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Notes

Convenient Depolymerization Route to Telechelic Polycarbonate Oligomers

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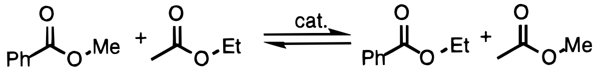
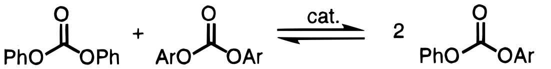
The development of methods for synthesizing telechelic polymers is an important area of research,[1] as these materials have useful properties and serve as foundations for the synthesis of block copolymers. Despite the industrial importance of Bisphenol A polycarbonate (PC), few PC telechelics are known.[2,3] Two general methods exist for the synthesis of telechelic polycondensates: (1) stoichiometric imbalance of difunctional monomers during polymerization, including the addition of monofunctional monomers, and (2) the depolymerization of polymers using reactive small molecules (e.g., glycolysis).[4,5] The former method has successfully yielded the known telechelic PCs; however, to the best of our knowledge, no telechelic PCs have been reported using the latter method.

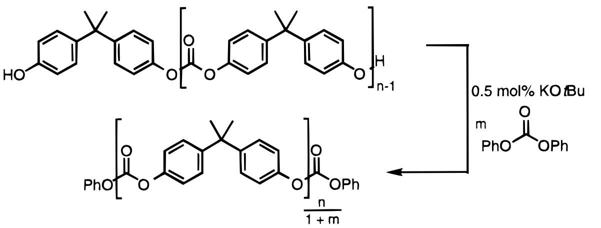


(1)



(2)

We recently reported that alkali-metal alkoxide clusters catalyze the ester interchange reaction under mild conditions and at high rates (up to 10^6 turnovers/h) (eq 1).[6] A demonstration of the successful extension to the carbonate interchange reaction (eq 2) has led to the depolymerization of PC in the presence of diaryl carbonates (DAC) (eq 3). Equilibrium incorporation of a DAC into a PC chain effectively reduces the average MW and moreover ensures that the majority of end groups are DAC-derived. This publication describes a convenient synthesis of telechelic PCs utilizing functionalized DACs.



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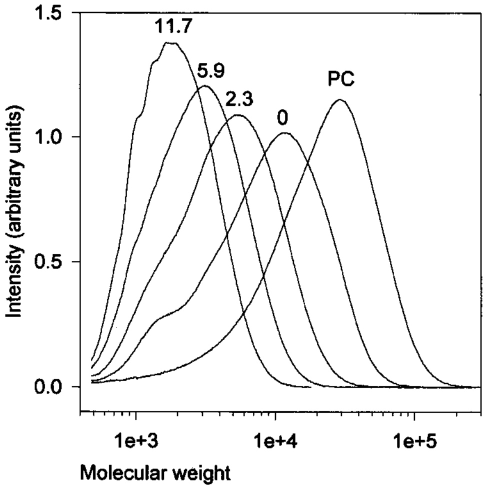

Figure 1. GPC curves of depolymerized commercial PC (M_n = 13 000, PDI = 2.3), using 0.5 mol % KO^tBu in the presence of variable quantities of diphenyl carbonate. Reactions were quenched after 240 min at room temperature in THF, and the polymers were precipitated into MeOH and dried in vacuo. PC refers to the starting polymer.

The reaction of commercial hydroxy-terminated PC[7] with 0−11.7 equiv of diphenyl carbonate per average chain and catalyst[8] in THF results in a controlled breakdown of the polymer's molecular weight as assayed by GPC, Figure 1 (Table 1, entries 2−7).[9] Initial breakdown is rapid, as early quenches (2−4 min) yield molecular weights near the final value. Longer reaction times and precipitation from MeOH further narrows the MW distribution to the GPC traces shown in Figure 1. The increased solubility of the low MW telechelics result in fractionation and reduced yields of the oligomers (entries 2−7).[10] Despite the fractionation, the trend of reduced PDI with increasing DAC remains true as unfractionated samples behaved similarly. The final MW of the telechelic is controlled by the initial ratio of diphenyl carbonate to PC and the degree of polymerization (DP) of the starting polymer.[7,11] Experiments with no or less than 2 equiv of DAC added (entries 2 and 3) lead to polymers whose measured DPs are significantly lower than the theoretical DPs calculated by introducing the catalyst as an end group (0.25 equiv per average polymer chain). However, with greater than 2 equiv of DAC, good agreement is observed between measured and calculated DPs.[12] At this point we do not have a satisfying explanation for this observation.

