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Accessing New Materials through Polymerization and Modification of a Polycarbonate with a Pendant Activated Ester

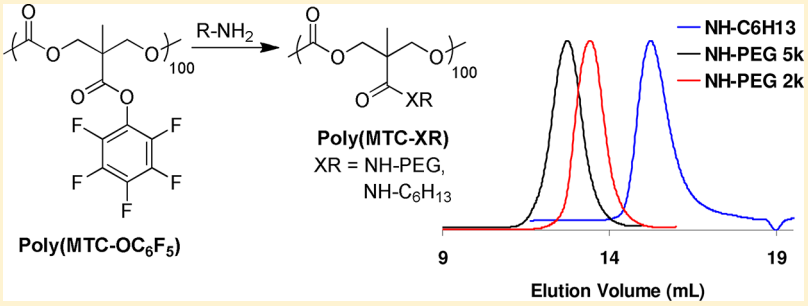
Amanda C. Engler,*[,†] Julian M. W. Chan,[†] Daniel J. Coady,[†] Jeannette M. O'Brien,[†] Haritz Sardon,[†,‡] Alshakim Nelson,[†] Daniel P. Sanders,[†] Yi Yan Yang,[§] and James L. Hedrick*[,†]

[†]IBM Almaden Research Center, 650 Harry Rd., San Jose, California 95120, United States

[‡]POLYMAT, Univ. of the Basque Country, Joxe Mari Korta Center-Avda. Tolosa, 72, 20018, Donostia-San Sebastian, Spain

[§]Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, Singapore 138669, Singapore

Supporting Information



ABSTRACT: Functionalized polycarbonates were synthesized by organocatalytic ring-opening polymerization (ROP) of a cyclic monomer with a pendant activated ester (MTC-OC_6F_5) followed by a postpolymerization modification with both small molecules and macromolecules. Controlled ROP to form homopolymers and diblock copolymers was realized using catalytic quantities of triflic acid. For the homopolymers, a linear relationship between $[M]_0/[I]_0$ and molecular weight (by GPC) demonstrated the living nature of the polymerization. Poly(MTC-OC_6F_5) was functionalized under mild reaction conditions with a variety of amines to obtain polymers with pendant primary, secondary, and tertiary amides. Graft polymers with a high grafting density of over 87% were synthesized using amine-terminated poly(ethylene glycol) of two different molecular weights (2 and 5 kDa). The preparation of poly(MTC-OC_6F_5) provides a means of accessing a wide range of functional polycarbonates with minimal synthetic steps. This new methodology for the formation of functionalized polycarbonates provides a simple and versatile platform for the synthesis of new and innovative materials.

INTRODUCTION

Aliphatic polycarbonates have received considerable attention for therapeutic delivery, polymer-based therapeutics, and tissue engineering because of their low toxicity, biocompatibility, and degradability. These polymers can be prepared with precise control through the ring-opening polymerization (ROP) of cyclic carbonates by cationic, anionic, coordination−insertion, organocatalytic, and enzymatic methods.[1] Tailoring the functionality of these materials has been successfully accomplished through the postfunctionalization of polycarbonates[2] as well as through the preparation of functionalized monomers.[2c,3] For postpolymerization modifications, various functional groups used for "click chemistry" have been incorporated into the polymer. For example, Dove and co-workers[2a] reported the synthesis of allyl-functionalized polycarbonates and demonstrated the postfunctionalization via the radical addition of thiols to the pendant allyl group. More recently, Sanyal et al.[2b] reported a polycarbonate containing a thiol-reactive maleimide. In both examples, the monomers, based on 2,2-bis-(hydroxymethyl)propanoic acid, were prepared using multiple steps and polymers were synthesized by ROP using the organocatalyst 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Another strategy that has been reported is the incorporation of a pendant activated ester leaving group, succinimide-*N*-oxycarbonyl.[2f] Although the activated ester allowed for convenient postpolymerization modification, these polycarbonates exhibited a broad polydispersity index (PDI).

For the preparation of functionalized monomers, a number of synthetic pathways have been explored.[3a] Most pathways involve several synthetic steps and the use of toxic phosgene derivatives. Recently, Hedrick and co-workers[3a] reported a two-step approach (Scheme 1a) to functionalized cyclic monomers based on 2,2-bis(hydroxymethyl)propanoic acid featuring a versatile pentafluorophenyl ester intermediate (MTC-OC_6F_5). This intermediate is easily synthesized on the gram to kilogram scale in high yields, without the use of phosgene and can be stored on the benchtop. Furthermore, a wide range of functional molecules can be easily prepared by reaction of

