Synthesis of Amine-Terminated Aliphatic Polycarbonates via $Al(Et)_2(OR)$-Initiated Polymerizations

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Received August 23, 1996; Revised Manuscript Received July 22, 1997[⊗]

ABSTRACT: New aliphatic polycarbonates derived from trimethylene carbonate (**1**) (TMC, 1,3-dioxan-2-one),have been prepared by ring opening polymerization. The synthesis is achieved by using new aluminum alkoxide initiators which allow for the incorporation of controlled functionality in the resulting polymer. The synthesis of poly(TMC) with nitrophenyl end groups was achieved by using initiators of the form, $Al(Et)_{3-x}(OR)_x$; where $x = 1-2$, $R = -(CH_2)_2PhNO_2$. The end groups could be reduced to give the corresponding aminophenyl end-capped poly(TMC). In these polymerizations, molecular weight is proportional to the monomer/intiator ratio, with each polymer chain containing one nitrophenyl or aminophenyl functionality.

Introduction

Interest in the development of specifically functionalized polymers and oligomeric materials has grown considerably in recent years. Controlled introduction of various functionalities has been sought for a variety of purposes including the development of bioactive materials, polymeric emulsifiers, and stabilizers and the creation of block and graft copolymers.

The aliphatic polycarbonate derived from trimethylene carbonate (1) (TMC, 1,3-dioxan-2-one), has been studied for its potential use as biocompatible or biodegradable materials.[1] The studies of the thermal degradation of poly(TMC) also indicate that it may be useful as a thermally labile component for the preparation of polyimide nanofoams.[2,3] For these and other applications, it is desirable to obtain poly(TMC) blocks of controlled molecular weight and functionality. Poly(TMC) can be synthesized by a number of means. Previous studies have shown that both solution and bulk polymerization with a variety of initiators can be used to yield poly(TMC) of controlled molecular weight.[4,5] End group functionalized poly(TMC) has been prepared by reacting the hydroxylic groups of poly(TMC) to give poly(TMC) with unsaturated polymerizable groups.[6] We now report the synthesis of poly(TMC) with nitrophenyl and aminophenyl end groups using aluminum alkoxide initiators. In these polymerizations, polymers of the desired molecular weight can be made by adjusting the initiator/monomer ratio. In the final materials, each polymer chain contains one functionality, and there is no need to derivatize a previously prepared polymer.

Experimental Section

Materials. All materials were commercially available and used as received unless otherwise noted. Anhydrous ethanol (Gold Shield) was distilled from $Mg(OEt)_2$ prior to use. All reactions were performed in an argon atmosphere drybox unless otherwise noted.

Analyses and Instrumentation. NMR spectra ($CDCl_3$) were recorded on an IBM WP 250 spectrometer operating at 250.1 MHz (^1H) and 62.9 MHz (^{13}C) with chemical shifts reported in ppm downfield from tetramethylsilane. Gel permeation chromatography (GPC) was performed utilizing a Waters 150-C fitted with a series of Waters Styragel columns (HR1, HR2, HR4, HR5E) using THF as eluent. GPC molecular weights are reported vs polystyrene standards (calibrated from 100 to 2×10^6).

Polymer Synthesis. Several representative examples are shown. The yields for most of the polymerizations were essentially quantitative (greater than 95%). Several lower molecular weight polymers had lower yields due to fractionation of the lower molecular weight oligomers (<1000).

Synthesis of Ethyl-Terminated Poly(TMC), PTMC-1. A 100 mL round-bottomed flask, fitted with a magnetic stir bar, was charged with 5 mL of $Cl_2CHCHCl_2$ (TCE), and 0.15 mL (0.29 mmol) of a 1.9 M solution of $Al(Et)_3$ in toluene was added slowly with stirring. To this mixture, 16.6 μL (0.29 mmol) of ethanol was added and ethane was evolved. When the addition of the alcohol co-initiator was complete, 3.0 g (29.4 mmol) of 1,3-dioxan-2-one (Dajac Labs) in 4 mL of TCE was added. The resulting clear mixture was stirred and heated to 100 °C for 12 h. A dramatic increase in viscosity was noted. The polymer was precipitated into methanol/water (50:1), and reprecipitated several times from CH_2Cl_2, giving 3.0 g of a white powder (100% yield).