End groups present in the commercial PC used in this study reduce the degree of functionality in the telechelic oligomers to less than the ideal value of 2.0 (eq 3 explicitly ignores this effect). We calculate that oligomers synthesized using 11.7 equiv of DAC per average chain length have an average degree of functionality of ∼1.82. Ring-opening techniques[13] or use of PC of even higher MW should push the functionality number of the oligomers closer to the more desirable value of 2.0.

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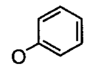
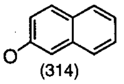
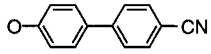
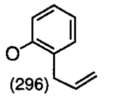
Table 1. GPC and DSC Data for Functionalized Polycarbonates[a]

Entry	DAC $(ArO)_2CO$ *(molecular weight)*	DAC *equiv.*	Mn *(uncorrected)*	Mn *(corrected)*	%Yield[b]	PDI	DP *(exptl.)*	DP *(theor.)*	Tg *°C*
1	Starting Material	-	23000	13000	-	2.3	50	-	149
2	OAr=  (214)	0	9100	5000	91(7)	2.4	19	40	140
3		0.6	8100	4500	90(8)	2.4	17	27	140
4		2.3	6100	3400	87(8)	2.0	13	14	126
5		4.1	4500	2500	83(14)	1.8	9.0	9.4	120
6		5.9	4000	2200	79(23)	1.6	7.8	7.0	113
7		11.7	2900	1600	67(10)	1.4	5.5	3.9	98
8	 (314)	5.9	3700	2000	81(16)	1.6	6.6	7	114
9	 (436)	11.7	3100	1700	67(32)	1.4	5.0	3.9	120
10	 (296)	5.9	4400	2400 (2200)[c]	81(15)	1.6	8.3 7.5	7.0 7.0	108

[a] See Experimental Section for reactions conditions; entry 9 was reacted at 60 °C. [b] Yields represent isolated solid from MeOH precipitation, the number in parentheses represents material recovered from the filtrate. [c] By end-group analysis (^{1}H NMR), not corrected for degree of functionality.

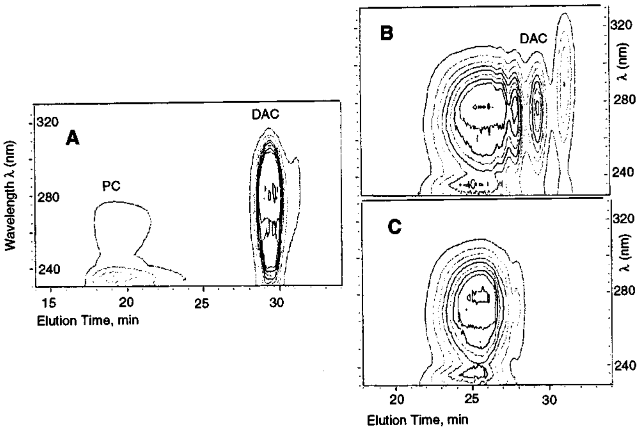


Figure 2. 2-D GPC/UV/vis of PC depolymerized with 11.7 equiv of CNBiPh at 0 (A), 4 (B), and 240 (C) min (after precipitation from MeOH).

Like diphenyl carbonate, alternative DACs were well-behaved and gave rapid reactions that yielded the expected telechelic materials, Table 1.[14] In addition to GPC characterization, the DP of the polymer in entry 10 was determined to be 7.5 by ^{1}H NMR, in good agreement with expectations. Thermal characterization (DSC) confirmed that the glass transition temperature (T_g) was sensitive to both the MW of the oligomer and the identity of the end group.