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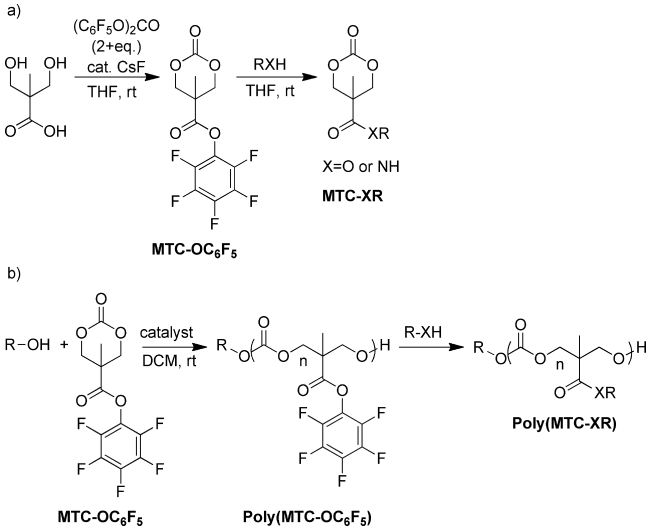
Scheme 1. General Synthetic Route to (a) Functional Carbonate Monomers Using MTC-OC_6F_5 Intermediate and (b) Functional Polycarbonates via Poly(MTC-OC_6F_5)



this intermediate with suitable nucleophiles such as amines and alcohols. While MTC-OC_6F_5 offers great versatility to create functional monomers, due to the nature of ROP, protection prior to ROP and deprotection steps after ROP are necessary to obtain some functionalities. Even then, some functionalities are difficult to access. For example, it can be challenging to polymerize some monomers containing secondary amides under basic conditions because the amide can be deprotonated leading to poor polymerization control.[4] Preparation of poly(MTC-OC_6F_5) by ROP of the MTC-OC_6F_5 intermediate would provide a means of realizing a wide range of functional polycarbonates, including those with pendant amides, with minimal synthetic steps (Scheme 1b). Notably, there are several reports in the literature of polymers bearing the activated pentafluorophenyl ester. Theato and Nilles[5] reported the polymerization of pentafluorophenyl methacrylate and pentafluorophenyl 4-vinylbenzoate via reversible addition−fragmentation chain transfer polymerization. Successful postpolymerization substitution with aniline and alphatic amines was reported at 100% conversion. Klok and co-workers[6] explored the feasibility of using poly(pentafluorophenyl methacrylate) to prepare a library of water-soluble polymers. Substitution percentages ranged from less than 50% to nearly quantitative, depending on the side-group functionality. They also demonstrated the sequential addition of different side groups to create statistical polymers.

Although the synthesis of MTC-OC_6F_5 has been reported, the ROP of MTC-OC_6F_5 has remained a challenge. There are many types of catalysts available for ROP of cyclic carbonates, including transition metal catalysts as well as basic and acidic organocatalysts. However, the high reactivity attributed to the pentafluorophenyl ester group makes catalyst selection for the ROP of MTC-OC_6F_5 a unique challenge. Transition metal catalysts have proven very reliable and efficacious ROP catalysts.[7] Unfortunately, for many applications, including biomaterials, transition metal catalysts are a poor choice for catalyzing ROP because they are oxophilic, making them difficult to remove from oxygen-rich polycarbonates. Basic organocatalysts have been used to synthesize a wide variety of functionalized polycarbonates;[1a,d] however, traditional basic organocatalysts such as DBU could react with the pentafluorophenyl ester, allowing the nucleophilic initiator to attack the activated ester rather than propagate ROP. Furthermore, the labile leaving group, pentafluorophenol could quench the catalyst. (−)-Sparteine has been used for the ROP of MTC-OC_6F_5[8] but is no longer commercially available.[9] Organic acid catalyzed ROP of MTC-OC_6F_5 could circumvent many of the limitations associated with base-catalyzed ROP. These catalysts have been explored for the ROP of lactides[10] and select cyclic carbonates.[4,11]

Organo-catalyzed ROP of cyclic carbonates enables the synthesis of a wide array of well-defined polymeric structures. In this work, we expand the library of available functional polymers with the ROP of MTC-OC_6F_5 and postfunctionalization of the polymer. Organic acids were screened to determine the best catalyst for the controlled ROP of MTC-OC_6F_5. Small molecule alcohols, benzyl alcohol and 1-pyrenebutanol, as well as methoxy-terminated poly(ethylene glycol) (mPEG-OH) were used as initiators. Diblock copolymers were synthesized to demonstrate the versatility and expand the range of possible applications. Postpolymerization functionalization with various small molecules and amine-terminated PEG under mild reaction conditions was also performed.

RESULTS AND DISCUSSION

Polymerization of MTC-OC_6F_5. MTC-OC_6F_5 was synthesized according to literature procedure.[3a] Several different acid catalysts, diphenyl phosphate (DPP), *p*-toluenesulfonic acid (PTSA), and triflic acid were screened for the ROP of MTC-OC_6F_5. For catalyst screening, polymerization of MTC-OC_6F_5 was performed at room temperature in dichloromethane using a 1 M concentration of MTC-OC_6F_5 and an initial monomer-to-initiator-to-catalyst ratio of ($[M]_0/[I]_0/[catalyst]$) of 100/1/10). Conversion of monomer to polymer was monitored using ^1H NMR by observing the disappearance of the cyclic carbonate doublets at 4.87 and 4.40 ppm and the appearance of the polycarbonate singlet at 4.48 ppm. DPP did not facilitate the ROP of MTC-OC_6F_5 after 48 h. When using PTSA, polymer was formed; however, the molecular weight of the polymer formed was significantly lower than what was predicted by the initial monomer-to-initiator ratio ($[M]_0/[I]_0$), indicating that the polymerization was not well controlled. Successful living polymerization of MTC-OC_6F_5 was accomplished using triflic acid, which was determined to be the optimal catalyst and utilized for the remaining studies.

