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Synthesis and Microstructural Characterization of Ethylene Carbonate−ε-Caprolactone/L-Lactide Copolymers Using One- and Two-Dimensional NMR Spectroscopy

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ABSTRACT: Copolymers containing ethylene carbonate (EC) and ε-caprolactone (CL)/L-lactide (LA) units of different compositions were synthesized by the ring-opening polymerization method using the SmI_2/Sm initiator system. EC was non-homopolymerizable using the same initiator. A maximum of 19 mol % EC was incorporated into the polycaprolactone backbone. The microstructure of these copolymers was analyzed by one- and two-dimensional NMR spectroscopies. The triad sequence distribution centered at CL has been obtained from ^{13}C NMR spectroscopy. 2D $^1H-^{13}C$ HMQC (heteronuclear multiple-quantum correlation) and HMBC (heteronuclear multiple-bond correlation) spectra were used to confirm the existence of EC as isolated units and CL/LA in the blocks. The complete and correct assignment of peaks in the ^{13}C NMR spectrum of previously reported EC−CL copolymers is also done on the basis of $^1H-^{13}C$ HMQC and HMBC spectroscopic techniques.

Introduction

Aliphatic polyesters, such as poly(ε-caprolactone) (PCL), poly(lactide) (PLA), and aliphatic polycarbonates are important as biodegradable and biocompatible materials in the fields of medicine, pharmacy, and agriculture. The recent research focus is on the ring-opening polymerization (ROP) method for their synthesis using metal catalysts, especially lanthanide catalysts.[1−12] Poly(ethylene carbonate) (PEC) is one of the polymers which undergoes rapid enzyme-mediated bioabsorption in vivo.[13,14] This property is highly useful for controlled release of drugs. However, PEC has attracted little attention in the past due to difficulty in the preparation of high molecular weight PECs under nontrivial reaction conditions and difficult processability due to its thermoelasticity.[15] Since the first report of Inoue et al.,[16] the copolymerization of ethylene oxide and carbon dioxide remained as the only method that was suitable for the preparation of high molecular weight PECs[17] as ROP of ethylene carbonate (EC) was not successful due to a positive enthalpy of polymerization. On the other hand, polyesters such as CL and PLA have vast commercial medical and pharmaceutical applications as homopolymers or copolymers.[18] Generally, copolymerization of aliphatic polyesters is carried out for modifying their physical properties and for tuning the degradability behavior. For example, PLA has a rigid macromolecular structure and has been copolymerized with various monomers to produce copolyesters, copoly(ester ether)s, and copoly(ester amide)s for increasing its flexibility.[19−21] A long methylene chain promotes biodegradability by imparting flexibility to the polymer, but at the same time will have poor mechanical properties. Therefore, copolymers of EC with L-lactide (LA) and CL could be of interest as biomaterials with improved properties over those of PLA and PCL. Although the copolymerization behavior of CL with γ-butyrolactone (BL), β-butyrolactone, valerolactone (VL), glycolide, and LA are available,[22−26] only a few reports regarding its copolymerization with EC are available.[27] The knowledge of the microstructure is essential to understand the macroscopic characterization of the polymers. The majority of these research groups have utilized only 1D (^1H and ^{13}C) NMR spectroscopy for microstructural characterization and sequence distribution for CL- and PLA-based copolymers.[22−27] Wakatsuki et al.[2] have used 2D NMR techniques for microstructure determination of CL−BL copolymers.

Previously we have reported the enhanced reactivity of the SmI_2/Sm system for polymerization of caprolactone and L-lactide.[28] EC was not polymerizable by the same system. Polymerization of CL using SmI_2 is reported only at reflux with very low yield and multimodal GPC curves by Evans et al.[29] The same authors have also reported the non-homopolymerizability of EC using SmI_2 and the formation of CL−EC copolymers in THF only at reflux with an EC content of about 5−6 mol %.[27a] Yasuda et al. have used $(C_5Me_5)_2SmMe(THF)$ initiator for copolymerization of EC and CL and showed the resulting copolymers to be random in structure using the ^1H NMR technique.[27b] Copolymers of LA and EC are not reported in the literature.

