Preparation of Soluble, Linear Titanium-Containing Copolymers by the Free-Radical Copolymerization of Vinyl Titanate Monomers with Styrene

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ABSTRACT: Linear, soluble copolymers containing titanium are of interest for use in targets for inertial-confinement fusion (ICF) experiments because the titanium is a useful spectroscopic probe for studying the nuclear fusion process. Some suitable copolymers have been prepared from vinyl titanate monomers and styrene via free-radical polymerization. Soluble copolymers with molecular weights between 70,000 and 100,000 daltons containing 0.1 atom % titanium can be reliably prepared. These copolymers have been incorporated into targets used in inertial-confinement fusion experiments at Lawrence Livermore National Laboratory. Attempts to prepare identical copolymers using macromolecular modification were unsuccessful and yielded insoluble materials upon reaction of the functionalized copolymers with titanium(IV) isopropoxide. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 190–199, 2000

Key words: laser fusion; titanium-containing copolymer; vinyl titanate; copolymerization; macromolecular modification

INTRODUCTION

Soluble, linear, carbon-based copolymers containing elements such as chlorine, iodine, or transition metals such as titanium are of interest for use in the production of targets for laser inertial-confinement fusion (ICF) experiments.[1–5] In an ICF implosion experiment,[6] a small plastic microballoon target containing gaseous deuterium (D_2) or deuterium–tritium (DT) is symmetrically exposed to extremely high-power radiation from a laser source. This radiation ablates the capsule wall and compresses the gaseous fuel to very high densities and temperatures, resulting in the initiation of nuclear fusion. Dopant atoms incorporated into the inner wall or "mandrel" of the capsule can provide spectroscopic probes of the capsule implosion process.[3,4] Titanium is a particularly interesting diagnostic atom because it gives rise to a relatively simple K-shell spectroscopic signal when the capsule wall is mixed into the hot, dense plasma during the implosion.[3,4]

For a titanium-containing material to be useful in mandrel preparation, it must have mechanical and solution properties similar to those of polystyrene, as well as the proper titanium content.[1,2,5] None of the titanium-containing polymeric materials described in the literature have this combination of characteristics.[5,7–20]

There are two general routes for the preparation of linear polymers containing transition-metal complexes as substituents: macromolecular modification and the polymerization of metal-containing monomers. Macromolecular modification involves the coordination of groups on polymer chains to metal precursor complexes. The appeal of macromolecular modification for the preparation of titanium-containing copolymers is that the reactive titanium-complex substituents are introduced after the polymerization has taken place and, thus, do not have to survive under the polymerization conditions. However, attempts to prepare soluble, linear polymers containing titanium via the macromolecular modification have only been partially successful. We have reported that the reaction of poly(styrene–methacrylic acid) with dichlorotitanocene yields a soluble, linear polymer only if a large excess of the dichlorotitanocene is used.[5] However, this polymer becomes insoluble when the excess dichlorotitanocene is removed. Camail and coworkers reported that the reactions of copolymers of alkyl methacrylates and methacrylic acid with titanium(IV) alkoxides yield soluble polymers only when large excesses of the titanium(IV) alkoxides are used.[20] These authors did not attempt to remove the excess titanium(IV) alkoxides from their polymers.

Because of the difficulties with the macromolecular modification approach, we have developed methods for the preparation of soluble, linear polystyrene copolymers containing titanium via copolymerization of styrene with vinyl titanate monomers. The results from these studies and from our attempts to prepare identical copolymers using a macromolecular modification approach are reported in this article.

EXPERIMENTAL

Materials

Benzene, toluene, hexanes, and N,N-dimethylformamide (DMF) were dried over activated molecular sieves. Tetrahydrofuran (THF) was dried by distillation from sodium and benzophenone. Dichloromethane was dried by distillation from calcium hydride. Inhibitor-free styrene (Fisher, Pittsburgh, PA) and 2-hydroxyethyl methacrylate (Fisher) were obtained by distilling the inhibited monomers under reduced pressure. The 2-(methacryloyloxy)ethyl acetoacetate (Aldrich, Milwaukee, WI), (2-methacryloxyethoxy)triisoproxytitanate (Gelest, Inc., Tullytown, PA), and titanium methacryloxy ethylacetoacetate triisoproxide (Gelest, Inc.) monomers and titanium(IV) isopropoxide (Aldrich) were used as received. Azobisisobutyronitrile (AIBN) was purified by recrystallization and dried under a vacuum prior to use. All oxygen- and water-sensitive materials were handled in a Vacuum Atmospheres glove box or with standard Schlenk techniques.