Several different initiators ranging from a small molecule to a macromolecule were explored for the formation of homopolymers and diblock copolymers. Homopolymers with varying degrees of polymerization were synthesized by initiation with either 1-pyrenebutanol or benzyl alcohol, as summarized in Table 1. The degree of polymerization determined by $[M]_0/[I]_0$ was varied from 20 to 200. As seen in Figure 1a, a linear relationship between molecular weight characterized by GPC and $[M]_0/[I]_0$ was observed, indicative of a living polymerization.

Polymerization studies were performed with a 1-pyrenebutanol initiator for convenient monitoring of the polymerization by GPC using both ultraviolet/visible (UV−vis) and refractive index (RI) signals. As shown in Figure 1b, the UV−vis and RI THF GPC traces for poly(MTC-OC_6F_5)$_{100}$ overlay, indicating that pyrene is on the initiating chain end, confirming end-group fidelity. The small shoulder on the higher molecular weight side of the peak is an artifact attributed to $\pi-\pi$ interactions, arising

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Table 1. Summary of All Unmodified Poly(MTC-OC_6F_5)

polymer	initiator	$[M]_0/[I]_0$	conv (%)	DP[a] by NMR	M_n (Da) by GPC	PDI
P200	PyBuOH	200	95	237	37 200	1.21
P100	PyBuOH	100	93	105	20 500	1.15
P50	PyBuOH	50	90	51	10 900	1.17
P25	PyBuOH	25	100	27	5 780	1.10
B200	BnOH	200	93		28 600	1.20
B100	BnOH	100	95		21 300	1.18
B50	BnOH	50	96		11 200	1.24
B20	BnOH	20	95		5 060	1.15

[a]Degree of polymerization (DP).

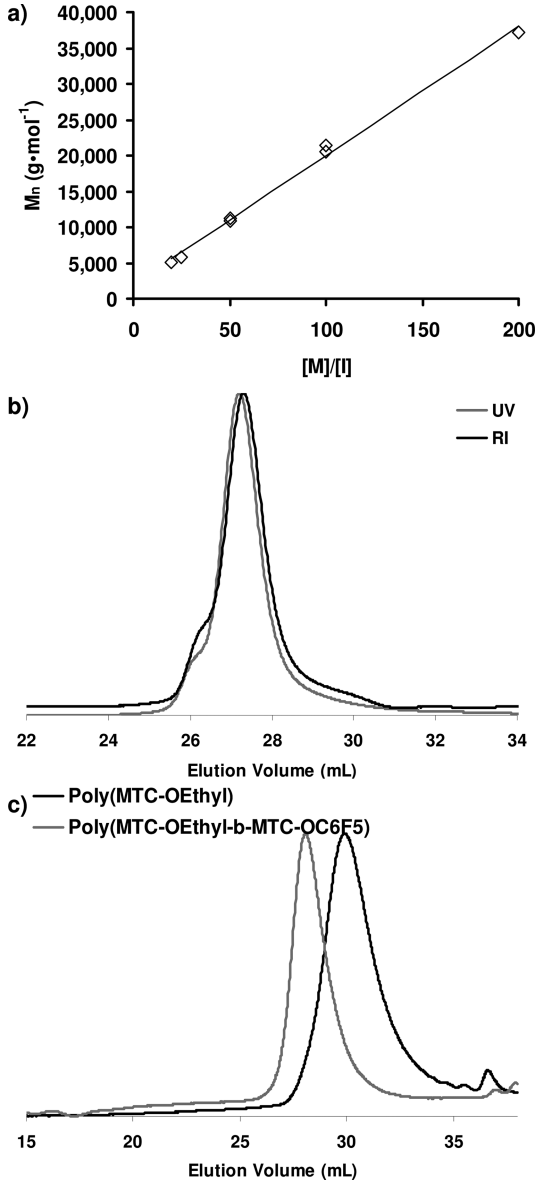

Figure 1. (a) Linearly increasing M_n by GPC as a function of $[M]_0/[I]_0$, (b) UV and RI GPC traces of poly(MTC-OC_6F_5)$_{100}$, and (c) GPC traces of diblock copolymer formed via sequential addition of monomers MTC-OEthyl and MTC-OC_6F_5.

from the pyrene moieties. This shoulder is not observed for the polymers initiated with benzyl alcohol (Figure S1). ^{1}H NMR spectroscopy was also used to confirm the degree of polymerization by comparing the integration between the polycarbonate signal at 4.48 ppm and the 1-pyrenebutanol signals at 7.87 ppm (d, 1H) and 3.4 ppm (t, 2H) for the lower degrees of polymerization (Figure S2). As shown in Table 1, the degree of polymerization determined by ^{1}H NMR analysis is in close agreement with $[M]_0/[I]_0$.

Synthesis of Diblock Copolymers. To further probe the polymerizability of MTC-OC_6F_5, diblock copolymers were synthesized using either a macroinitiator or by sequential addition of MTC monomers. Commercially available poly(ethylene glycol) monomethyl ether (PEG, 5 kDa) was used as a macroinitiator. When characterized by THF-GPC, a distinct shift in molecular weight was observed (Table 2) with minimal broadening of the PDI, indicating chain extension of the PEG–OH_{5K}. Diblock copolymers consisting of poly(MTC-OEthyl-*b*-MTC-OC_6F_5) and poly(MTC-OC_6F_5-*b*-MTC-OEthyl) were polymerized by sequential addition of the monomers in a one-pot reaction sequence. Polymerization with the first monomer was initiated with 1-pyrenebutanol, and after >90% conversion was observed, the second monomer was added. Monomer conversion was monitored by ^{1}H NMR, and molecular weight was monitored by THF-GPC. As shown in Figure 1c and Figure S3, a shift in molecular weight was observed after the addition of the second monomer. Sequential addition of the monomer in either order resulted in diblock copolymers of similar molecular weight and polydispersity (Table 2).

