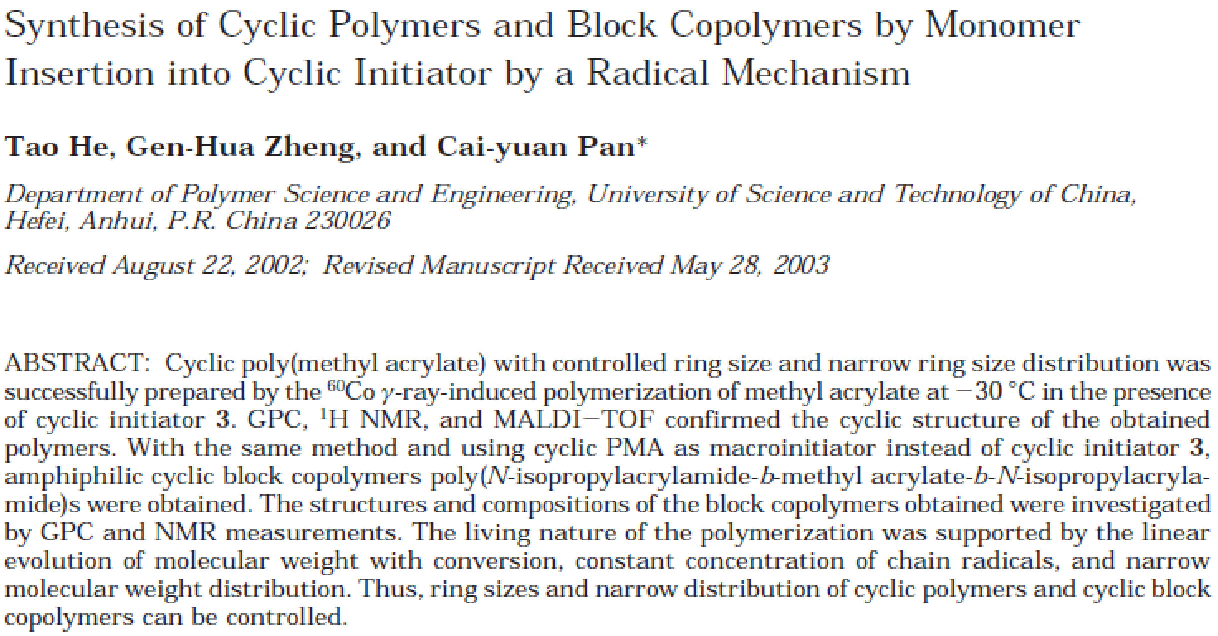
Cyclic RAFT/MADIX CT Agents

by Robert B. Login

rloginconsulting.com

Cyclic RAFT CTA's can polymerize vinyl monomers into cyclic polymers.

Cyclic polymers because of their unique properties compared to their linear counterparts include reduced hydrodynamic volume, lower intrinsic viscosity and distinctive fluorescence enhancement, higher Tg, higher refractive index. Cyclic polymers exhibit endless topologically with more stringent restrictions on the backbone conformation and the absence of chain ends (JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY 2016, 54, 1447–1458).



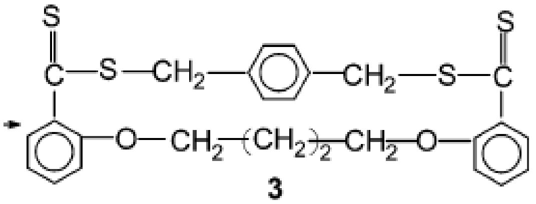
Synthesis of Cyclic Polymers and Block Copolymers by Monomer Insertion into Cyclic Initiator by a Radical Mechanism

Tao He, Gen-Hua Zheng, and Cai-yuan Pan*

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui, P.R. China 230026

Received August 22, 2002; Revised Manuscript Received May 28, 2003

ABSTRACT: Cyclic poly(methyl acrylate) with controlled ring size and narrow ring size distribution was successfully prepared by the ^{60}Co γ-ray-induced polymerization of methyl acrylate at −30 °C in the presence of cyclic initiator **3**. GPC, ^{1}H NMR, and MALDI−TOF confirmed the cyclic structure of the obtained polymers. With the same method and using cyclic PMA as macroinitiator instead of cyclic initiator **3**, amphiphilic cyclic block copolymers poly(*N*-isopropylacrylamide-*b*-methyl acrylate-*b*-*N*-isopropylacrylamide)s were obtained. The structures and compositions of the block copolymers obtained were investigated by GPC and NMR measurements. The living nature of the polymerization was supported by the linear evolution of molecular weight with conversion, constant concentration of chain radicals, and narrow molecular weight distribution. Thus, ring sizes and narrow distribution of cyclic polymers and cyclic block copolymers can be controlled.