Characterization Methods

The ^{1}H-NMR spectra were recorded on either a GE NT-300 or a Bruker ARX-300 multinuclear NMR spectrometer and were referenced to internal tetramethylsilane (TMS).

Size-exclusion chromatography (SEC) was carried out on a system incorporating a Waters 510 pump, a Waters 410 differential refractive index detector, and two Waters linear Ultrastyragel columns in series at 30°C using a flow rate of 1 mL/min. Injections of 20 mL of THF solutions containing between 0.1 and 0.2% (w/v) of the polymer were used. Weight-average ($\bar{M}_w$), number-average ($\bar{M}_n$), and z-average ($\bar{M}_z$) molecular weights and polydispersities ($\bar{M}_w/\bar{M}_n$) were calculated using a polystyrene calibration curve.

Thermal analyses of polymer samples were performed on a Mettler-Toledo TA8000 thermal analysis system. Differential scanning calorimetry (DSC) measurements were made using the DSC402 module. Each sample (5 mg) was heated to 130°C for 10 min to remove any traces of solvent under nitrogen gas. Three scans from 25 to 200°C at a rate of 10°C/min were run. The midpoint of the glass transition of each polymer was calculated using Mettler software. The averages of the second and third scans are reported. Thermogravimetric analyses (TGA) were performed using the TG50 402 module. Samples ranging from 9.0 to 11.0 mg were heated from 50 to 600°C at a rate of 20°C/min under a nitrogen atmosphere. The temperatures at 20% weight loss are reported as the decomposition onset temperatures.

Atom percent titanium analyses[21,22] were performed on a Fizon Omicron X-ray fluorescence

spectrometer using a Mo anode source. Data were acquired at 1 mA/40 kV and under conditions that did not require corrections for absorption. Measurements were calibrated using a dichlorotitanocene calibration curve.

Preparation of Poly(styrene-*co*-2-hydroxyethyl methacrylate) in Toluene (PSHEMA1)

A solution of 200 mL of toluene, 20 mL of inhibitor-free styrene, 20 mL of inhibitor-free 2-hydroxyethyl methacrylate, and 0.10 g of AIBN was prepared in a 500-mL Schlenk flask capped with a rubber septum. The contents of the flask were degassed by first evacuating the flask for 10 min while it was cooled to $-78°C$ in a dry ice/isopropanol bath and then filling the flask with N_2. After the degassing procedure was repeated three times, the reaction mixture was allowed to warm to room temperature and then was heated to 60 $\pm$ 1°C under N_2 in an oil bath. After only 1 h, a significant amount of white solid was observed in the flask. After 21.5 h, the reaction mixture had become a solid white mass with little liquid evident. The liquid in the reaction mixture was decanted, and the white solid was removed from the flask and washed exhaustively with hexanes. Approximately 30 g (70%) of the product was isolated. This polymer was completely insoluble in both THF and DMF.

Preparation of Poly(styrene-*co*-2-hydroxyethyl methacrylate) in DMF (PSHEMA2 and PSHEMA3)

Two soluble, copolymers were prepared in DMF. The first copolymer (PSHEMA2) was prepared as follows: A solution of 10 mL of inhibitor-free styrene, 10 mL of inhibitor-free 2-hydroxyethyl methacrylate, and 0.050 g of AIBN in 100 mL of DMF (16.7% total monomer) was prepared in a 500-mL Schlenk flask. The contents of the flask were degassed by first evacuating the flask for 10 min while it was cooled to $-78°C$ in a dry ice/isopropanol bath and then filling the flask with N_2. After the degassing procedure was repeated three times, the reaction mixture was warmed to room temperature and then heated under N_2 at 60 $\pm$ 1°C for 70 h. Finally, the clear reaction mixture was added to 300 mL of hexanes to precipitate the product as a white solid. The crude product was collected by vacuum filtration and then was dissolved in 150 mL of dichloromethane. This solution was poured into 300 mL of hexanes,

and the precipitated polymer was allowed to settle. The precipitate was isolated by vacuum filtration, washed with 100 mL hexanes, and dried on the vacuum line. The yield of the final product was 8.2 g (41%). This copolymer was readily soluble in THF.