Postpolymerization Modification with Small Molecules. Convenient single-step postpolymerization modification of poly(MTC-OC_6F_5) provides access to polycarbonates exhibiting a wide variety of functionality. Furthermore, a single backbone with a narrow PDI can be synthesized, onto which various functionalities can be installed, allowing for direct comparison of their resultant properties. Several model small molecules were selected for postpolymerization modification studies to obtain primary, secondary, and tertiary amides (Table 3). For the formation of a primary amide, the precursor polymer was dissolved in DMF and excess ammonium acetate was added to the solution. Within 20 min, complete conversion of activated ester to amide was observed, and the polymer precipitated into diethyl ether. To obtain secondary amides, preliminary functionalization studies were carried out at room temperature in $CDCl_3$ using 1-hexylamine at a 1:1.05 OC_6F_5 ester:1-hexylamine ratio. The reaction proceeded to ~50% conversion after 20 min but did not proceed to completion, which indicates that the acidic pentafluorophenol was sequestering the basic primary amines, thereby inhibiting further reaction. After 1.05 equiv of triethylamine (TEA) was added to the reaction mixture, quantitative functionalization was observed. Running the reaction in optimum conditions (Table 1) resulted in quantitative functionalization of 1-hexylamine and benzylamine in all cases examined (Table 1). Figure 2 shows the ^{1}H NMR spectrum of poly(MTC-OC_6F_5) and polymer with amide and *N*-hexylamide moieties. For both substituted polymers, the proton signal of the newly formed amide is visible, and the signal on the ^{1}H NMR spectrum integrated as expected for complete conversion of activated ester into amide. For the formation of tertiary amides, *N*-ethylmethylamine was reacted with poly(MTC-OC_6F_5). Functionalizations promoted by TEA in THF/DMF solvent mixture, the reaction proceeded at a significantly slower rate compared with primary amine reactants and lower substitution was also observed (Table 3). When running the reaction in DMF with excess *N*-ethylmethylamine, the reaction rate significantly increased and higher substitution was achieved

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Table 2. Characterization of First Block (b1) and Second Block (b2) of Diblock Copolymers Containing Poly(MTC-OC_6F_5)

polymer	initiator	DP		M_n (Da) by GPC		PDI by GPC	
		b1	b2	b1	b2	b1	b2
PEG-*b*-poly(MTC-OC_6F_5)	PEG-OH (5 kDa)	114	10	6680	9 520	1.04	1.13
poly(MTC-OC_6F_5-*b*-MTC-OEthyl)	PyBuOH	50	50	8770	12 480	1.20	1.24
poly(MTC-OEthyl-*b*-MTC-OC_6F_5)	PyBuOH	50	50	5290	11 200	1.17	1.19

Table 3. Summary of Substituted Polymers

side chain	backbone	rxn promoter[a]	solvent	rxn time	funct[b,c] (%)	M_n (Da) GPC	PDI
amide							
	B100	AA	DMF	20 min	>98	13 800	1.22
	B50	AA	DMF	20 min	>98	8 050	1.32
	B20	AA	DMF	20 min	>98	5 920	1.21
1-hexylamide							
	B100	none	$CDCl_3$	20 min	50		
	B200	TEA	THF	20 min	>98	32 200	1.19
	B100	TEA	THF	20 min	>98	25 800	1.19
	B50	TEA	THF	20 min	>98	16 800	1.2
	B20	TEA	THF	20 min	>98	8 010	1.21
benzylamide							
	B200	TEA	THF	20 min	>98	25 100	1.27
	B100	TEA	THF	20 min	>98	22 200	1.23
	B50	TEA	THF	20 min	>98	12 100	1.42
	B20	TEA	THF	20 min	>98	7 720	1.24
N-ethylmethylamide							
	B200	TEA	THF/DMF	24 h	86		
		EMA	DMF	3 h	95	14 800	1.30
	B100	EMA	DMF	3 h	98	14 000	1.31
	B50	EMA	DMF	3 h	98	8 680	1.25
	B20	EMA	DMF	3 h	>98	4 740	1.24
PEG (2 kDa)							
	B200	TEA	THF	23 h	90	147 400	1.32
	B100	TEA	THF	23 h	89	110 600	1.21
	B50	TEA	THF	23 h	92	64 900	1.17
	B20	TEA	THF	23 h	93	44 400	1.11
PEG (5 kDa)							
	B100	TEA	$CDCl_3$	24 h	88	192 000	1.28

[a]Triethylamine (TEA), *N*-ethylmethylamine (EMA), ammonium acetate (AA). [b]Percent functionalization was determined by ^{1}H NMR with sample spectra shown in the Supporting Information. [c]As determined by ^{1}H NMR with error of ±2%.

(>95%). Under both reaction conditions, some side groups were hydrolyzed, most likely a result of adventitious water in the system (Figure S4).