3

Macromolecules 2003, 36, 5960-5966.

Reactive & Functional Polymers 80 (2014) 33–39

Cyclic poly(vinylcarbazole) *via* ring-expansion polymerization-RAFT (REP-RAFT)

Ajaykumar Bunha, Peng-Fei Cao, Joey Dacula Mangadlao, Rigoberto C. Advincula *

Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, OH 44106, US

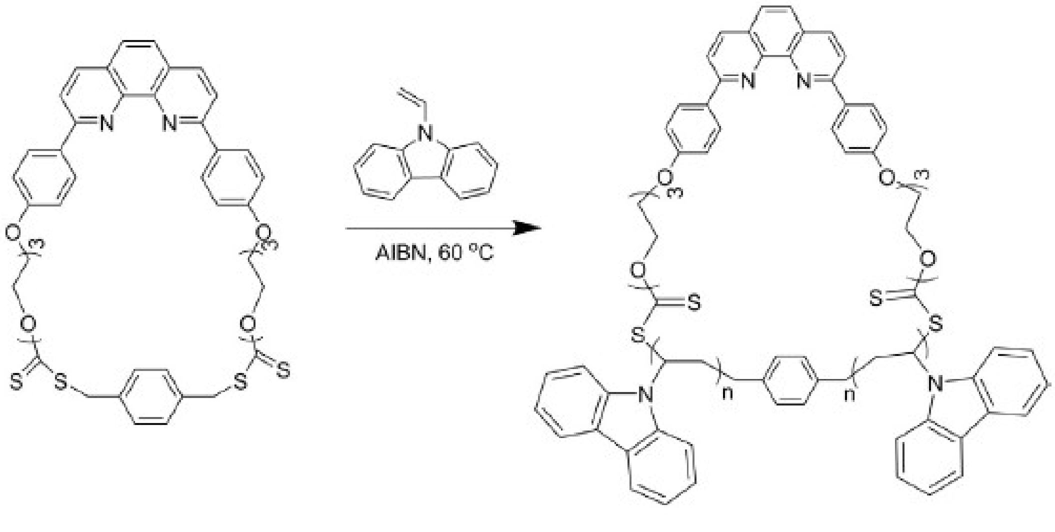
ARTICLE INFO

Article history:
Received 29 October 2013
Received in revised form 27 February 2014
Accepted 2 March 2014
Available online 20 March 2014

Keywords:
Ring-expansion polymerization
Cyclic RAFT initiator
N-vinylcarbazole (NVK)

ABSTRACT

In this paper, we demonstrate the formation of cyclic poly(vinylcarbazole) *via* a ring-expansion polymerization reversible addition-fragmentation chain transfer (REP-RAFT). A cyclic dixanthate RAFT chain transfer agent (CTA) was synthesized and employed for controlled free radical polymerization of N-vinylcarbazole (NVK). The molecular weight in relation to polymerization time suggested the formation of a polymer with well-controlled molecular weight and ring size. The obtained macromolecules were characterized by nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS) and dynamic light scattering (DLS). Atomic force microscopy (AFM) was also employed to directly observe the cyclic polymers with different ring sizes.



Scheme 2. RAFT polymerization of N-vinylcarbazole using cyclic CTA (1).