In this paper we report the enhanced reactivity of SmI_2/Sm for the synthesis of copolymers of EC at room temperature and at 50 °C with CL and LA, respectively. The complete structural assignment of the copolymers using one- and two-dimensional NMR spectroscopies such as ^1H, ^{13}C, ^{13}C DEPT (distortionless enhancement by polarization transfer), $^1H-^{13}C$ HMQC (heteronuclear multiple-quantum correlation), $^1H-^{13}C$ HMBC (heteronuclear multiple-bond correlation), and COSY techniques is also given. Reassignment of the reported[27a] EC peaks in the ^{13}C NMR spectrum is mentioned on the basis of the two-dimensional $^1H-^{13}C$ HMQC and HMBC spectra.

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Table 1. SmI_2/Sm-Based Copolymerizations of EC with CL/LA at Room Temperature (20 °C) ([SmI_2]:[CL] = 1:44; [SmI_2]:[LA] = 1:35)

run	EC:CL/LA (molar ratio)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n	polymer composition EC content (%)[a]
1	00:100	98	3.79	1.67	0.0
2	25:75	85	2.80	1.60	09.0
3	40:60	65	2.60	1.52	14.7
4	56:44	41	2.51	1.30	19.0
5[b]	14:86	67	1.24	1.50	02.5
6[b]	44:66	60	1.14	1.57	03.0
7[b]	62:38	42	1.08	1.58	04.2

[a] Calculated from ^1H NMR. [b] LA is the comonomer, and the polymerization temperature is 50 °C.

Experimental Section

Materials and Instrumentation. THF was purified by distillation over potassium under nitrogen. CL (Aldrich) was dried over CaH_2 for 2 days, distilled under reduced pressure, and degassed by the freeze−thaw method (two times). LA (Aldrich) was recrystallized from dried ethyl acetate. SmI_2 was prepared as a 0.1 M solution in THF by reacting 10 mmol of Sm (Aldrich, 40 mesh) with 5 mmol of diiodoethane.[30] The molecular weight of the polymers were determined by GPC using the Knauer system equipped with two columns of PSS−SDV (linear, 10 μL, 60 • 0.8), a differential refractive index detector, and a UV photometer using THF as eluent at a flow rate of 0.83 mL/min.

^1H (400.13 MHz), ^{13}C (100.21 MHz), ^{13}C DEPT, and COSY NMR spectra were recorded on a Bruker DRX-400 spectrometer. Neat $CDCl_3$ was used, and ^1H and ^{13}C were referenced to residual solvent signals. $^1H-^{13}C$ correlation experiments were performed on a Bruker DRX-500 spectrometer, with a 5 mm multinuclear gradient probe and using gs-HMQC[31] and gs-HMBC[32] pulse sequences. The HMQC experiment was optimized for C−H coupling of 140 Hz, with decoupling applied during acquisition, while the HMBC experiment was optimized for coupling of 8 Hz, without decoupling during acquisition. 2D NMR data were acquired with 2048 points in t_2, the number of increments for t_1 was 256.4, eight scans were used for HMQC and HMBC experiments, respectively, and four dummy scans were used for both the experiments. A relaxation delay of 1 s was used for all 1D experiments and 2 s for all 2D experiments. The typical experiment time was about 1.5 and 3.0 h for HMQC and HMBC, respectively.

A Typical Procedure for Copolymerization Reactions. In general, all copolymerization reactions were carried out under dry conditions in an argon atmosphere due to the air and moisture sensitivity of Sm(II) compounds. A typical procedure for copolymerization of CL with EC is given here (run 4, Table 1). In the glovebox, EC (1.0 g, 11.36 mmol) was weighed in a predried Schlenk tube. Addition of CL (1.0 g, 8.77 mmol) was done outside the glovebox, under argon by a syringe. To the stirred mixture of two monomers was added SmI_2 (2 mL (0.1 M solution in THF), 0.2 mmol) at room temperature, 20 °C. The color of the solution remained blue. The reaction was stopped after 18 h. The contents were dissolved in THF and precipitated in cold methanol containing a few drops of HCl, dried in a vacuum at room temperature overnight, and weighed (0.81 g, 41% yield). Purification of the copolymers was done by again dissolving in THF and reprecipitating in methanol−HCl. A similar procedure was used for copolymerization of LA and EC except both were weighed in the glovebox and the polymerization temperature was kept at 50 °C. Different copolymers were made by changing the molar ratio of CL/LA and EC (Table 1).