For all substituted polymers, GPC traces were obtained to determine if there was any degradation to the backbone during side-group functionalization (Figure S5). THF was used as the eluent for poly(MTC-OC_6F_5) but was not a suitable solvent for all substituted polymers. In the case of substituted polymers, DMF spiked with 0.01 M LiBr was used as the carrier solvent. Not only were the polymers fully soluble in DMF, but the LiBr additive also helps disrupt the intra- and interchain hydrogen bonds which could give rise to GPC artifacts. The same molecular weight trends were observed for the substituted polymers as poly(MTC-OC_6F_5) when looking at the degree of polymerization versus molecular weight, characterized by GPC (Table 3 and Figure S4). Furthermore, there was minimal broadening of the PDI as indicated by the narrow PDI values observed before and after functionalization.

PEG Grafting onto Poly(MTC-OC_6F_5). Polymer grafting using a "grafting onto" approach typically results in polymers with a low grafting density of polymeric brushes.[12] To improve grafting density using this approach, a large excess of side chains can be added; however, these side chains are often difficult to remove during the purification process. Another strategy is to utilize highly efficient reactions such as the 1,3-cycloaddition between an azide and an alkyne (i.e., "click chemistry").[12,13] To determine the feasibility of forming densely packed graft polymers on poly(MTC-OC_6F_5) using a "grafting onto" approach, grafting was performed using a model PEG system. PEG was selected for ease of analysis and for comparison to similar grafting systems in the literature.[6,12−14]

Amine-terminated PEG (2 and 5 kDa) was grafted onto the poly(MTC-OC_6F_5) at a 1.05:1 PEG:OC_6F_5 ester ratio, using TEA to promote the reaction (1.05 equiv for 2 kDa PEG and 1.77 equiv for 5 kDa PEG). A large shift in molecular weight was observed by GPC (Tables 2 and Table 3, Figure 3) without a broadening of PDI, indicating the backbone remained intact during the grafting reaction. As seen in Figure 3, there is a consistent increase in molecular weight with increasing degree of polymerization. The small secondary peaks observed in the GPC traces of the reaction solution are the unreacted PEG side

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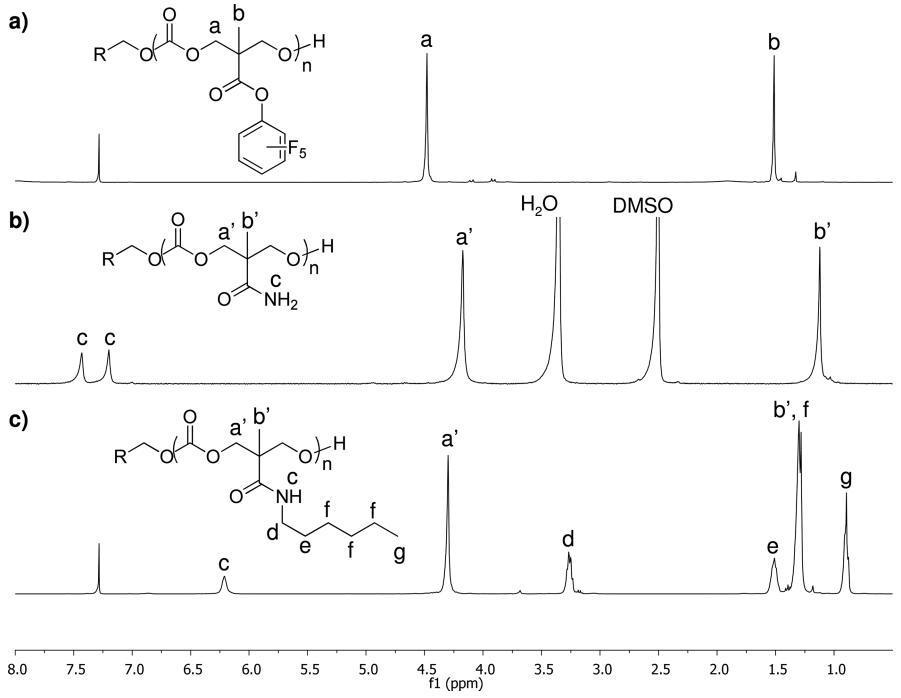

Figure 2. ^{1}H NMR of (a) poly(MTC-OC$_6$F$_5$) in CDCl$_3$, (b) poly(MTC-OC$_6$F$_5$) with primary amide side groups in DMSO-d_6, and (c) poly(MTC-OC$_6$F$_5$) with *N*-hexylamide side groups in CDCl$_3$.

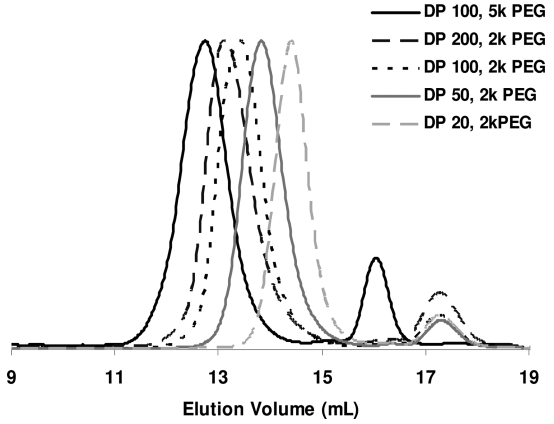

Figure 3. DMF GPC traces of various molecular weights of poly(MTC-OC$_6$F$_5$) grafted with 2 and 5 kDa PEG.

chains (2 or 5 kDa PEG). These unreacted side chains can easily be removed by dialysis.