Synthesis of Nitrophenyl-Terminated Poly(TMC), PTMC-8. A 100 mL round-bottomed flask, fitted with a magnetic stir bar, was charged with 22 mL of $Cl_2CHCHCl_2$ (TCE), and 2.06 mL (3.92 mmol) of a 1.9 M solution of $Al(Et)_3$ in toluene was added slowly with stirring. To this stirred mixture was slowly added (over a 30 min period) a solution of phenethyl alcohol, 0.655 g (3.91 mmol), in TCE. When the addition of the co-initiator was complete, 1,3-dioxan-2-one, 30.0 g (294.1 mmol), in 60 mL of TCE was added. The resulting clear yellow mixture was stirred and heated to 85 °C for 2 h. A dramatic increase in viscosity was noted. The polymer was precipitated into methanol, dissolved in CH_2Cl_2, and reprecipitated several times and dried under high vacuum. The yield was quantitative.

Synthesis of Aminophenyl-Terminated Poly(TMC), PTMC-8R. A Parr hydrogenation bottle was charged with 6.0 g of PTMC-**8**, 100 mL of dry THF and 0.6 g of palladium on charcoal (10% Pd). The bottle was pressurized with 45 psi of hydrogen and allowed to shake for 10 h. The flask was then carefully evacuated and filled with dry nitrogen. The solution was ultracentrifuged and filtered (0.2 μm) and the solution reduced in volume to 20 mL by rotary evaporation. The polymer was precipitated into methanol/water (1:1), rinsed with methanol (3×100 mL), and dried in a vacuum oven, yielding 5.6 g of a white powder.

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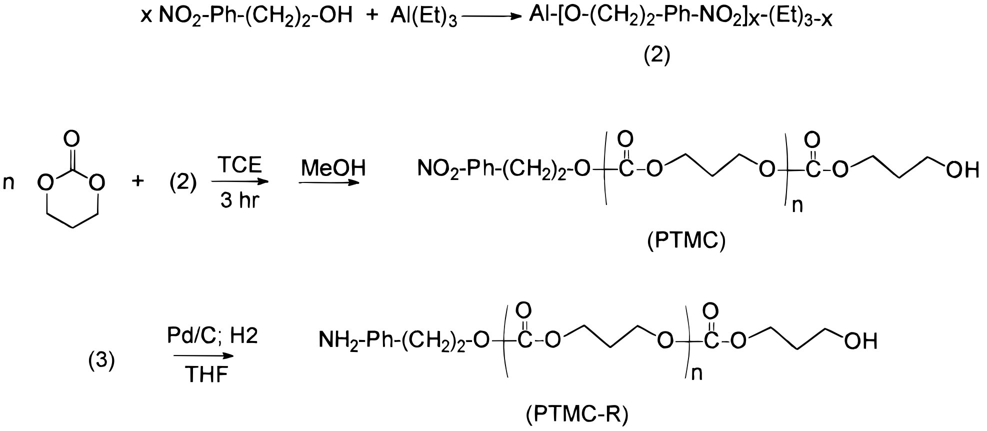
⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S0024-9297(96)01275-2 CCC: $14.00

Scheme 1. Synthesis of Aminophenyl-Terminated Poly(trimethylene carbonate)



Results and Discussion

It is well-known that aluminum alkoxides are active initiators in the ring-opening polymerization of various cyclic aliphatic lactides and lactones.[7] Though aluminum isopropoxide has been used as an initiator for the melt polymerization of TMC in bulk,[4] the use of aluminum alkoxides for solution polymerization of TMC has not been reported. The report of the use of functionalized aluminum initiators of the following type,[8] in the polymerization of lactides and lactones has spurred a great deal of interest in generating polylactides and polylactones with controlled end group functionality.[7,9,10] Attempts to synthesize amine-terminated poly(caprolactone) using intiators like **2**, where R = $-(CH_2)_3NH_2$, failed to give the desired materials due to amide linkage formation.[11]

$$\mathrm{Al(Et)_{3-x}(OR)_x}$$

2

$x = 1-3$;
R = $-(CH_2)_2Br$; $-(CH_2)_2CH{=}CH_2$; $-(CH_2)_2NEt_2$

A functionalized initiator approach has been used to attach a 4-nitrophenyl group to the end of poly(TMC) chains. The nitrophenyl groups can then be easily reduced to give the corresponding amine (see Scheme 1). The nitrophenyl containing poly(TMC) was made by reacting 1,3-dioxan-2-one with **2** where R = $-(CH_2)_2$-$PhNO_2$ and $x = 1, 2$ in 1,1,2,2-tetrachloroethane (TCE).

