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Absence of tetramethylene diradical intermediates in Lewis acid catalyzed group transfer polymerization

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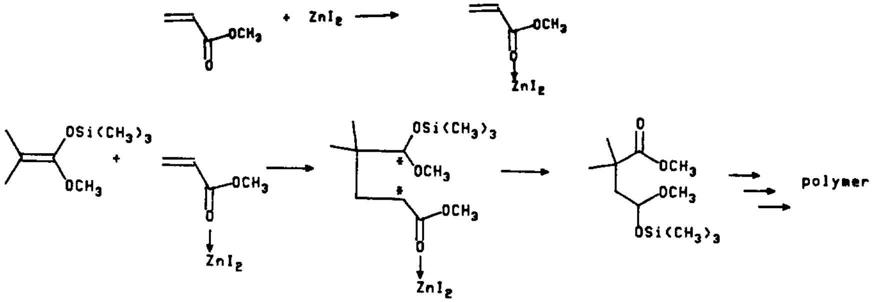
Summary

A diradical tetramethylene intermediate in Lewis acid catalyzed Group Transfer Polymerization of methyl acrylate is unlikely based on the lack of incorporation of styrene during methyl acrylate polymerizations.

Introduction

Lewis acid catalyzed group transfer polymerization (GTP) has been described by Hertler and coworkers.[1] Unlike anion catalyzed GTP, in which the initiator is activated, the Lewis Acid catalyst activates the monomer (see Figure). Lewis acid catalysts which can be used are zinc halides and dialkylaluminum halides and oxides. These catalysts are more active when used with acrylates rather than with methacrylates. Webster has proposed a zwitterionic mechanism in both initiation and propagation for GTP.[2] However, based on our Organic Chemist's Periodic Table[3], a tetramethylene possessing such terminal donor and acceptor groups would exhibit diradical behavior rather than zwitterionic. If this is the case, copolymerization should occur with a co-monomer that polymerizes by radical polymerization, even if it does not homopolymerize under GTP conditions.

In this study, we will investigate the Lewis acid catalyzed group transfer polymerization of methyl acrylate in the presence of styrene or inhibitor to test for possible radical intermediates.



, = +,- Webster's Proposed Mechanism

, = ·,· Hall's Proposed Mechanism

Experimental

^1H NMR spectra were recorded on a Bruker WM-250 Nuclear Magnetic Resonance Spectrometer at 250MHz. Molecular weights were measured by size exclusion chromatography on a Shodex A-804 column, calibrated with polystyrene standards using chloroform as the eluent and a Waters refractive index detector.

Methyl acrylate, styrene, p-butylstyrene, dichloroethane and toluene were dried over calcium hydride and distilled before use. Zinc iodide was dehydrated by heating over a Bunsen burner flame for 15 minutes under vacuum immediately before use. 1-Methoxy-1-trimethylsiloxy-2-methyl-1-propene was obtained from Petrarch Systems Inc. 3-t-Butyl-4-hydroxy-5-methylphenyl sulfide was obtained from Aldrich. Both were used without further purification.

Group transfer polymerizations were carried out in Y-tubes under argon. Zinc iodide and methyl acrylate were put in one arm of the tube. The second monomer and the trimethylsilylketene acetal initiator were put in the other arm. Concentration of both monomers after mixing was 5M. Five mole percent zinc iodide was used. Mixtures were degassed before opening under argon and the polymerization was started by mixing. The reaction times were approximately one half hour.

Photochemical reactions were degassed and opened under argon. Tubes were put in a photochemical reactor (wavelength = 254 nm) for approximately 14 hours.

Work ups were done according to the literature.[1]

Results and Discussion

Using styrene as a comonomer is a more sensitive test for an intermediate diradical species than using a radical inhibitor. Styrene monomers do not polymerize under group transfer methods (see Table). Zinc iodide does not initiate the polymerization of styrene, nor does the GTP initiator 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene. Styrene does not polymerize in the presence of ZnI_2 and ethyl acetate, used as a model compound. Styrene is readily polymerized in the presence of radical initiators. Hence, styrene should be incorporated into the acrylate polymer if the reaction is radical in nature. The resulting copolymer would be easily isolated, regardless of the concentration of the radical species. Small molecules obtained from the reaction of the radical species with an inhibitor will be very few and these may easily be overlooked.

Methyl acrylate was polymerized under GTP conditions in both dichloroethane and toluene to give poly(methyl acrylate)

Table. Copolymerization Reactions of Methyl Acrylate and Styrene Monomers

Monomer 1	Monomer 2	Solvent	Initiator	Additives	Results	Yield	Mn Molecular Wt.	$\frac{Mw}{Mn}$
MA	—	DCE	GTP[a], ZnI_2	—	PMA	50%	3300	1.5
MA	—	$\emptyset CH_3$	GTP, ZnI_2	—	PMA	50	945	1.4
styrene	—	$\emptyset CH_3$	ZnI_2	—	no polymer	0	—	—
styrene	—	$\emptyset CH_3$	ZnI_2	EtOAc	no polymer	0	—	—
styrene	—	$\emptyset CH_3$	GTP, ZnI_2	—	no polymer	0	—	—
MA	styrene	$\emptyset CH_3$	AIBN, $h\nu$	—	copolymer	72	18,900	2.6
MA	t-BuSty	$\emptyset CH_3$	AIBN, $h\nu$	—	copolymer	98	41,200	1.9
MA	styrene	$\emptyset CH_3$	AIBN, $h\nu$	ZnI_2	copolymer	100	94,800	1.4
MA	t-BuSty	$\emptyset CH_3$	AIBN, $h\nu$	ZnI_2	copolymer	100	128,000	1.3
MA	styrene	DCE	GTP, ZnI_2	—	PMA	58	1000	1.2
MA	t-BuSty	DCE	GTP, ZnI_2	—	PMA	84	440	2.5
MA	t-BuSty	$\emptyset CH_3$	GTP, ZnI_2	—	PMA	88	520	1.8
MA	—	$\emptyset CH_3$	GTP, ZnI_2	inhibitor[b]	MA	96	1600 330	1.1 1.2

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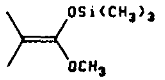

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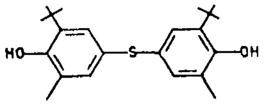

(see Table). Copolymerization reactions of methyl acrylate with both styrene and t-butylstyrene in toluene under GTP conditions gave only poly(methyl acrylate). The lack of copolymer in the reactions involving styrene monomers indicates that the reaction is not proceeding via a diradical intermediate. This statement is further supported by the fact that methyl acrylate does copolymerize with both styrene and t-butylstyrene by radical polymerization using AIBN as an initiator.

Poly(methyl acrylate) is obtained under GTP conditions in the presence of the sulfide inhibitor, 3-t-butyl-4-hydroxy-5-methylphenyl sulfide. Therefore, it is again unlikely that a radical intermediate is involved in group transfer polymerization.

The results presented here indicate that Lewis acid catalyzed group transfer polymerization does not proceed by way of a tetramethylene diradical.

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