Results and Discussion

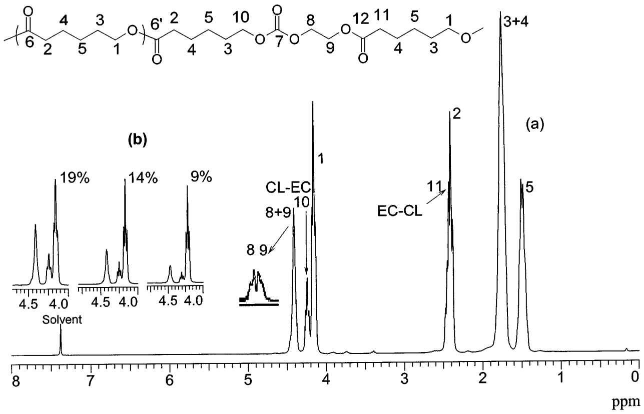

Figure 1. (a) ^1H NMR spectrum of the EC−CL copolymer (run 4, Table 1). (b) Parts of the ^1H NMR spectra with different EC compositions; the values attached are the EC mole percent.

Copolymerizations of CL/LA and EC were carried out using SmI_2/Sm as an initiator. SmI_2 prepared by the reaction of Sm metal with diiodoethane in THF was directly employed (without removal of excess Sm metal, 5 mmol). It was taken by syringe from a vigorously stirred suspension. Our previous studies showed enhanced reactivity of this SmI_2/Sm system for homopolymerization of CL and LA as compared to the studies reported by Evans et al. for homopolymerization of CL using SmI_2.[28,29] EC was found to be non-homopolymerizable using the same initiator. Various copolymerizations of EC with CL/LA were tried by changing the EC content in the feed, and the results are tabulated in Table 1. High molecular weight polymers with moderate polydispersity, unimodal GPC curves, and rubbery natures were obtained ($M_n = (2.5-2.6) \times 10^4$; $M_w/M_n = 1.3-1.6$) in the case of EC−CL copolymers. There was a decrease in the yield of the polymer obtained on increasing the EC content in the feed.

Structural characterization of the polymers obtained was done using one- and two-dimensional NMR spectroscopic techniques. The representative one-dimensional ^1H NMR spectrum of the polymer obtained from run 4 (Table 1) (CL−EC copolymer) is shown in Figure 1. Besides characterizable peaks of PCL ($-OCH_2CH_{2-}$, 4.16 ppm, 1; $-C(O)CH_2CH_{2-}$, 2.41 ppm, 2; $-C(O)CH_2CH_{2-} + -OCH_2CH_{2-}$, 1.75 ppm, 4 + 3; $-CH_2CH_2CH_{2-}$, 1.48 ppm, 5), EC signals were present very close to each other at 4.44 ppm ($-C(O)OCH_{2-}$, 8) and 4.33 ppm ($-OCH_2CH_{2-}$, 9). The absence of peaks between 3.1 and 3.3 ppm clearly indicates the absence of ether units which are generally formed as defects by decarboxylation of EC. Also the PCL signals at 4.16 and 2.41 ppm were split into major (1, 2) and minor (10, 11) peaks. The ratio of the intensity of the minor peaks to some characterizable peak of PCL (for example, $-OCH_2CH_{2-}$, 4.16 ppm, 1) decreases in intensity as the EC content decreases (Figure 1b). Also the minor peaks have almost the same intensity as the EC peaks $-C(O)OCH_{2-}$ (8) and $-OCH_2CH_{2-}$ (9) individually. Therefore, the minor peaks (10 and 11) from the signals at 4.16 and 2.41 ppm could be assigned to diad heterosequences such as *CL*−EC and EC−*CL*. The correctness of the assigned EC and the minor peaks of PCL is confirmed from 2D COSY measurement. Protons 10 showed a cross-peak to protons 3, and protons 11 showed a cross-peak to protons 4 (Figure 2); no cross-peak was observed for protons 8 and 3. The EC content of the copolymers (Table 1) was determined from the ratio of the areas of peaks 8 + 9 (EC protons; $-C(O)OCH_{2-}$ and $-OCH_2CH_{2-}$) and peak 1 (PCL proton; $-OCH_2CH_{2-}$) in Figure 1