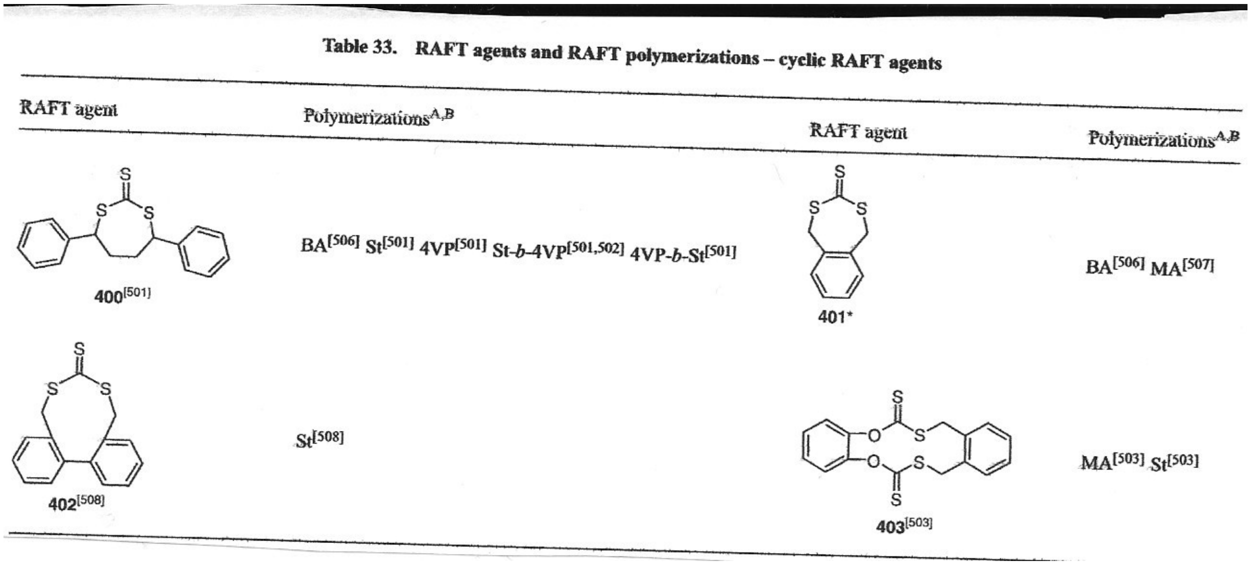
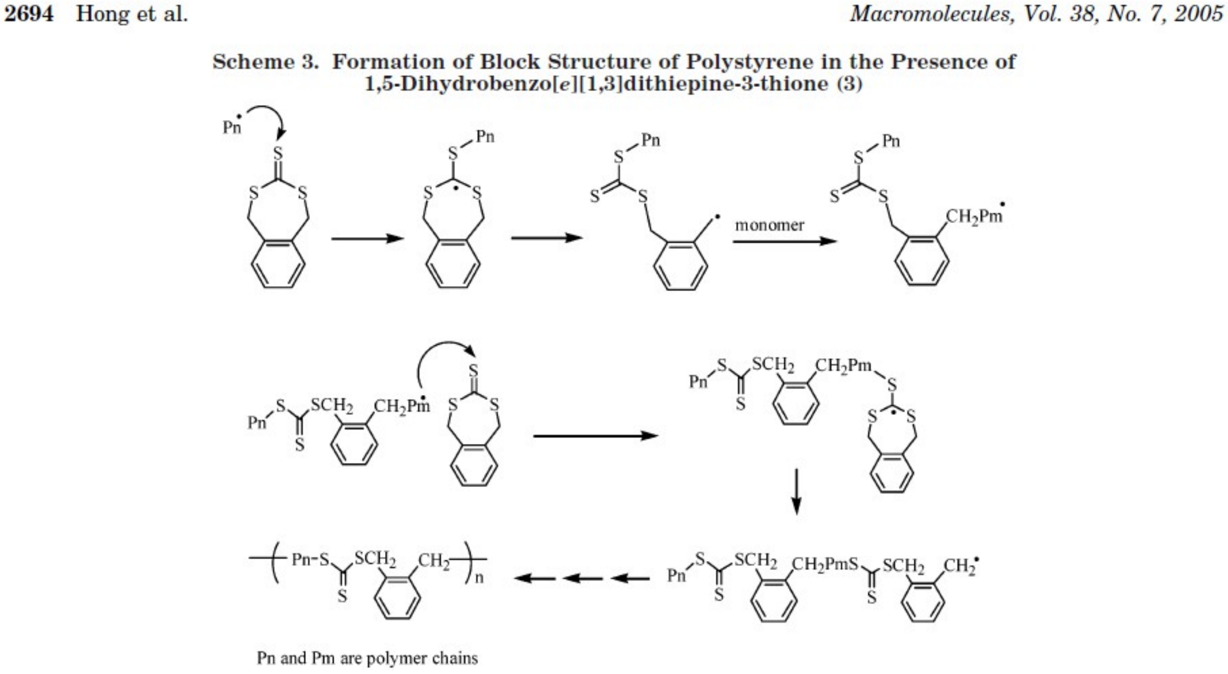


Table 33. RAFT agents and RAFT polymerizations – cyclic RAFT agents

RAFT agent	Polymerizations[A,B]	RAFT agent	Polymerizations[A,B]
400[501]	BA[506] St[501] 4VP[501] St-*b*-4VP[501,502] 4VP-*b*-St[501]	**401***	BA[506] MA[507]
402[508]	St[508]	**403**[503]	MA[503] St[503]

Moad et. al. Aust. J. Chem. 2009, 62, 1402-1472.