The second, soluble copolymer (PSHEMA3) was prepared as follows: A solution of 16.7 mL of inhibitor-free styrene, 3.3 mL of inhibitor-free 2-hydroxyethyl methacrylate, and 0.10 g of AIBN in 100 mL of DMF was prepared in a 500-mL Schlenk flask. The contents of the flask were degassed by first evacuating the flask for 10 min while it was cooled to $-78°C$ in a dry ice/isopropanol bath and then filling the flask with N_2. After the degassing procedure was repeated three times, the reaction mixture was warmed to room temperature and then heated under N_2 at 60 $\pm$ 1°C for 50 h. The reaction mixture was then poured into 1 L of methanol and 1 L of deionized water to yield a sticky white solid and a milky emulsion. The liquid was decanted, and the solid was dissolved in 50 mL of acetone. This solution was poured into 1.8 L of hexanes, and a sticky white solid precipitated. The supernatant liquid was decanted, and the solid was dried under a high vacuum to yield 5.6 g (28%) of the copolymer. This copolymer was soluble in THF.

Preparation of Poly(styrene-*co*-2-acetoacetoxyethyl methacrylate) (PSAM)

A solution of 15 mL of inhibitor-free styrene, 25 mL of 2-acetoacetoxyethyl methacrylate, and 0.081 g of AIBN in 200 mL of benzene (16.7% total monomer with a styrene to 2-acetoacetoxyethyl methacrylate ratio of 3 : 5) was prepared in a 500-mL Schlenk flask. The contents of the flask were degassed by first evacuating the flask for 10 min while it was cooled to $-78°C$ in a dry ice/isopropanol bath and then filling the flask with N_2. After the degassing procedure was repeated three times, the reaction mixture was warmed to room temperature and then heated under N_2 at 60 $\pm$ 1°C for 263 h. Next, a degassed solution of 0.080 g of AIBN in 5 mL of benzene was added to the reaction mixture, and the reaction mixture was heated for an additional 72 additional h at 60°C (335 h total). Finally, the reaction mixture was poured into 1.8 L of hexanes to precipitate the crude polymer. The supernatant liquid was decanted, and the solid residue was dissolved in 150 mL of dichloromethane. This solution was

poured into 1.8 L of hexanes, and a sticky white solid precipitated. The supernatant liquid was decanted, and the solid was dried under a high vacuum to yield 29.8 g (74%) of copolymer that was soluble in THF.

Reaction of Poly(styrene-*co*-2-hydroxyethyl methacrylate) with Ti(OPr^i)$_4$

A solution of 2.00 g of very dry PSHEMA3 in 50 mL of THF was stirred under N_2 as a solution of 1.9 g (0.0070 mol) of Ti(OPr^i)$_4$ in 100 mL of THF was added dropwise over a period of 20 min. As the addition proceeded, the reaction mixture became cloudy. The reaction mixture was then stirred for 3 h. After vacuum filtration and drying under a high vacuum, 2.05 g of a sticky white solid that was completely insoluble in THF, DMF, and acetone was obtained.

Reaction of Poly(styrene-*co*-2-acetoacetoxyethyl methacrylate) with Ti(OPr^i)$_4$

A solution of 1.08 g of very dry PSAM in 100 mL of CH_2Cl_2 was stirred under N_2 as a solution of 1.1 g (0.0039 mol) of Ti(OPr^i)$_4$ in 100 mL of THF was added over a 20-min period. As the addition proceeded, the solution turned light yellow in color and became cloudy. After the addition was completed, the solution was stirred for 2 h. After vacuum filtration and drying under a high vacuum, 0.96 g of a sticky white solid was obtained. This solid was insoluble in THF and DMF.

Preparation of Poly[styrene-*co*-(2-methacryloxyethoxy)triisopropoxytitanium(IV)] (PSTM1) and Poly[styrene-*co*-(methacryloxyethylacetoacetonato)triisopropoxy-titanium(IV)] (PSTM2)