The cyanobiphenyl functionality (entry 9) has a unique UV absorbance that makes it a useful end group-specific spectroscopic probe.[2a] A 2-dimensional contour plot of the GPC/UV/vis spectrum of a mixture of dicyanobiphenyl carbonate (CNBiPh) and PC prior to the addition of catalyst is shown in Figure 2A. The lack of PC tailing to wavelengths greater than 290 nm is readily apparent while the DAC absorbs strongly to 320 nm. After 4 min at room temperature (Figure 2B), the retention time increases and the polymer absorbs to longer wavelengths. The fine structure reveals low molecular weight oligomers and DAC. After 4 h (Figure 2C), the precipitated polymer shows a uniform absorbance profile which tails to 320 nm, indicating a homogeneous distribution of cyanobiphenyl end groups.[10]

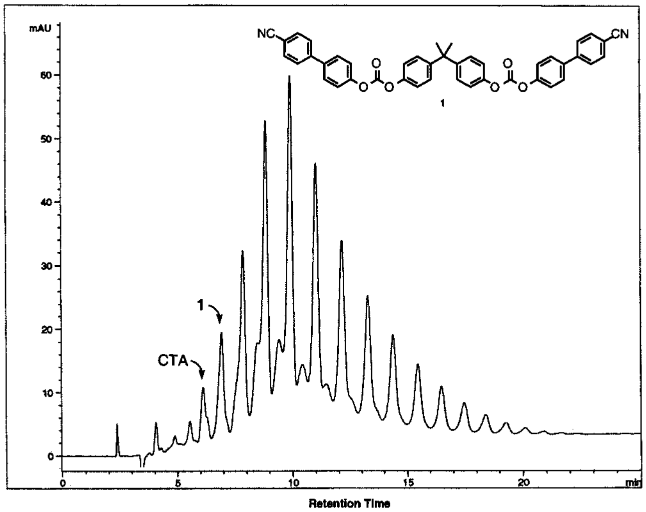


Figure 3. HPLC trace of precipitated cyanobiphenyl terminated PC obtained using 11.7 equiv of DAC and 0.5 mol % of KO^{t}Bu. The trace was recorded at 300 nm.

The distribution of DAC end groups within the polymer chains was also conveniently monitored by HPLC (Figure 3) as the majority of the oligomers could be cleanly separated. The pattern and relative intensity of peaks in the chromatograms obtained at 300 and 254 nm were superimposable, confirming the uniform distribution of end groups in each oligomer chain and the absence of cyclics.[13] To facilitate the assignment of the absorbances in the HPLC trace, **1**, the smallest PC telechelic, and CNBiPh were spiked into the oligomer solutions. Although crude, counting the major peaks to maximum gives DP = 4, close to expected for this experiment, entry 9, Table 1.

In summary, we report our preliminary observations on the utilization of a "new" catalyst for the aromatic carbonate interchange reaction which depolymerizes PC in the presence of DACs.[15] The depolymerization methodology gives good MW control and is kinetically well-behaved as judged by the uniform distribution of end groups and low polydispersities.

Experimental Section

Materials. Poly(Bisphenol A carbonate) was purchased from Aldrich (Catalog no. 18,162-5), dissolved in unstabilized THF (10 wt/v), filtered, and precipitated into an 8-fold excess of MeOH. The precipitate was filtered and dried for 24 h at room temperature and for 2 h at 120 °C under high vacuum (10 mTorr). ^{1}H NMR confirmed the absence of any solvent. THF was distilled from purple Na/benzophenone under argon prior to use. KO^{t}Bu (Aldrich, 95%) was sublimed, and stored under nitrogen in a drybox. Diphenyl carbonate (Aldrich, 99%) was recrystallized from hexanes/MeOH (10/1 v/v), 2-naphthol (Aldrich, 99%) was used as received, and 2-allylphenol (Aldrich, 98%) was distilled prior to use. 4′-Hydroxy-4-biphenylcarbonitrile (Aldrich, 97%) was purified by flash chromatography, using silica gel (E. Merck Science, Silica Gel 60 Geduran) and ether/pentane (1/3 v/v) as eluent. Pentane was passed through an alumina column before being used.[16] Triphosgene (Aldrich, 98%) was used as received. Triethylamine was freshly distilled from CaH_2 under nitrogen prior to use. *p*-Toluenesulfonic acid monohydrate (Aldrich, 98.5+%), 4-(dimethylamino)pyridine (DMAP) (Aldrich, 99%) and Bisphenol A bis(chloroformate) (Aldrich, 96%) were used as received.