PEG grafting density was determined using ^{1}H NMR, by integrating the methyl peak on the polycarbonate backbone for unsubstituted, b, and substituted, b′, repeat units (Figure 4). The grafting density was further verified by monitoring the conversion of PEG-amine into grafted PEG-amide, using ^{1}H NMR. Unreacted PEG-amine has a peak at 1.83 ppm (peak e, Figure S6) that shifts to 1.74 ppm (peak e′, Figure S6), after amide formation. For all graft polymers, a high degree of grafting density was observed, over 88%. For 5 and 2 kDa PEG-grafted poly(MTC-OC$_6$F$_5$)$_{100}$, little difference was observed in grafting density between the two different molecular weights (90% and 88%, respectively).

The kinetics of the PEG-amine grafting reaction was studied using both 2 and 5 kDa PEG and poly(MTC-OC$_6$F$_5$)$_{100}$. The reaction was carried out in CDCl$_3$ with TEA at 1.06 equiv for 2 kDa PEG and 1.77 equiv for 5 kDa PEG. ^{1}H NMR spectra were taken at various time points over a 24 h period, and the

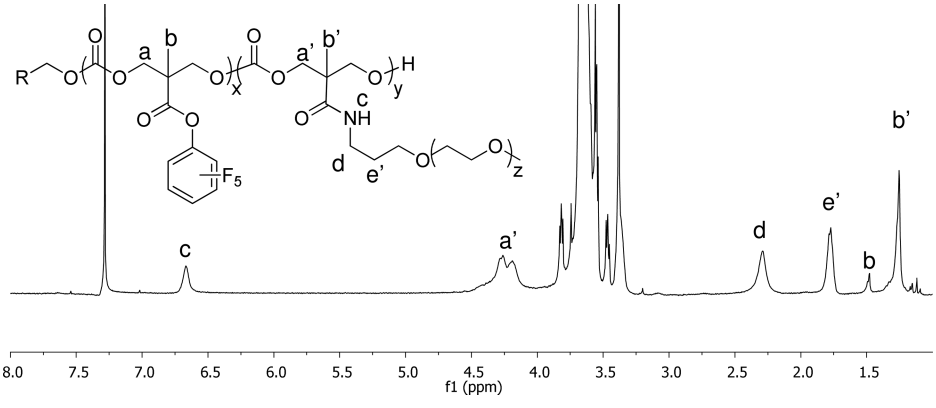

Figure 4. ^{1}H NMR of poly(MTC-OC$_6$F$_5$) grafted with 2 kDa PEG.

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conversion of activated ester into amide was monitored by comparing the methyl peak on the polycarbonate backbone for unsubstituted and substituted repeat units (Figure S6). As shown in Figure 5, for both TEA loading levels, 70% grafting

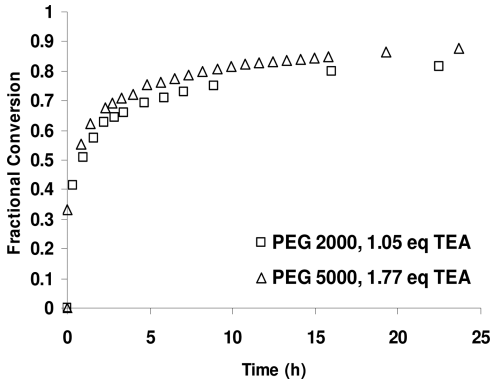

Figure 5. Fractional conversion of activated ester to PEG-amide graft as a function of time for poly(MTC-OC_6F_5) grafted with 2 and 5 kDa PEG.

was accomplished within 5 h. High TEA levels (1.77 equiv) increased the reaction rate slightly, but both polymers had similar grafting densities after 24 h. As expected, as the grafting density increased, the reaction rate decreased due to the shielding of the activated ester groups on the polymer backbone by the densely packed PEG brushes.

When comparing this grafting system to similar ones presented in the literature, the grafting densities observed are higher or comparable to systems that utilize various "click chemistry" reactions. Several systems utilize the 1,3-cycloaddition reaction between an azide and alkyne. Goa and Matyjaszewski[12] grafted PEG-N_3 (750 Da) onto a poly(HEMA) backbone; the highest grafting efficiency attained was 88.4% with an alkyne/PEG-N_3 ratio of 1:8.5. Engler, Lee, and Hammond[13] grafted PEG-N_3 onto a polypeptide backbone containing an alkyne on each repeat unit. Near-quantitative grafting efficiencies were observed for this system, which was attributed to the rigid α-helical backbone of the polypeptide increasing the availability of the alkyne groups. Gibson, Fröhlich, and Klok grafted short amine-terminated PEG (560 Da) onto poly(pentafluorophenyl methacrylate) and observed grafting densities between 60 and 70%.[6] Parish and Emrick reported a PEG-grafted aliphatic polyester system with grafting efficiencies between 70 and 80%.[14]

CONCLUSION

Herein we demonstrated the organo-catalyzed ROP of MTC-OC_6F_5 and postfunctionalization of the polymer with both small molecule and macromolecular amines. The controlled ROP of MTC-OC_6F_5 to form homopolymers and diblock copolymers was achieved through the use of the acid catalyst, triflic acid. For the homopolymers, a linear relationship between $[M]_0/[I]_0$ and molecular weight determined by GPC analysis demonstrated the living nature of the polymerization. Poly(MTC-OC_6F_5) was postfunctionalized under mild reaction conditions with a variety of amines. Graft polymers with a high grafting density of over 87% were synthesized using amine-terminated PEG of two different molecular weights. In summary, the facile preparation of poly(MTC-OC_6F_5) and its postfunctionalization provides rapid access to a wide range of functional polycarbonates with minimal synthetic steps.