These copolymers were prepared either in a Schlenk flask fitted with a rubber septum and connected to a N_2/vacuum manifold or in a sealed glass reaction vessel under a vacuum. A number of polymerizations were performed with different total monomer concentrations (9.1–28.5% total monomer, v/v), different relative amounts of styrene and titanate monomer (50 or 60 mol %), and different AIBN concentrations (2.0×10^{-4} to 5.4×10^{-4} g/mL). The general procedure for the polymerizations is as follows: The appropriate amounts of styrene and the titanate monomer, AIBN, and benzene or toluene were placed in a Schlenk flask or in a flask connected to the vac-

uum line. The solution was first cooled in a dry ice/isopropanol bath and then evacuated to 0.02–0.03 mmHg (manifold) or approximately 1×10^{-6} mmHg (vacuum line). The degassing procedure was repeated three times. If the polymerization was conducted on a manifold, the Schlenk flask was filled with N_2 after the final degassing cycle. If the polymerization was conducted on a vacuum line, the flask was sealed under a vacuum before the reaction mixture was thawed during the final degassing cycle. The flask was then placed in an oil bath at $60 \pm 1°C$. In some syntheses, a fine white solid settled had settled to the bottom of the flask after about 12 h. In most cases, a second charge of AIBN was added after 3–4 days to improve the yields of the polymerizations. For polymerizations run under N_2, this was accomplished by injecting a solution of AIBN in benzene into the reaction mixture through the rubber septum. For polymerizations run under a vacuum, the second charge of AIBN was added by fracturing a break-seal between the vessel containing the reaction mixture and a tube containing a benzene solution of AIBN. The polymerizations were allowed to proceed for 162–211 h depending upon the particular experiment. The copolymers were isolated by pouring the reaction mixtures into dry, degassed hexanes in the glove box. After approximately 12 h, the supernatant liquids were decanted, and the solid polymers were dissolved in THF or dichloromethane. These solutions were filtered, and the filtrates were evaporated to dryness. The final products, which were tough yellow–white solids, were dried under a high vacuum. All the copolymers were soluble in THF, dichloromethane, and chloroform.

RESULTS AND DISCUSSION

For a titanium-containing polymer to serve as a mandrel material for use in inertial confinement fusion experiments, it must meet a rather stringent set of conditions. Mandrels may be prepared either by droptower or microencapsulation techniques.[1] Both processes have been optimized for polystyrenelike polymers: The former requires solubility in a volatile organic solvent such as dichloromethane, while the latter requires a water-immiscible solvent with density close to 1.0 g/cm^3. In either case, polymer weight-average molecular weights ($\bar{M}_w$) of at least 50,000 daltons and preferably 100,000 daltons are required to

provide adequate strength. Finally, to provide useful spectroscopic information, the titanium content of the copolymers must be at least 0.1 atom %.*

In a recent article,[5] we briefly reviewed the titanium-containing polymeric materials reported in the literature and noted that none of these polymers are suitable for mandrel production. We also described our attempts to prepare titanium-containing copolymers suitable for mandrel production by reacting polystyrene copolymers bearing carboxylic acid groups with titanocene derivatives. Our results indicated that these copolymers became insoluble in the absence of a large excess of the molecular titanocene complex. More recently, Camail and coworkers reported that the reactions of titanium(IV) alkoxides with alkyl methacrylate–methacrylic acid copolymers yield insoluble, crosslinked materials unless large excesses of the titanium(IV) alkoxides are used.[20]

Camail et al.'s results were quite promising, and we have attempted to prepare titanium-containing polymers that are appropriate for mandrel formation from titanium(IV) alkoxides. The copolymerization of styrene and functionalized monomers followed by reaction of the copolymers with $Ti(OPr^i)_4$, a procedure similar to that reported by Camail and coworkers, yielded insoluble polymers. In contrast, the free-radical catalyzed copolymerization of styrene and two titanium complexes derived from 2-hydroxyethyl methacrylate, shown in Figure 1, yielded copolymers with suitable titanium contents that are readily soluble in THF and dichloromethane. Microshells produced from one of the copolymers also have sufficient mechanical strength to serve as target mandrels.

Preparation and Characterization of Copolymers of Styrene with 2-Hydroxyethyl Methacrylate (PSHEMA) and 2-Acetoacetoxyethyl Methacrylate (PSAM)

Camail and coworkers reported that it is possible to prepare soluble titanium-containing polymers by the reactions of titanium(IV) alkoxides with alkyl methacrylate/methacrylic acid copolymers if large excesses of the titanium(IV) alkoxides are used.[20] Unfortunately, no molecular weights were