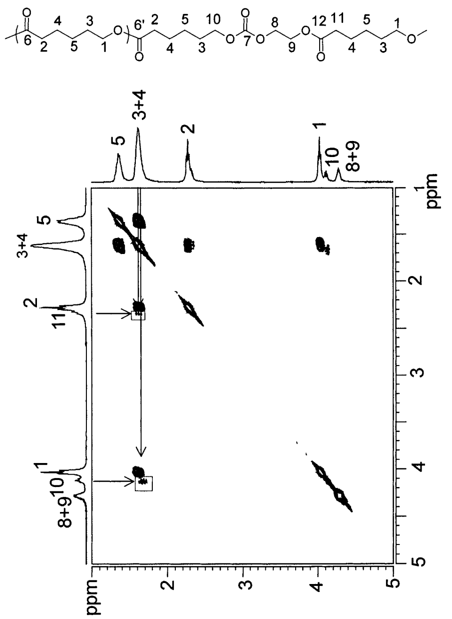

Figure 2. COSY spectrum of the EC−CL copolymer (run 4, Table 1).

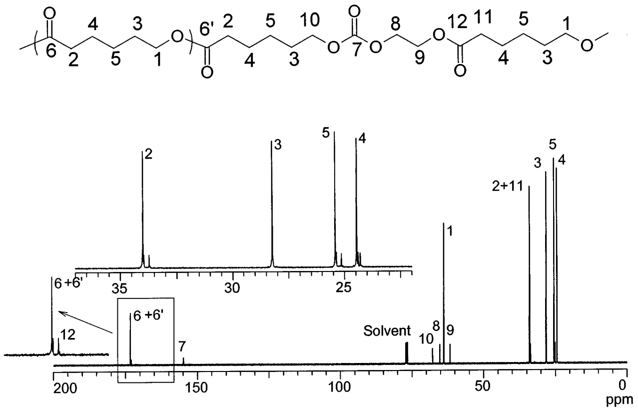

Figure 3. ^{13}C NMR spectrum of the EC−CL copolymer (run 4, Table 1).

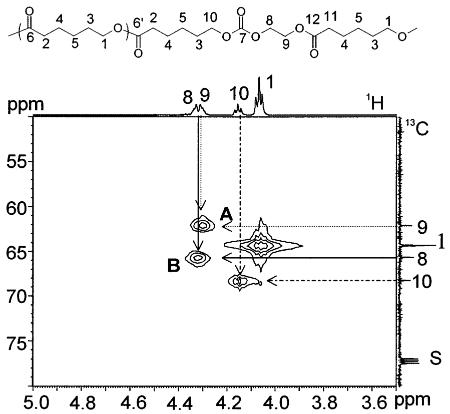

Figure 4. ^{1}H−^{13}C HMQC NMR spectrum of the EC−CL copolymer (run 4, Table 1) in the regions (^{1}H) 3.5−5.0 ppm and (^{13}C) 50−80 ppm.

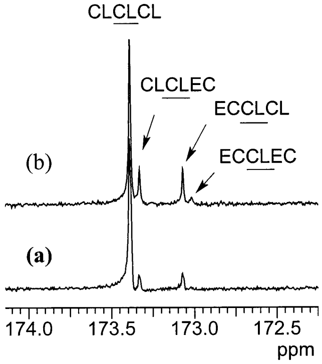

Figure 5. ^{13}C NMR expanded carbonyl carbon spectrum of the EC−CL copolymer with EC contents of (a) 9 mol % and (b) 14.7 mol %.