In order to assess whether aluminum alkoxides could be used to initiate the polymerization of TMC, a simple ethoxy-initiator was prepared: **2** where R = $-(CH_2)_2H$ and $x = 1$. The reactions were carried out in TCE at 80 °C. Polymerization was evidenced by an increase in solution viscosity, and the reactions were terminated after 3 h by reaction with methanol (PTMC-**1**) or by allowing the polymerization mixture to react with 4-nitrobenzoyl chloride (PTMC-**2**−**4**) in solutions. All of the polymers were precipitated into methanol followed by filtration and vacuum drying. The characterization data for these polymers are shown in Table 1.

Molecular weights were determined by GPC (calibrated with polystyrene standards) and by examining end groups by ^{1}H NMR. Though there is good agreement of molecular weights by these two techniques, the M_n derived from NMR is probably more reliable as the GPC molecular weights values are obtained from polystyrene standards.

It was possible to vary the molecular weight of the materials by adjusting the monomer to initiator ratio. Though strict control, as seen with true "living" polymerizations was not observed, a good agreement between calculated molecular weight and actual molecular weight was observed in most cases. An examination of the molecular weights of the polymers listed in Table 1 shows a close agreement of the observed molecular weight with the predicted molecular weight from the monomer/initiator ratio. The exception in this series is PTMC-**4**, which has a higher than expected M_n. This is most likely due to fractionation of the lower molecular weight oligomers during polymer isolation and the lower polydispersity of this sample supports this assumption. These polymerizations proceed by a ring-opening insertion reaction and are clearly not living polymerizations as evidenced by the molecular weight distributions. NMR experiments indicated that the endcapping reaction of hydroxy-functionalized polymers with 4-nitrobenzoyl chloride was not quantitative. Comparison of the number of ethoxy end groups to the number of 4-nitrobenzoyl end groups showed that functionalization approaching 60% could be achieved. For this reason, initiators containing the desired functionality were prepared to ensure quantitative functionalization of the polymer chains.

Table 1. Characterization Data for Ethoxy-Initiated Poly(TMC)

sample entry	[M]/ [Al]	[EtOH]/ [Al]	M_n (^{1}H NMR)	M_n (GPC)	M_w/M_n (GPC)
PTMC-**1**[a]	100	1	9000	9500	2.26
PTMC-**2**[b]	75	1	7900	8900	1.90
PTMC-**3**[b]	50	1	5600	6600	1.86
PTMC-**4**[b]	25	1	3300	4800	1.52

[a] Hydroxy-terminated. [b] 4-Nitrobenzoyl-terminated.

4-Nitrophenethanol was reacted with triethylaluminum in TCE to afford the desired initiators. TMC was added, and polymerizations were terminated with methanol after reaction for 3 h at 80 °C. The characteristics of the 4-nitrophenethoxy-initiated polymers are shown in Table 2. The molecular weights of the polymers were determined by both gel permeation chromatography (GPC) and ^{1}H NMR. In the NMR experiments, the ratio of the peak areas of the aromatic protons vs the areas of the protons of the polycarbonate backbone were used to determine molecular weights (Figure 1).

It was observed that when equimolar amounts of trialkylaluminum and 4-nitrophenethyl alcohol were used, a polymer of roughly twice the expected molecular weight is obtained. When 2 mol of 4-nitrophenethyl alcohol are reacted with 1 mol of trialkylaluminum, an initiator that gives the desired molecular weight control is achieved. We believe that an interaction involving the nitro group of the first nitrophenethoxy group gives

Table 2. Characterization Data for 4-Nitrophenethoxy-Initiated Poly(TMC)

sample entry	[M]/[Al]	[ROH]/[Al]	M_n (^{1}H NMR)	M_n (predicted)[b]	M_n (GPC)	M_w/M_n (GPC)
PTMC-**5**[a]	75	1	11300	7700	15300	1.79
PTMC-**6**[a]	75	1	14700	7700	16300	1.74
PTMC-**7**[a]	75	1	15300	7700	15900	1.97
PTMC-**8**[a]	25	1	5900	2600	8200	2.06
PTMC-**9**[a]	78	2	5100	8000	5300	1.91
PTMC-**10**[a]	75	2	7900	7700	6600	1.5
PTMC-**11**[a]	50	2	5300	5100	4400	1.79

[a] Hydroxy-terminated. [b] Based on the expectation that each molecule of alcohol would yield one polymer chain.