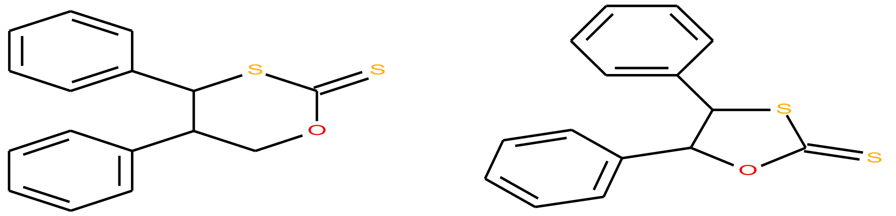
2694 Hong et al. *Macromolecules, Vol. 38, No. 7, 2005*

Scheme 3. Formation of Block Structure of Polystyrene in the Presence of 1,5-Dihydrobenzo[*e*][1,3]dithiepine-3-thione (3)

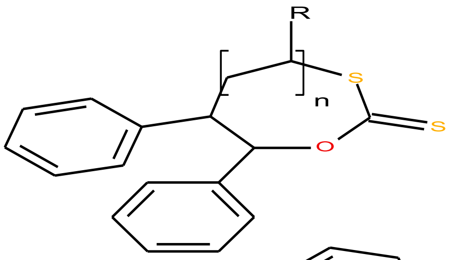
Pn and Pm are polymer chains

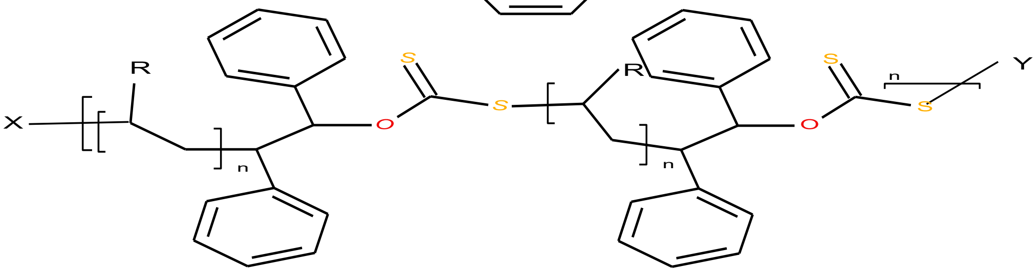
The above were really the few references I found for RAFT ring expansion polymerization(REP). They appear to require a macrocycle CTA so that ring strain is not a factor or can ring strain enhance the polymerization?

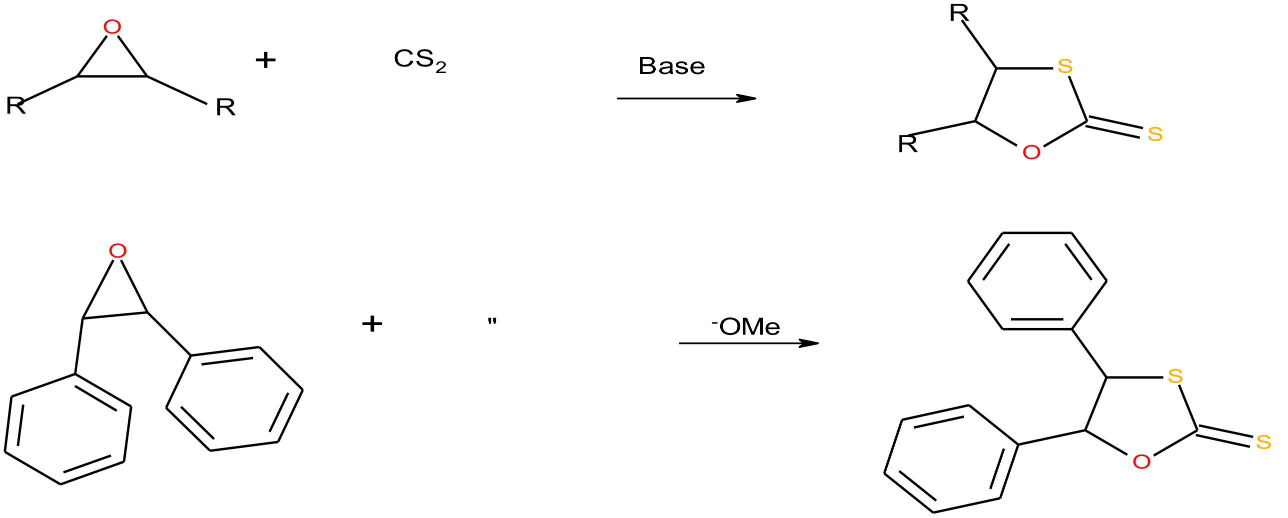
To explain my ideas the following figures are referred to:



Phenyl derivatives are shown but other derivatives are possible





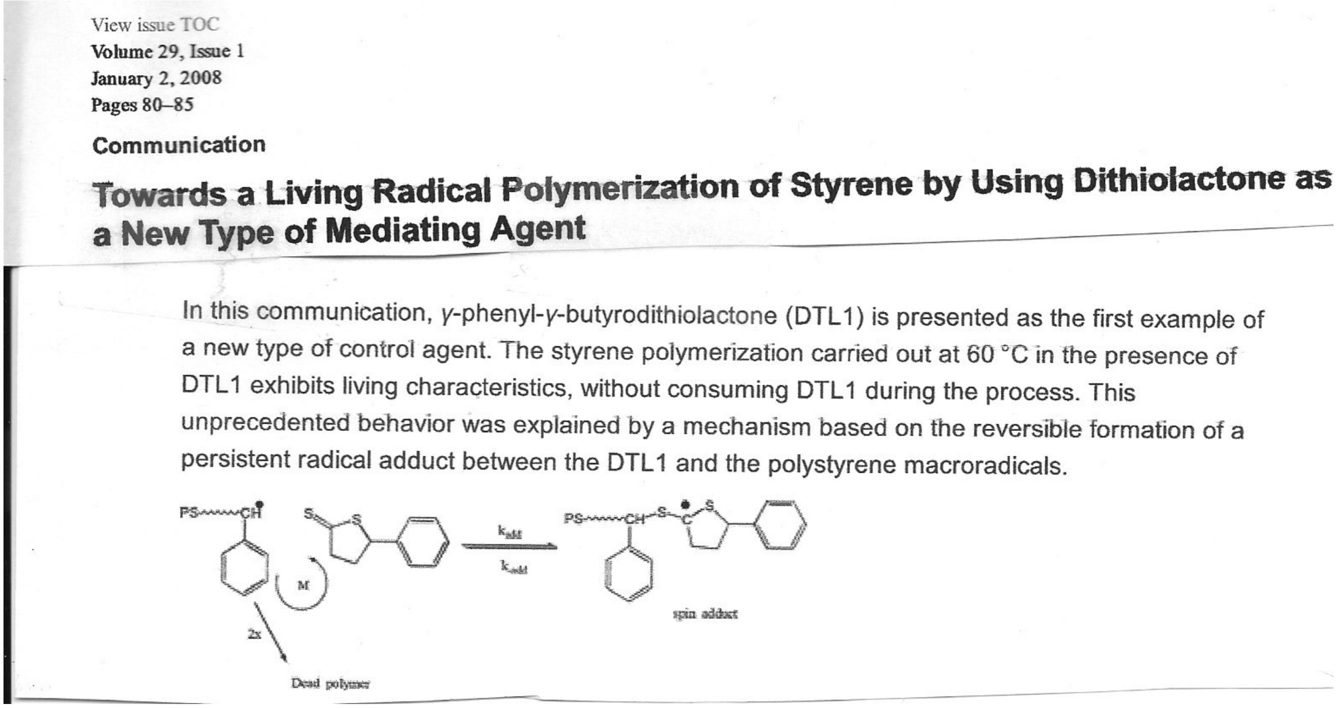


Synthesis of the 4,5-Diphenyl-1,3-oxathiolane-2-thione monomer in 86% yield: I. Yavari et. al. Synlett 2008(6), 889-891.