EXPERIMENTAL SECTION

Materials. MTC-OC_6F_5 was obtained from Central Glass and purified by crystallizing twice from a mixture of ethyl acetate and hexanes. Amine-terminated PEG was purchased from NOF Corporation. Dichloromethane was dried using activated alumina columns and stored over molecular sieves (3 Å). All other materials were purchased from Sigma-Aldrich and used as received.

Methods. ^{1}H NMR spectra were obtained on a Bruker Avance 400 instrument at 400 MHz. Gel permeation chromatography (GPC) was performed in tetrahydrofuran (THF) using a Waters system equipped with four 5 μm Waters columns (300 mm × 7.7 mm) connected in series with an increasing pore size (100, 1000, 10^5, and 10^6 Å), a Waters 410 differential refractometer, and a 996 photodiode array detector. The system was calibrated with polystyrene standards. GPC analysis was also performed in dimethylformamide (DMF) spiked with 0.01 M LiBr using a Waters system equipped with two Agilent PolyPore columns (300 mm × 7.5 mm) connected in series, a Waters 410 differential refractometer. The system was calibrated with poly(methyl methacrylate) standards.

General Procedure for Synthesis of Poly(MTC-OC_6F_5). In a nitrogen-purged glovebox, a small vial was charged with 1-pyrenebutanol (0.003 g, 0.01 mmol), MTC-OC_6F_5 (0.357 g, 1.09 mmol), and 1.45 g of dichloromethane (1 M with respect to initial concentration of MTC-OC_6F_5). The solution was stirred until the 1-pyrenebutanol was fully dissolved. The MTC-OC_6F_5 only partially dissolves at this concentration. Trifluoromethanesulfonic acid (triflic acid) (0.008 g, 0.05 mmol) was added to the stirring solution. As the reaction proceeded, the undissolved MTC-OC_6F_5 slowly went into solution. The reaction was monitored by ^{1}H NMR. Once the reaction was complete (~12 h at this catalyst loading and degree of polymerization), the polymer was precipitated into hexanes, isolated, and dried to obtain a white solid (yield: 0.356 g, 98.9%). (If excess triflic acid was added, the polymer turned a slight brown color.) ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.48 (s, CH_2, 4H), 1.51 (s, CH_3, 3H). GPC (RI): M_n (PDI) = 20 500 Da (1.15).

General Procedure for Synthesis of Poly(MTC-OC_6F_5)-*b*-Poly(MTC-OEthyl). In a nitrogen-purged glovebox, a small vial was charged with 1-pyrenebutanol (0.006 g, 0.02 mmol), MTC-OC_6F_5 (0.357 g, 1.09 mmol), and 1.45 g of dichloromethane (1 M with respect to MTC-OC_6F_5). The solution was stirred until the 1-pyrenebutanol was fully dissolved. The MTC-OC_6F_5 only partially dissolves at this concentration. Triflic acid (0.008 g, 0.06 mmol) was added to the stirring solution. As the reaction proceeded, the undissolved MTC-OC_6F_5 slowly went into solution. The reaction was monitored by ^{1}H NMR. Once >95% conversion of MTC-OC_6F_5 was observed, MTC-OEthyl (0.205 g, 1.09 mmol) was dissolved in minimal dichloromethane and added to the polymerization mixture. Once the conversion of MTC-OEthyl to polymer was greater than 90%, the polymer was precipitated into hexanes, isolated, and dried to obtain a white solid (yield: 0.476 g, 84.7%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.48 (s, CH_2 poly(MTC-OC_6F_5), 4H), 4.26 (m, CH_2 poly(MTC-OEthyl), 4H), 4.20 (m, CH_2CH_3 poly(MTC-OEthyl), 2H), 1.51 (s, CH_3, 3H) poly(MTC-OC_6F_5), 1.26 (m, CH_3 poly(MTC-OEthyl), 3H), 1.26 (m, CH_2CH_3 poly(MTC-OEthyl), 3H). GPC (RI): block 1 M_n (PDI) = 8770 Da (1.20); blocks 1 and 2 M_n (PDI) = 12 500 Da (1.24).

Synthesis of PEG-*b*-Poly(MTC-OC_6F_5). In a nitrogen-purged glovebox, a small vial was charged with PEG_{5K}–OH (0.600 g, 0.120 mmol), MTC-OC_6F_5 (0.391 g, 1.20 mmol), and 1.60 g of dichloromethane (1 M with respect to MTC-OC_6F_5). The solution was stirred until the PEG_{5K}-OH was fully dissolved. The MTC-OC_6F_5 only partially dissolves at this concentration. Triflic acid (0.008 g, 0.06 mmol) was added to the stirring solution. As the reaction proceeded, the undissolved MTC-OC_6F_5 slowly went into solution. The reaction was monitored by ^{1}H NMR. Once the reaction was complete, the polymer was precipitated into diethyl ether, isolated, and dried to

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obtain a white solid (yield: 0.616 g, 62.1%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.48 (s, CH_2, 4H), 3.65 (s, CH_2CH_2, 4H), 1.51 (s, CH_3, 3H). GPC (RI): M_n (PDI) = 9520 Da (1.13).