General Procedure for Depolymerizing PC. A 550 mg (0.037 mmol) sample of PC, DAC, and a stir bar were added to a 25 mL predried flask, capped with a rubber septum, and purged with argon for 5−10 min. After 10 mL of THF was added via syringe, the solution was stirred under argon until all the material had dissolved (10−30 min). A 1.3-fold excess of catalyst was weighed in a 4 mL vial in the drybox, which was capped with a rubber septum and transferred out, and 2.5 mL of THF was added via syringe. Of this solution, an aliquot of 1.2 mg (0.01 mmol) of KO^{t}Bu was syringed into the polymer/DAC solution to initiate the depolymerization reaction. In the case of CNBiPh, 225 mg (0.018 mmol) of PC and 0.6 mg (0.005 mmol) of KO^{t}Bu were used, and the reaction was run at 60 °C to ensure a homogeneous solution. All other reactions were run at room temperature. With higher loadings of DAC successful MW breakdown was immediately observable as the PC solution became less viscous upon catalyst addition. After 4 h the polymer solution was pipetted into 80 mL of stirring MeOH. The precipitate was filtered and dried at room temperature for 24 h in vacuo (10 mTorr). The solvents were removed from the filtrate, and the residue was dried in the same way.

Characterization. GPC. Molecular weight distribution was determined by GPC in THF at 35 °C on a Waters 150-CV GPC in THF against PS standards. The column set used were based on Styragel HR columns (Waters Corp.) with pore sizes of 10^4, 10^3, 500, and 100 Å. Corrections for the MW of PC utilized the universal calibration method, using the following values: $K_{PS} = 0.013$, $K_{PC} = 0.039$, $\alpha_{PS} = 0.71$, and $\alpha_{PC} = 0.70$.[17]

HPLC. Chromatograms were obtained on a Hewlett-Packard 1100 instrument using a cyano-terminated silica gel column (LiChrosphere 100CN) (250 × 4 mm, 5 μm pore size, 100 μm particle size). Polymer samples were run at 1 mL/min in THF/hexanes (30/70 v/v) with a gradient elution of 0.5% THF/min to 45% THF. A UV diode array detector was used for analysis.

DSC. Thermal properties of polymers were determined on a Seiko SSC/5200 DSC 220C, calibrated with In. The heating/cooling rates were 20 °C /min. The second heating was selected for calculating T_g.

NMR. ^{1}H NMR were recorded at either 200 or 300 MHz; ^{13}C NMR spectra were recorded at either 50 or 75 MHz. For end group analysis of 2-allylphenyl-terminated PC (entry 8, Table 1) a delay time of 10 s was selected.

Melting points are uncorrected and were measured on a Thomas-Hoover capillary melting point apparatus. The mp for CNBiPh was measured by DSC (heating rates 20 °C/min) and for compound **1**, on a microscope equipped with a Linkam heating stage.

Synthesis of DAC. Two general routes to synthesizing DACs were chosen: (a) melt−transesterification of the aryl acetate with diphenyl carbonate with 1−2 mol % of KO^{t}Bu at 120 °C under vacuum (removal of phenylacetate) for 10−30 min or (b) use of triphosgene.[18] *Caution*! always wear personal protective equipment! Although triphosgene is a solid (mp = 86 °C), it rapidly reacts with protic compounds and should only be handled in a hood and weighed in closed containers.

2-Naphthyl Acetate. To 28.8 g (0.2 mol) of 2-naphthol dissolved in 70 mL acetic anhydride was added a catalytic amount of *p*-toluenesulfonic acid and the solution refluxed under Ar for 2 h. After the reaction mixture was cooled to room temperature, it was poured into water to precipitate the desired product. The crude product was recrystallized three times from ethanol/water (3/1) affording 11.4 g (30%) of white crystals; mp = 68 °C (lit. 70 °C).[19] ^{1}H NMR and ^{13}C NMR spectra match the reported data.[20]

Di-2-naphthyl Carbonate. A 1.85 g (0.01 mol) sample of 2-naphthyl acetate, 1.07 g (0.01 mol) of diphenyl carbonate, and 11.4 mg (0.1 mmol) of KO^{t}Bu were added to a Schlenk flask with a transfer arm attached to a second Schlenk flask, cooled with liquid nitrogen. The mixture was then heated to 120 °C for 10 min while vacuum was applied through the empty Schlenk flask to remove the phenyl acetate. The resulting solids were dissolved in ethyl acetate, filtered through silica, and recrystallized three times from ethyl acetate, yielding 0.65 g (41%) of white platelets; mp = 175−6 °C (lit. 178 °C).[21] ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 8H), 7.45 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 152.4, 148.6, 133.6, 131.6, 129.7, 127.8, 126.8, 126.1, 120.2, 118.1.