The facile reaction of CS2 with epoxides is the reason I'm interested in this xanthate's MADIX potential. The reason for the 1,2 epoxy derivative is that the reaction affords the unwanted isomer (5 position) if a mono-substituted epoxide is employed (Other synthesis routes could be proposed that would afford the mono derivative attached to the 4-carbon next to sulfur). This 4 substituent however must be capable of stabilizing radicals that are reactive enough to start the MADIX polymerization. The benzyl group is known to do this. The initial small amount of added initiator adds to the 2-thione group, then generates the carbon radical stabilized by the benzyl group(Hong et. al. shown above is an example). More detailed explanation of RAFT/MADIX can be found in several reviews such as D.J. Kiddie et. al. Macromol. 2012, 45, 5321-5342.
References for Xanthate synthesis:
N. Kihara et. al. JOC 1995, 60, 473-475.
R. Maggi et. al. Synthesis 2008(1), 53-56.
W. Clegg et. al. JOC 2010, 75, 6201-6207.
Y. Taguchi et. al. Bull. Soc. Jpn., 61, 921-925 (1988).
W. Choi et. al. Macromolecules, 1998, 31, 2454-2460.

My idea is to use this type of cyclic xanthates in RAFT/MADIX CTA polymerization. With the above CTA's, the polymerization could possibly go two ways; cyclic formation of a macrocyclic or a cyclicpolymer containing multiple xanthate moieties. X and Y are attached in a very large macrocycle. R can be from the various monomers such as NVP, Vac, MA, MMA etc. that could be employed in this polymerization.

What follows is what should be an example of this idea.



View issue TOC
Volume 29, Issue 1
January 2, 2008
Pages 80–85

Communication

Towards a Living Radical Polymerization of Styrene by Using Dithiolactone as a New Type of Mediating Agent

In this communication, γ-phenyl-γ-butyrodithiolactone (DTL1) is presented as the first example of a new type of control agent. The styrene polymerization carried out at 60 °C in the presence of DTL1 exhibits living characteristics, without consuming DTL1 during the process. This unprecedented behavior was explained by a mechanism based on the reversible formation of a persistent radical adduct between the DTL1 and the polystyrene macroradicals.

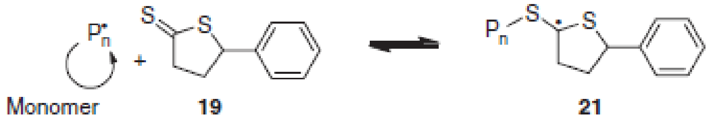
Macromolecular Rapid Communications; Soriano-Moro et. al.

I don't understand why the benzyl group doesn't stabilize the carbon radical? Only 4 references cited this reference, indicating to me that the above interpretation of the reaction was not of interest or valid. If their interpretation is correct then they would have to indicate what's at the other end of the polystyrene? The terminal of the polymer would be hard to distinguish with all the styrene phenyls if indeed it was a benzyl in possibly a cyclic motif? Since no attempt to try this CTA with MMA etc. which would clearly show the terminal moiety if it was benzyl; therefore, I believe my interpretation is valid. However their synthesis of the dithiolactone itself is useful.

Here's what the experts say! Aust. J. Chem. 2009, 62, 1402–1472

Graeme Moad,[A,B] Ezio Rizzardo,[A,B] and San H. Thang[A,B]

“The thiolactone 19 was proposed to control the polymerization of St by a similar addition–fragmentation process (Scheme 2).[83] The mechanism as shown seems unlikely since, for control, most of the propagating species would need to be present as the dormant species 21. ESR experiments showed that a high concentration of radicals were not present during polymerization. The mechanism would suggest that the final product should also have structure 21." Clearly this is not the case.



Scheme 2. Reversible addition–fragmentation mechanism for dithiolactone.

Numerous references clearly show the generation and stability of the benzyl's group's interaction with the carbon radical and its ability to start the MADIX polymerization, the same mechanism should be at play here also.

Living Cationic Cyclic Polymerization

Recently several very interesting papers have appeared concerning the application of RAFT CTA's that work with cationic CLP. With the RAFT agent, block polymers of vinyl ethers are easily synthesized, not only that but cationic followed by CRP polymerization is possible.