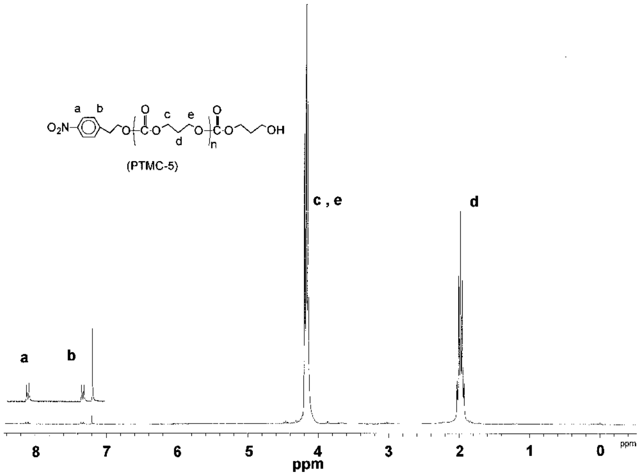


Figure 1. ^{1}H NMR spectrum of 4-nitrophenyl-terminated poly(trimethylene carbonate).

rise to a complex in solution. The second molecule of 4-nitrophenethyl alcohol then coordinates at the alkoxy end of the molecule, forming the initiating species. A yellow/brown gel was observed to form shortly after generation of the initiator. This gel quickly disappears upon addition of the monomer. It is well-known that nearly any molecule having unshared electron pairs can complex with organoaluminum compounds.[12] It is likely that the unshared electrons of the nitro group can coordinate to form a weak complex. Spectroscopic evidence shows that a reversible complex forms between triethylaluminum and nitroaromatic compounds. We believe that the first equivalent of nitrophenethyl alcohol forms a coordination complex through the nitro group while the second equivalent forms the active initiator species through the alcohol group.

The nitro group of the polymer chains underwent facile reduction by standard methods (Pd/C and H_2) to yield the desired amino-terminated polymers which has been confirmed by NMR analysis (Figure 2). A small degree of fractionation of lower molecular weight polymer chains occurs during the reprecipitation after reduction. This is manifested in a higher observed molecular weight and smaller polydispersities as shown in Table 3.

Summary

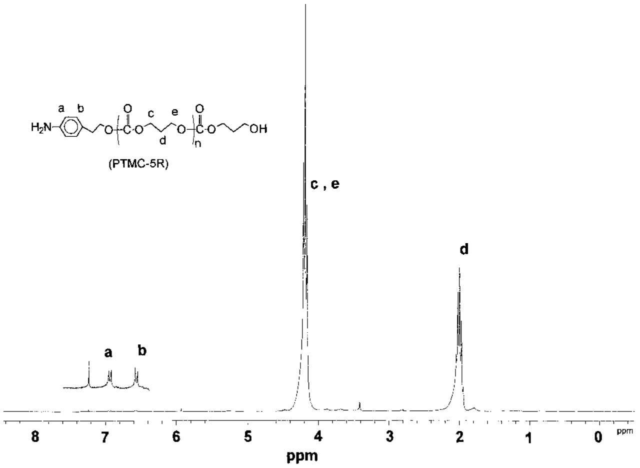


Figure 2. ^{1}H NMR spectrum of 4-aminophenyl-terminated poly(trimethylene carbonate).

Table 3. Characterization Data 4-Amino-Terminated Poly(TMC)

sample entry	[M]/[Al]	[ROH]/[Al]	M_n (^{1}H NMR)	M_n (predicted)[c]	M_n (GPC)	M_w/M_n (GPC)
PTMC-**5**[a]	75	1	11300	7700	15300	1.79
PTMC-**5**R[b]	75	1	17900	7700	18500	1.67
PTMC-**6**[a]	75	1	14700	7700	16300	1.74
PTMC-**6**R[b]	75	1	21600	7700	20700	1.51
PTMC-**9**[a]	78	2	5100	8000	5300	1.91
PTMC-**9**R[b]	78	2	7000	8000	5800	1.79
PTMC-**10**[a]	75	2	7900	7700	6600	1.5
PTMC-**11**[a]	50	2	5300	5100	4400	1.79
PTMC-**11**R[b]	50	2	5300	5100	4600	1.47

[a] Before reduction. [b] After reduction. [c] Based on the expectation that each molecule of alcohol would yield one polymer chain.

Initiators of the formula $Al(Et)_{3-x}(OR)_x$, where $x = 1$, 2, have been shown to be efficient initiators for the solution polymerization of 1,3-dioxan-2-one. We were able to incorporate nitrophenyl groups into the initiators, thereby generating new polymers with each chain terminated by a single nitrophenyl group. These nitro groups undergo a facile reduction under mild reaction conditions, yielding aminophenyl-terminated polycarbonates. The polymers' molecular weights could be controlled by proper adjustment of the initiator/monomer ratio. The utility of these new polymers is currently under investigation in our laboratories and will be the subject of future reports.

Acknowledgment. The authors acknowledge that this work was funded, in part, by NIST (ATP Contract No. 70NAAB-3H1-365).

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MA961275V