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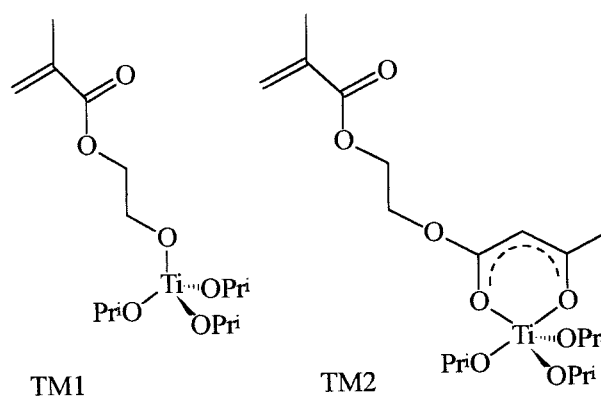* Atom percent titanium is defined as the number of titanium atoms per 100 total atoms.

Figure 1   The (2-methacryloxyethoxy)triisopropoxytitanium(IV) (TM1) and (methacryloxyethylacetoacetonato)triisopropoxytitanium(IV) (TM2) monomers used to prepare the titanium-containing copolymers PSTM1 and PSTM2.

reported for these polymers, and both the excess of titanium(IV) alkoxide and the nature of the polymer make them unsuitable for mandrel production. However, these results were sufficiently promising that we attempted to prepare titanium-containing copolymers via the stoichiometric reactions of $Ti(OPr^i)_4$ with either a styrene–2-hydroxyethyl methacrylate copolymer (PSHEMA) or a styrene–2-acetoacetoxyethyl methacrylate copolymer (PSAM). Neither copolymer was commercially available, and each was prepared by free-radical copolymerization.

The rate of the copolymerization of styrene and 2-hydroxyethyl methacrylate (HEMA) was sensitive to the nature of the solvent. In toluene, polymerization occurred very rapidly, and the product, PSHEMA1, precipitated from the solution. After 21.5 h, the percent conversion of the polymerization was greater than 70%. The PSHEMA1 copolymer was insoluble in both THF and DMF, suggesting that it had a very high molecular weight. The copolymer was also swollen with monomer, suggesting that one or both of the monomers had a higher affinity for the polymer than for the toluene. This suggests that the rapid polymerization and high molecular weight of the copolymer may be due to absorption of one or both monomers by the propagating polymer chains to give a high concentration of the monomer(s) around the propagating chain ends.

The copolymerization of styrene and HEMA also occurred rapidly in DMF, but a soluble product was obtained. In one polymerization, a reac-

Table I   Reaction Stoichiometry, Copolymer Composition, and Molecular Weight Data

Copolymer	% Total Monomer	Volume Fraction Styrene	AIBN (g/mL × 10^4)	Percent Conversion	Mol Fraction Styrene (n)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_z \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
PSTM1a	19.8	0.50	4.0	36	0.87	34.4	51.1	72.4	1.48
PSTM1b	18.0	0.40	2.0	16	0.82	52.0	76.2	109	1.46
PSTM1c	22.0	0.40	2.0	21	0.81	50.8	85.8	133	1.69
PSTM1d	27.0	0.40	2.0	13	0.81	61.7	105	166	1.70
PSTM2a	16.7	0.50	4.2	20	0.93	23.4	53.8	280	2.30
PSTM2b	15.6	0.46	4.2	23	0.89	25.5	49.9	122	1.95
PSTM2c	23.1	0.37	5.8	18	0.84	31.3	49.8	80.8	1.59
PSHEMA2	16.7	0.50	4.2	50	0.50	108	706	3110	6.56
PSHEMA3	16.7	0.83	8.3	28	0.77	32.1	53.1	76.2	1.65
PSAM	16.7	0.38	3.4	74	0.48	60.7	141	329	2.32

tion mixture that was 16.7% total monomer with a 1 : 1 styrene-to-HEMA ratio and 4.2×10^{-4} g/mL of AIBN gave a 50% conversion after only 70 h and one charge of AIBN. The product, PSHEMA2, had a very high molecular weight and a high polydispersity. These results contrast with copolymerizations involving TM1, discussed subsequently, in which both the molecular weights and polydispersities of the polymers are significantly lower.

The PSHEMA2 copolymer was not a suitable precursor for reaction with $\text{Ti}(\text{OPr}^i)_4$ because of its broad molecular weight distribution and low mol fraction of styrene (n). A more suitable copolymer, PSHEMA3, was prepared using 16.7% total monomer that was 83% styrene and 17% HEMA and 8.3×10^{-4} g/ml of AIBN. This polymer had an n of 0.77, $\bar{M}_w$ of about 50,000 daltons, and a reasonably narrow molecular weight distribution.