General Procedure for Postpolymerization Modification with Ammonium Acetate. Poly(MTC-OC_6F_5) (50 mg, 0.15 mmol/repeat unit) was dissolved in 0.5 mL of DMF. A small amount (5−10 mg) of ammonium acetate was added to the stirring solution. The reaction mixture was left to react for 20 min. Undissolved ammonium acetate was removed from solution, and the product was precipitated into diethyl ether to yield a white powder (yield: 0.021 g, 84%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.31 (d, NH_2, 2H), 4.17 (s, CH_2CCH_2, 4H), 1.12 (s, CCH_3, 3H).

General Procedure for Postpolymerization Modification with Hexylamine and Benzylamine. Poly(MTC-OC_6F_5) (100 mg, 0.307 mmol/repeat unit) was dissolved in 0.5 mL of THF and cooled in an ice bath. A solution containing hexylamine (0.033 g, 0.32 mmol) and triethylamine (0.033 g, 0.32 mmol) in 0.5 mL of THF was added dropwise. The reaction mixture was allowed to warm to room temperature, and the product was precipitated into diethyl ether to yield a white solid (yield: 0.063 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.20 (s, *NH*, 1H), 4.30 (s, CH_2CCH_2, 4H), 3.27 (q, $NHCH_2$, 2H), 1.51 (t, $NHCH_2CH_2$, 2H), 1.30 (m, CCH_3 and $CH_2CH_2CH_2CH_3$, 3H and 6H), 0.89 (t, CH_2CH_3, 3H). With benzylamine, the reaction mixture gelled during the course of the functionalization. Before precipitation, the reaction mixture was heated until the gel became a free-flowing liquid. This liquid was then pipetted into diethyl ether to precipitate the target polymer as a white solid (yield: 0.067 g, 87%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 8.41 (brs, *NH*, 1H), 7.20, 7.12 (m, C_6H_5, 5H), 4.24 (d, $NHCH_2$, 2H), 4.19 (brs, CH_2CCH_2, 4H), 1.12 (s, CCH_3, 3H).

General Procedure for Postpolymerization Modification with *N*-Ethylmethylamine. Poly(MTC-OC_6F_5) (100 mg, 0.307 mmol/repeat unit) was dissolved in 0.5 mL of THF. A solution containing *N*-ethylmethylamine (0.019 g, 0.32 mmol) and triethylamine (0.033 g, 0.32 mmol) in 0.5 mL of THF was added. The solution turned turbid, and a minimal volume of DMF was added until the solution cleared. The reaction mixture was left to react for 24 h (86% functionalization *N*-ethylmethylamine was achieved, while the remaining pentafluorophenol esters hydrolyzed). For a sample ^{1}H NMR spectra, see Figure S4.

Alternative protocol: poly(MTC-OC_6F_5) (30 mg, 0.092 mmol/repeat unit) was dissolved in 0.5 mL of DMF, and *N*-ethylmethylamine (0.022 g, 0.37 mmol) was added. The solution turned turbid, and additional DMF (0.25 mL) was added until the solution cleared. The reaction mixture was left to react for 3 h (95% functionalization *N*-ethylmethylamine was achieved, while the remaining pentafluorophenol esters hydrolyzed). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 4.25 (dd, CH_2CCH_2, 4H), 3.33 (s, $NHCH_2$, 2H), 2.93 (s, $NHCH_3$, 3H), 1.23 (s, CCH_3, 3H), 0.99 (s, $NHCH_2CH_3$, 3H).

General Procedure for Postpolymerization Modification with PEG-NH_2. Poly(MTC-OC_6F_5) (30 mg, 0.092 mmol/repeat unit) was dissolved in 0.5 mL of THF. A solution containing PEG-NH_2 (CH_3O-$(CH_2CH_2O)_{45}$-$CH_2CH_2CH_2NH_2$, 0.193 g, 0.0966 mmol) and triethylamine (0.0095 g, 0.097 mmol) in 0.5 mL of THF was added dropwise. The solution was stirred at room temperature for 24 h. The product was precipitated twice into diethyl ether to yield a white solid (yield: 0.128 g, 65.0%). ^{1}H NMR ($CDCl_3$, 400 MHz): see Figure 4.

General Procedure for Kinetic Study of Postpolymerization Modification with PEG-NH_2. Poly(MTC-OC_6F_5) (10 mg, 0.031 mmol/repeat unit) was dissolved in 0.4 mL of $CDCl_3$. A solution containing PEG-NH_2 (CH_3O-$(CH_2CH_2O)_{45}$-$CH_2CH_2CH_2NH_2$, 0.064 g, 0.032 mmol) and triethylamine (0.009 g, 0.03 mmol) in 0.4 mL of $CDCl_3$ was added dropwise. ^{1}H NMR was taken at various time points over a 24 h period.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional ^{1}H NMR and GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: acengler@us.ibm.com (A.C.E.); hedrick@us.ibm.com (J.L.H.).

Notes

The authors declare no competing financial interest.

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