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Dihydroxy Capped Triblock DTC and CL Oligomers Prepared by an Alkyl Glycol/Yttrium Phenolate System

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Abstract: Dihydroxy capped triblock oligomers of 2, 2-dimethyltrimethylene carbonate (DTC) and ε-caprolactone (CL) with number-average molecular weight from 3,000 to 12,000 g/mol have been synthesized by alkyl glycol initiator in the presence of yttrium tri(2, 6-di-*tert*-butyl-4-methylphenolate)s ($Y(OAr)_3$) catalyst. They are expected to be used as macroinitiators for the design of new polymeric materials.

Keywords: Rare earth catalyst, block oligomer, 2, 2-dimethyltrimethylene carbonate, ε-capro lactone.

Some catalysts containing poly(ethylene glycol) (PEG) for block copolymerization of DTC, CL or lactide have been reported[1-5]. This paper describes the preparation of triblock oligomers of DTC or CL with two OH end groups by a catalytic system composed of alkyl glycol and $Y(OAr)_3$.

DTC and $Y(OAr)_3$ were prepared as reported[4] while CL and PEG were commercial products. All polymerizations were carried out in previously flamed and argon purged ampoules with Schlenk techniques. As a typical example, PEG400 ($M_n \approx 400$ g/mol) and $Y(OAr)_3$ were dissolved in tetrahydrofuran (THF) and aged for 15 min at 40 ºC. Then the THF solution of DTC monomer was added. The product was washed by dilute HCl aqueous solution, precipitated in *n*-hexane and dried under vacuum.

Table 1 summarizes the polymerizations of DTC and CL with PEG, ethylene glycol (EG) or neopentyl glycol (NG) initiators in the presence of $Y(OAr)_3$. The system exhibits high activity toward the ring-opening polymerizations of DTC or CL. Oligomers obtained have monomodal GPC curves as shown in **Figure 1**. The number average of molecular weights (M_n) of DTC triblock oligomers poly(DTC-*b*-PEG -*b*-DTC)s decrease with the lowering molar ratio of [DTC]/[PEG] (run 1-4 in **Table 1**) retaining narrow MWD (M_w/M_n = 1.3-1.8).

The active species of $-CH_2O-Y<$were generated by a reversible reactions of PEG400 and $Y(OAr)_3$, which initiated the ring opening polymerization of DTC monomers, as shown in **Scheme 1**. The rapid reversible reaction between $-CH_2O-H$ and $-CH_2O-Y<$ controlled the propagations of the oligomers with different chain lengths.

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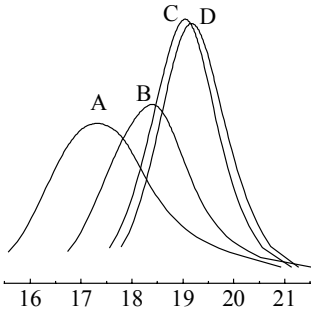
Thus, alkyl glycols acted as molecular weight modifiers and yttrium phenolate as a catalyst.

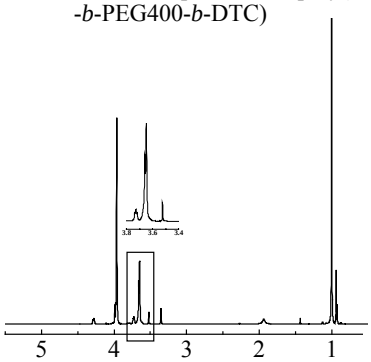
The structure of triblock DTC oligomer (run 4 in **Table 1**) has been characterized by ^{1}H NMR (**Figure 2**) recorded on a Bruker Avance DMX500 spectrometer. The triplet signal at 4.3 ppm contributed by the direct link unit of [PEG]OCH$_2$C*H*$_2$OCO[DTC] and no triplet signal at about 3.6 ppm for –CH$_2$CH$_2$– in the –OH ending unit of PEG400 indicate that the product has an ABA block structure. Moreover, the end group of DTC block gives single peak at 3.5 ppm (–C(CH$_3$)$_2$C*H*$_2$OH) caused by the reaction of–CH$_2$O–Y< with HCl. The obtained dihydroxy end oligomers can be further used as macroinitiator to develop multiblock copolymers.