The ^{1}H-NMR spectra of the PSHEMA3 copolymer has four broad peaks. Resonances of the phenyl protons of the styrene are observed between 6.4 and 7.3 ppm. Two resonances of the methylene protons in the 2-hydroxyethyl groups of the HEMA are observed between 2.5 and 4.2 ppm. The resonances of the methylene and methyne protons of the styrene and the methylene and methyl protons in the methacrylate groups of the HEMA are observed between 0.5 and 2.4 ppm. The mol fractions of the styrene (n) in the PSHEMA copolymers were calculated from the relative integrations of the phenyl protons and the aliphatic protons using eq. (1):

$$\frac{I(\text{aromatic})}{I(\text{aliphatic})} = \frac{5n}{4(1-n)} \qquad (1)$$

where I(aromatic) is the value of the integral of the broad resonance between 6.4 and 7.3 ppm and I(aliphatic) is the value of the broad resonance between broad resonances between 2.5 and 4.2 ppm. The calculated n values for the polymers are given in Table I.

A copolymer of styrene and 2-acetoacetoxyethyl methacrylate (PSAM) was prepared in benzene at 60°C. The rate of polymerization for this system is similar to those observed for systems with the titanium-containing monomers; after 335 h and addition of a second charge of AIBN, the polymerization had reached 74% conversion. The molecular weight is reasonable for a copolymer prepared using 16.7% total monomer and an AIBN concentration of 3.4×10^{-4} g/mL. The copolymer has a broader molecular weight distribution and a higher mol fraction of 2-acetylacetoxyethyl methacrylate than was desired for our application due to the high percent conversion. However, no attempt was made to optimize these parameters because, as discussed below, the reaction of PSAM with $\text{Ti}(\text{OPr}^i)_4$ yielded insoluble products.

The ^{1}H-NMR spectrum of PSAM contains a number of broad peaks. Resonances of the phenyl protons of the styrene are observed between 6.5 and 7.3 ppm. Resonances of the methylene protons in the 2-acetoacetoxyethyl groups in the 2-acetoacetoxyethyl methacrylate are observed between 2.9 and 4.5 ppm. Resonances of the other aliphatic protons in the styrene and 2-acetoacetoxyethyl methacrylate are observed between 0.2 and 2.9 ppm. A resonance between 11.9 and 12.1 ppm is assigned to enol protons in the enol tautomer of the 2-acetylacetoxy groups. The mol frac-

tion of the styrene (n) was calculated from the relative integrations of the phenyl protons and the aliphatic protons using eq. (2):

$$\frac{I(\text{aromatic})}{I(\text{aliphatic})} = \frac{5n}{3n + 14(1 - n)} \qquad (2)$$

where $I(\text{aromatic})$ is the value of the integral of the phenyl resonances between 6.4 and 7.3 ppm and $I(\text{aliphatic})$ is the integral of the resonances between 0.2 and 4.5 ppm. The n values for the polymers are given in Table I.

Reaction of PSHEMA3 and PSAM with Ti(OPr^i)$_4$

The reactions of titanium(IV) alkoxides with alkyl methacrylate–methacrylic acid copolymers were reported to yield insoluble polymers unless the titanium(IV) alkoxides were used in excess.[20] To determine if variations in either the nature of the comonomer (styrene versus alkyl methacrylate) or the coordinating group (carboxylate versus hydroxyl or β-diketonate) would yield soluble polymers, the stoichiometric reactions of Ti(OPr^i)$_4$ with both PSHEMA3 and PSAM were examined. Both reactions yielded insoluble products. It is unclear why these reactions yield insoluble products, because, as discussed below, the copolymerizations of styrene with the titanium-containing monomers, TM1 and TM2, yield soluble polymers with the same functional groups.