Di-4-carbonitrile-4′-biphenyl Carbonate (CNBiPh). To 1.17 g (6.0 mmol) of purified 4′-hydroxy-4-biphenylcarbonitrile dissolved in 20 mL of THF under Ar was added 0.9 mL (6.6 mmol) of triethylamine. A solution of triphosgene (320 mg, 1.1 mmol) in 5 mL of THF was added dropwise by addition funnel to the precooled (−10 °C) phenolic solution over 15 min. To compensate for salt precipitation an additional 20 mL of THF was added after 30 min. The reaction was allowed to come to room temperature overnight, and, after a total of 24 h, it was precipitated into water and the THF allowed to evaporate. The crude material was filtered, washed with water, and dried (1.08 g). Two recrystallizations from dioxane/ethanol (2.5/1) afforded 980 mg (75%) of only slightly soluble white crystals; mp = 229 °C. ^{1}H NMR (DMSO-d_6): δ 7.9 (m, 11H), 7.54 (d, J = 8.6 Hz, 5H). ^{13}C NMR (DMSO-d_6): δ 151.0, 143, 136, 132.8, 128.5, 127.6, 121.9, 110.2.

Di-4-carbonitrile-4′-biphenyl Carbonate of Bisphenol A (1). 640 mg (3.3 mmol) of 4′-hydroxy-4-biphenylcarbonitrile was dissolved in 3.2 mL of 1 N NaOH and stirred for 4 h at room temperature under Ar followed by addition of 5 mL of MeOH and overnight stirring. All solvents were removed, and the crude product was suspended in 20 mL of dry ether. To this slurry was slowly added 520 mg (1.6 mmol) of Bisphenol A bis(chloroformate) in 20 mL of dry ether. After 3 h water was added and the product extracted into ethyl acetate. Drying the organic phase over $MgSO_4$, filtering, and removing the solvent in vacuo yielded 1.03 g of crude product. TLC on silica (ether/petroleum ether 1/1 v/v) revealed some starting material. The crude product was resubjected to acylating conditions over 12 h (20 mL of THF, 0.37 mL (2.66 mmol) of triethylamine, catalytic DMAP, and another 420 mg of Bisphenol A bis(chloroformate)). Extracting into ethyl acetate, drying over $MgSO_4$, filtering through a silica plug, and solvent removal yielded 1.27 g of crude material. Several recrystallizations from dioxane/ethanol (1/10 v/v) yielded 73 mg (7%) of white crystalline product; mp = 184 °C. ^{1}H NMR ($CDCl_3$): δ 7.6 (m, 12H), 7.33 (m, 4H), 7.16 (m, 8H), 1.63 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 152.0, 151.3, 148.9, 148.5, 144.5, 137.3, 132.7, 128.5, 128.0, 127.7, 121.7, 120.3, 118.8, 111.2, 42.6, 30.9.

Di-2-Allylphenyl Carbonate. A 1.20 g (9.0 mmol) sample of freshly distilled 2-allylphenol was dissolved in 20 mL of THF and 1.25 mL of triethylamine under Ar. A solution of 450 mg (1.55 mmol) of triphosgene in 5 mL of THF was added via addition funnel to a precooled (−10 °C) stirring solution of the phenol over 5 min. After 1 h, the reaction was filtered and the solvent removed in vacuo. The yellow oil (1.27 g) was dissolved in 35 mL of diethyl ether and washed with water (25 mL), a 5% $NaHCO_3$ solution (3 × 20 mL), and water (2 × 20 mL), dried over $MgSO_4$, and filtered, and the solvent was removed to yield 1.12 g (84%) of a clear liquid. ^{1}H NMR ($CDCl_3$): δ 7.25 (m, 8H), 5.97 (m, 2H), 5.15 (m, 4H), 3.45 (d, J = 6.3 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 151.9, 149.2, 135.7, 131.8, 130.6, 127.6, 126.7, 121.8, 116.6, 34.4.