HCl·Et_2O-Catalyzed Metal-Free RAFT Cationic Polymerization: One-Pot Transformation from Metal-Free Living Cationic Polymerization to RAFT Radical Polymerization[1]

Shinji Sugihara,*[†,‡] Naoto Konegawa,[†] and Yasushi Maeda[†] *Macromolecules* 2015, 48, 5120–5131

Thioether-Mediated Degenerative Chain-Transfer Cationic Polymerization: A Simple Metal-Free System for Living Cationic Polymerization

Mineto Uchiyama,[†] Kotaro Satoh,*[†,‡] and Masami Kamigaito*[†] *Macromolecules* 2015, 48, 5533–5542

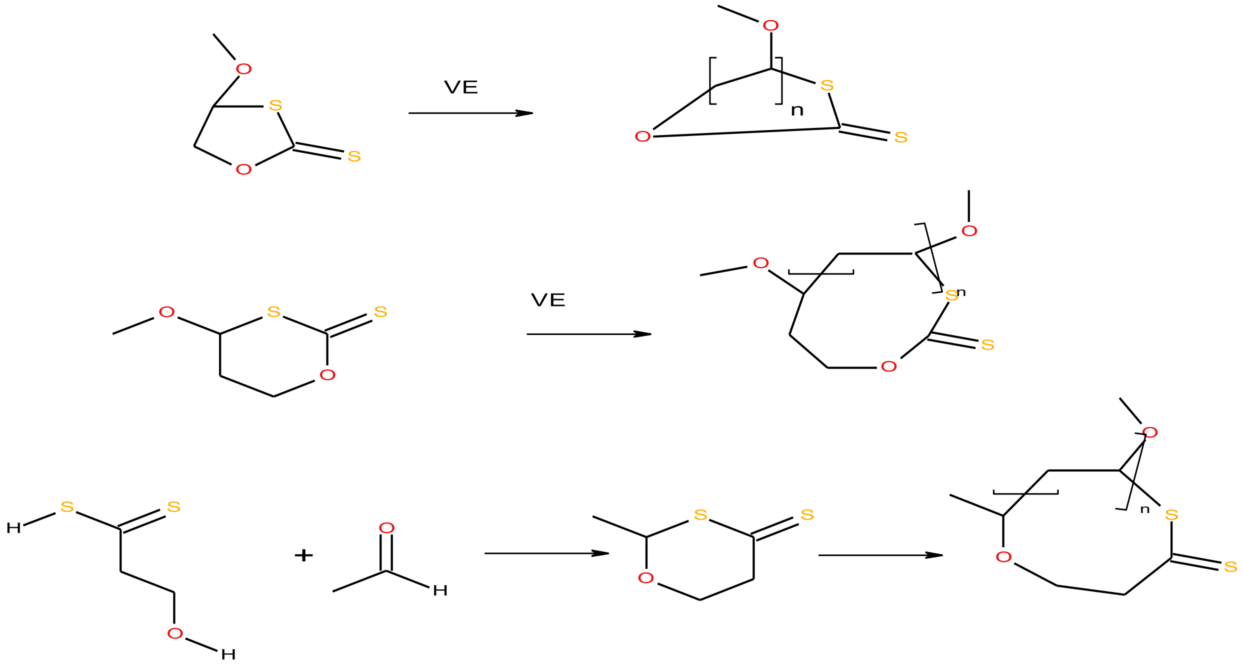
Macromolecules 2012, 45, 794–804

Transformation of Living Cationic Polymerization of Vinyl Ethers to RAFT Polymerization Mediated by a Carboxylic RAFT Agent

Shinji Sugihara,* Kenta Yamashita, Keiji Matsuzuka, Isao Ikeda, and Yasushi Maeda

Although these papers illustrate how selected RAFT CTA's can be used, I could not find any example of their use to form cyclic polymers of vinyl ethers. Considering my previous paper concerning cyclic RAFT CTA's, it would seem obvious that or similar RAFT CTA's would result in well controlled cationic cyclic polymerization.

I can visualize several interesting applications for cyclic cationic polymerization.
In analogy with the crown ethers, cyclic methyl vinyl ether or other VE's or mixtures or CRP following cationic can all be accomplished with RAFT/MADIX CTA's. Such large macrocycles having ether groups, for example, projecting in or out of the cyclic chain would have unusual complexing behavior. Conducting said cationic polymerization in the presence of a complexing agent should control orientation of the ether groups much like a cation controls the preparation of crown ethers.



Rather than draw all RAFT/MADIX CTA possibilities, the above are suggested.

Cyclic cationic polymerization followed by CRP would afford copolymers of MVE and NVP for example (many monomer combinations are obviously possible), that would lead to cyclics exhibiting unique complexing ability. Fluorine derivatives might even have use as blood substitutes.

I hope you found these proposals interesting. Thanks for reading!
Dr. Robert B. Login, rloginconsulting.com