Preparation of Poly[styrene-*co*-(2-methacryloxyethoxy)triisopropoxytitanium(IV)] (PSTM1) and Poly[styrene-*co*-(methacryloxyethylacetoacetonato)triisopropoxy-titanium(IV)] (PSTM2)

Because the reactions of Ti(OPr^i)$_4$ with both PSHEMA3 and PSAM gave insoluble products, the copolymerization of styrene with monomers (TM1 and TM2 shown in Fig. 1) were carried out. The copolymers were prepared either in a Schlenk flask fitted with a rubber septum and connected to a N$_2$/vacuum manifold or in a glass reaction vessel sealed under a vacuum. A number of polymerizations were performed with different total monomer concentrations (9.1–28.5% total monomer, v/v), different relative amounts of styrene and the titanium-containing monomer (50 or 60 mol %), and different AIBN concentrations (2.0 $\times$ 10^{-4} to 5.4 $\times$ 10^{-4} g/mL). The polymerizations

were allowed to proceed for 162–211 h, and the products were tough yellow solids that were soluble in THF, dichloromethane, and chloroform.

Preparation and Characterization of Copolymers (PSTM1) from Styrene and TM1

High molecular weight copolymers with intact titanium complexes can be prepared from styrene and TM1 if air- and moisture-free conditions are maintained. Both Schlenk and vacuum line techniques allowed the preparation of good quality copolymers. Schlenk techniques were used to prepare the majority of these copolymers because this method was less expensive and less labor intensive than was the vacuum line technique. The polymers were prepared from the inhibited TM1 monomer because attempts to remove the inhibitor resulted in polymerization of the TM1. It is interesting that HEMA is much more reactive than is TM1. This difference may be due to the free hydroxyl group in HEMA that may allow monomer aggregation and rapid polymerization.

The ^{1}H-NMR spectra of the copolymers exhibited four broad peaks. Resonances of the phenyl protons were observed between 6.3 and 7.2 ppm. Two resonances of the methylene protons in the oxyethyl groups of the TM1 and the methyne protons in the isopropoxy groups of the TM1 are observed between 3.7 and 4.9 ppm. Resonances of the methyl protons in the isopropoxy groups of the TM1, the methyne and methylene protons of the styrene, and the methylene and methyl protons in the methacrylate groups of the TM1 are observed between 0.1 and 2.6 ppm. The mol fraction of the styrene (n) in the PSTM1 copolymers was calculated from the ^{1}H-NMR integrations using eq. (3):

$$\frac{I(\text{aromatic})}{I(\text{aliphatic})} = \frac{5n}{3n - 26(1 - n)} \qquad (3)$$

where $I(\text{aromatic})$ is the value of the integral of the resonances between 6.3 and 7.2 ppm and $I(\text{aliphatic})$ is the integral of the resonances between 0.1 and 2.6 ppm. The values of n calculated for the PSTM1 copolymers are given in Table I. These data show that a monomer feed of 40% styrene and 60% TM1 gives copolymers with an n of 0.81–0.82, suggesting that styrene is more reactive than is TM1 under the polymerization conditions.

Table II   Atom Percent Titanium Data for the PSTM1 Copolymers

Copolymer	n	Atom Percent Ti
PSTM1a	0.87	~ 0.06
PSTM1b	0.82	0.10
PSTM1c	0.81	0.12
PSTM1d	0.81	0.12

The titanium contents in these copolymers were determined using X-ray fluorescence and are given in Table II. The data indicate that copolymers with n from 0.81 to 0.82 have titanium contents of about 0.1 atom %, the optimum value for use in ICF implosion experiments. Copolymers with higher values of n, not shown in Table II, typically had titanium contents that were too low for use in ICF implosion experiments.

The molecular weights and polydispersities for the PSTM1a–d copolymers were obtained from SEC and are given in Table I. The molecular weight reproducibility using different lots of the TM1 monomer under the same reaction conditions was rather poor. These inconsistencies appear to be due, in large part, to differences in the purity of the TM1 monomer used in these polymerizations (this monomer is very reactive and polymerizes even when stored under high purity nitrogen at $-10°C$). To avoid batch-to-batch problems with monomer purity, the PSTM1 copolymers in Tables I and II were simultaneously prepared from the same lot of TM1. Under these conditions, the molecular weight of the copolymer clearly increases as the total monomer concentration is increased (PSTM1b–d) and as the AIBN concentration is decreased (PSTM1a, PSTM1b, and PSTM1c). Also, increasing the relative amount of styrene in the reaction mixture increases the ratio of styrene to TM1 in the copolymer (PSTM1a, PSTM1b, and PSTM1c).