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References and Notes

(1) For general references on telechelic polymers see: (a) *Telechelic Polymers: Synthesis and Applications*; Goethals, E. J., Ed., CRC Press: Boca Raton, FL, 1989. (b) Percec, V.; Pugh, C.; Nuyken, O.; Pask, S. D. In *Macromonomers, Oligomers, and Telechelic Polymers. Comprehensive Polymer Science*; Eastmon, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds., Pergamon Press: New York, 1989, Vol. 6, pp 282−357.

(2) For examples of hydroxy terminated PC see: (a) Mork, C. O.; Priddy, D. B. *J. Appl. Polym. Sci.* **1992**, *45*, 2289−2301. (b) Riffle, J. S.; Shchori, E.; Banthia, A. K.; Freelin, R. G.; Ward, T. C.; McGrath, J. E. *J. Polym. Sci., Polym. Chem. Div.* **1982**, *20*, 2289−2301.

(3) For examples of non-hydroxy-terminated telechelic PC's see: (a) Marks, M. J.; Scott, D. C.; Guilbeaux, B. R.; Bales, S. E. *J. Polym. Sci., Polym. Chem. Div.* **1987**, *35*, 385−390. (b) Marks, M. J.; Sekinger, J. K. *Macromolecules* **1994**, *27*, 4106−4113. (c) Degree, P.; Jérôme, R.; Teyssie, P. *Polymer* **1994**, *35*, 371−376.

(4) Papaspyrides, C. D.; Poulakis, J. D. Regarding Plastics. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL 1996; Vol. 10, pp 7403−7419.

(5) (a) Marmo, J. C.; Wagener, K. B. *Macromolecules* **1993**, *26*, 2137−2138. (b) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 718−721.

(6) (a) Stanton, M. G.; Gagné, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 5075−5076. (b) Stanton, M. G.; Gagné, M. R. *J. Org. Chem.* **1997**, *62*, 8240−8242.

(7) By universal calibration, we calculate that M_n = 13 000, corresponding to a DP of 50 (see Experimental Section). Ratios of DAC/polymer and theoretical DPs were calculated using this DP.

(8) On the basis of a polymer DP of 50, we utilize 0.51 mol % KO^{t}Bu per carbonate repeating unit; this corresponds to 0.25 equiv of KO^{t}Bu per average chain.

(9) In the absence of catalyst no breakdown in molecular weight occurs.

(10) In the case of entry 9, HPLC analysis of the MeOH filtrate indicates the presence of DAC, **1** (major), and several higher oligomers.

(11) *Principles of Polymerization*, 3rd ed.; Odian G., Ed.; John Wiley & Sons: New York, 1991; p 87.

(12) At high DAC loadings, poorer agreement are observed (e.g., entries 7 and 9); however, we feel that this is due to poor GPC performance in this MW regime.

(13) Brunelle, D. J.; Boden, E. P.; Shannon, T. G. *J. Am. Chem. Soc.* **1990**, *112*, 2399−2402.

(14) All attempts to characterize the oligomers by electrospray mass spectrometry have been unsuccessful. We are currently synthesizing telechelic PCs with cation coordinating endgroups to facilitate their detection.

(15) A proof-of-principle demonstration of the application of this methodology for PC recycling was achieved by depolymerizing a pair of lab safety glasses with 11.7 equiv of diphenyl carbonate and 0.5 mol % of KO^{t}Bu in THF. The presence of a UV stabilizer (of unknown structure) in the PC lens (M_n = 13 000) did not affect the depolymerization as analyzed by GPC and HPLC. This material was qualitatively similar to the polymer generated from commercial PC, demonstrating the feasibility of recycling PC into telechelic polymers.

(16) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−20.

(17) Kurata, M. and Tsunashima, Y. *Viscosity-Molecular Weight Relationships and Unperturbed Dimensions of Linear Chain Molecules, in Polymer Handbook*, 3rd ed.; Brandrup, J., and Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; Chapter VII, pp 1−60.

(18) Eckert, H.; Forster, B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 894−895.

(19) Hodgson, H. M.; Foster; C. K. *J. Chem. Soc.* **1942**, 747−748.

(20) Pal, A.; Pal, T. *Indian J. Chem., B.* **1996**, *35B*, 157−160.

(21) Einhorn, A.; Hollandt, F. *Justus Liebigs Ann. Chem.* **1898**, *301*, 95−115.

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