The ^{13}C NMR spectrum of a EC−CL copolymer with an EC content 19 mol % (run 4) is shown in Figure 3. One set of six strong signals at 173.4 (6), 64.3 (1), 34.0 (2), 28.3 (3), 25.4 (5), and 24.5 (4) ppm was identical with that of homo-PCL and can easily be assinged to the PCL units of the copolymer. The carbonyl carbon of EC was obtained as a single peak at 155 ppm (7). Three new peaks were also observed in the region 62.0−68.0 ppm (62.5, 65.5, and 68.0 ppm). The origin of two peaks could be from the 8 and 9 carbons of the EC component, which should also appear in the same region. The available literature[27a] shows the peaks at 68.0 and 65.5 ppm to be from EC, but on the basis of only one-dimensional ^{13}C NMR data, the peak assignments cannot be made with certainty.

Further, the two-dimensional ^{1}H−^{13}C HMQC technique was used for correct and complete ^{13}C NMR peak assignments. From the ^{1}H−^{13}C HMQC spectrum shown in Figure 4, two separate cross-peaks (A and B) can easily be seen by correlation of protons 9 at 4.33 ppm with the carbon signal at 62.5 ppm and that of protons 8 at 4.44 ppm with the carbon signal at 65.5 ppm. On the basis of this, the signals at 62.5 and 65.5 ppm could easily be assigned to the carbon atoms attached to protons 9 and 8 of the EC unit, respectively. Analogously, the signal at 68.0 ppm goes to carbon atom 10. It is worthwhile to mention here that the ^{13}C NMR signals of the 8 and 9 carbons of EC are significantly shifted toward higher and lower field from carbon signal 1 of PCL as assigned by HMQC. In a previous study[27a] the ^{13}C NMR signals of EC in the region 62−68 ppm are incorrectly assigned.

All the PCL peaks in the ^{13}C NMR spectrum of EC−CL copolymers (Figure 3) (except the peak at 28.3 ppm) were split into a major and a minor peak. This also confirms the existence of diad homo- and heterosequences. The major signals of the PCL component were from the homosequence (CL−*CL*) because of the agreement with the peaks of homo-PCL. Also, the almost equal intensity of the ^{13}C signals of EC and that of the minor ones of PCL show the origin of these minor signals is from the diad heterosequences (EC−*CL* and *CL*−EC). Further splitting (into doublets) within these diad fractions can be assigned to triad compositional sequences, and the observed four peaks can be assigned to CL*CL*CL, CL*CL*EC, EC*CL*CL, and EC*CL*EC triads (Figure 5). Nonsplitting of the carbonyl carbon of EC clearly shows its presence as a discrete unit. This clearly suggests the following random structure for the copolymers with mainly blocks of CL separated by EC:

CL CL CL CL CL CL CL EC CL CL CL
EC CL EC CLCL

This suggested structure is confirmed by the two-dimensional ^{1}H−^{13}C HMBC NMR technique (Figure 6). The ^{1}H−^{13}C HMBC spectrum clearly shows that the ^{1}H NMR signals on carbon atoms 8 and 10 (at 4.44 and

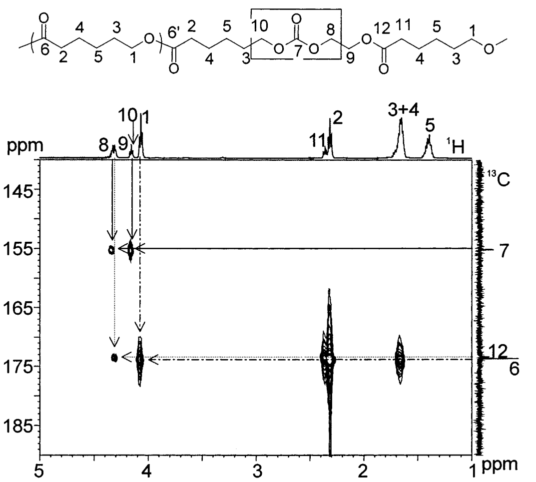

Figure 6. ^{1}H$-$^{13}C HMBC NMR spectrum of the EC$-$CL copolymer (run 3, Table 1) in the regions (^{1}H 1.0$-$5.0 ppm and (^{13}C) 140$-$190 ppm.