Preparation and Characterization of Copolymers of Styrene and TM2 (PSTM2)

Copolymers of styrene and TM2 were prepared using the same techniques used to prepare the PSTM1 copolymers. The ^{1}H-NMR spectra of these polymers contain a number of broad peaks. Resonances of the phenyl protons of the styrene are observed between 6.4 and 7.3 ppm. Resonances the methylene protons in the oxyethyl group of

the TM2, the methyne protons in the acetoacetonate groups of the TM2, and the methyne protons in the isopropoxy groups of the TM2 are observed between 3.7 and 4.8 ppm. Resonances of the methyl protons in the isopropoxy groups of the TM2, the methylene and methyne protons of the styrene, and the methylene and methyl protons in the methacrylate group of the TM2 are observed between 0.1 and 2.6 ppm. The mol fraction of styrene (n) in the PSTM2 polymers was calculated from the NMR integrations using eq. (4):

$$\frac{I(\text{aromatic})}{I(\text{aliphatic})} = \frac{5n}{3n - 31(1 - n)} \qquad (4)$$

where $I(\text{aromatic})$ is the integral of the resonances between 6.3 and 7.2 ppm and $I(\text{aliphatic})$ is the integral of the resonances between 0.1 and 2.6 ppm. The values of n for PSTM2a–c are shown in Table I. The n values for these copolymers depend upon the volume fraction of styrene in the total monomer feed. The n values for PSTM2 are consistently higher than are those for PSTM1. This indicates that TM2 is not incorporated into PSTM2 to same the degree that TM1 is incorporated into PSTM1 under similar reaction conditions and suggests that TM2 is not as reactive as is TM1 in copolymerizations with styrene. Because PSTM2a–c did not form acceptable mandrels in preliminary experiments, no attempt was made to prepare PSTM2 copolymers with higher values of n.

The molecular weights and polydispersities for PSTM2a–c were obtained from SEC, and their $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_w/\bar{M}_n$ values are given in Table I. These data suggest that the molecule weights of the copolymers depend on the AIBN and monomer concentrations but not on the titanium-containing monomer that is used.

Thermal Analyses of PSTM1a–d and PSHEMA3

The preparation of the mandrels for laser fusion experiments by the droptower technique involves exposing the polymers to relatively high temperatures ($\sim 200°C$),[1] and, thus, thermally stable polymers are required. Both DSC and TGA measurements on some of the copolymers were carried out to determine if they are sufficiently thermally stable to be used in these experiments. The glass transition temperatures, T_g's, and the decomposition onset temperatures of PSTM1a–d

Table III Glass Transition and Decomposition Onset Temperature for the PSTM1 and PSHEM3 Copolymers

Copolymer	T_g (°C)[a]	Decomposition Onset Temperature (°C)[b]
PSHEMA3	104	389
PSTM1a	86	397
PSTM1b	86	382
PSTM1c	86	384
PSTM1d	87	380

[a] Midpoint of the glass transition.
[b] Temperature at 20% weight loss.

and PSHEMA3 were measured and are listed in Table III. The T_g's for PSTM1a–d are lower than that of polystyrene ($T_g \sim 100$°C), as is expected for copolymers comprised primarily of styrene repeat units and a smaller amount of repeat units containing bulky groups such the $Ti(OPr^i)_3$ in the side chain. The value of T_g for PSHEMA3 is surprisingly close to that of pure polystyrene. The T_g for PSHEMA3 is also significantly higher than those of PSTM1a–d because of the hydrogen bonding that can occur between HEMA repeat units in the copolymer chains.

The decomposition onset temperatures of PSTM1a–d and PSHEMA3 are lower than that of polystyrene (417°C) but higher than that of poly-(methyl methacrylate) (360°C). As expected, there is a rough correlation between the decomposition onset temperatures and the mol fractions of styrene in the copolymers. The thermal properties of the PSTM1a–d copolymers are sufficiently close to that of polystyrene to allow them to be used in the fabrication of ICF targets.

CONCLUSIONS

We have successfully prepared titanium-containing copolymers suitable for use in ICF targets via the free-radical copolymerization of styrene with a titanium-containing monomer, TM1. Copolymers with weight-average molecular weights of about 100,000 daltons and titanium contents of about 0.1 atom % were obtained using a monomer feed that is 60% titanate monomer and 40% styrene. Attempts to prepare identical copolymers by macromolecular modification were unsuccessful. These studies demonstrate that the copolymeriza-

tion of styrene and vinyl monomers containing titanium is the method of choice for the preparation of titanium-containing copolymers suitable for use in ICF targets.

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