Figure 1 GPC curves of poly(DTC-*b*-PEG400-*b*-DTC)s



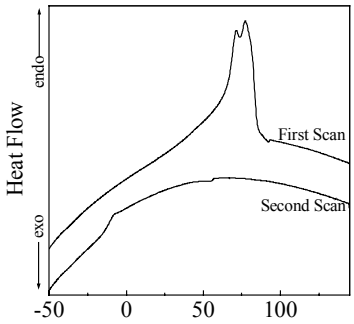
A, B, C, D: run 1, 2, 3, 4 in **Table 1**, respectively.

Figure 2 ^{1}H NMR spectrum of poly(DTC-*b*-PEG400-*b*-DTC)



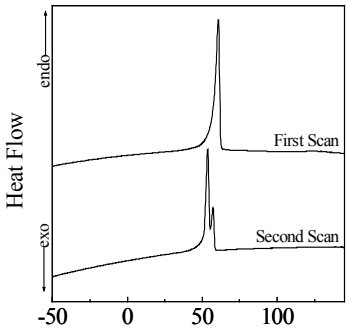
Run 4 in **Table 1**.

Figure 3 DSC curves of poly(DTC-*b*-PEG400-*b*-DTC)



Run 2 in **Table 1**.

Figure 4 DSC curves of poly(CL-*b*-PEG200-*b*-CL)



Run 6 in **Table 1**.

Scheme 1 Mechanism of propagation with alkyl glycol/$Y(OAr)_3$ catalyst, HOROH = PEG400

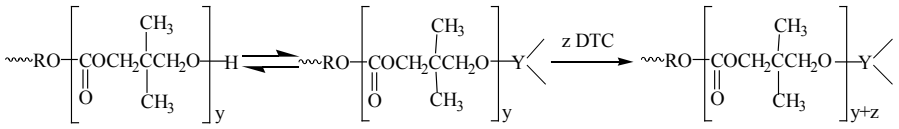


Table 1 Polymerizations initiated by alkyl glycol and $Y(OAr)_3$

Run	Monomer	Initiator	$\frac{[Monomer]}{[Y(OAr)_3]}$ [a]	$\frac{[Monomer]}{[glycol]}$ [a]	Conv. (%)	M_n [b]$\times10^{-3}$ ($g\cdot mol^{-1}$)	MWD [b]
1 [c]	DTC	PEG400	100	50	84	13	1.8
2 [c]	DTC	PEG400	100	30	74	7.7	1.5
3 [c]	DTC	PEG400	100	22	77	5.3	1.3
4 [c]	DTC	PEG400	100	17	73	4.6	1.3
5 [d]	CL	PEG400	150	46	95	12	1.7
6 [d]	CL	PEG200	150	32	97	10	1.5
7 [c]	CL	EG	100	26	99	4.6	1.8
8 [c]	CL	NG	100	12	99	3.1	1.5

[a] Molar ratio. [b] GPC measurement, carried out on a Waters 208 apparatus in THF (1.5 mL/min) calibrated with polystyrene standard. [c] 20 min, 40 ºC in THF. [d] 10 min, 40 ºC in toluene.

Thermal behaviors of the samples, as shown in **Figure 3** and **Figure 4**, were recorded on a Perkin Elmer Pyris 1 DSC instrument by the second heating scan (10 ºC/min, -50 to 150 ºC) with thermal history eliminated. Homopolymers of DTC exhibit two melting peaks at about 80-90 ºC and 115-125 ºC in the first heating scan, while the former always disappears in the second heating scan[4,6]. Poly(DTC-*b*-PEG-*b*-DTC) shows one T_g of -11 ºC and no T_m. Poly(CL-*b*-PEG-*b*-CL) gives two T_ms at 54 ºC and 57 ºC.

Acknowledgments

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