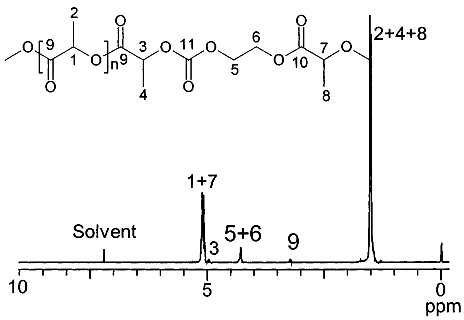

Figure 7. ^{1}H NMR spectrum of the EC$-$LA copolymer (run 7, Table 1).

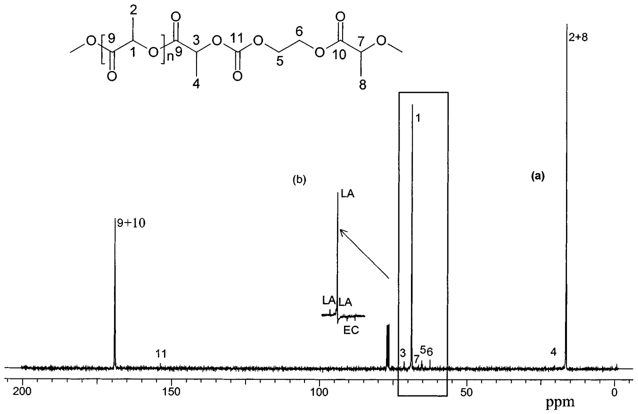

Figure 8. (a) ^{13}C NMR carbon spectrum of the EC$-$LA copolymer (run 6, Table 1). (b) A part of the DEPT spectrum of the EC$-$LA copolymer (run 6, Table 1).

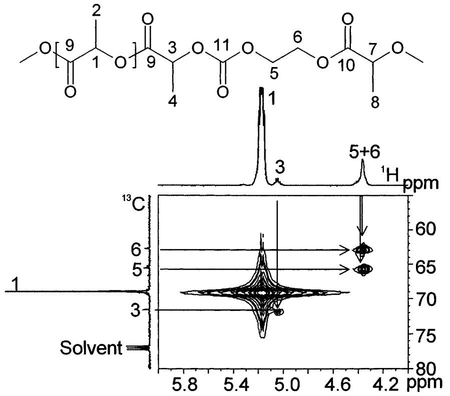

Figure 9. ^{1}H$-$^{13}C HMQC spectrum of the EC$-$LA copolymer in the regions (^{1}H) 4.0$-$6.0 ppm and (^{13}C) 55.0$-$80.0 ppm (run 6, Table 1).

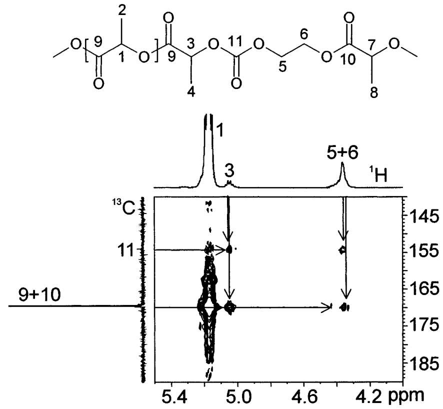

Figure 10. 2D ^{1}H$-$^{13}C HMBC NMR spectrum of the EC$-$LA copolymer (run 6, Table 1) in the regions (^{1}H) 4.0$-$5.5 ppm and (^{13}C) 40.0$-$190.0 ppm.

4.21 ppm, respectively) are both related to that of carbon atom 7 (155 ppm) of the EC unit. This suggests that protons 8 and 10 are involved with proton$-$carbon correlations through couplings over two bonds with carbon atom 7 in the polymer chain and that the signals were therefore correctly assigned to protons 8 (from EC) and 10 (from the connecting CL unit). Moreover, the proton attached to carbon atom 9 (at 4.33 ppm) has a correlation with carbon atom 12 at 173.1 ppm. This confirms that the proton attached to carbon 9 (from EC) has the carbonyl carbon of the linking CL unit as its neighbor. The correlation of protons 10 and 9 with carbons 7 and 12, respectively, shows the connection between the EC and CL units (Figure 6).

The representative ^{1}H NMR spectrum of the EC$-$LA copolymer is shown in Figure 7. PLA peaks at 1.52 ppm ($-$O$-$CH(CH_3)C(O)$-$, 2) and 5.1 ppm ($-$O$-$CH(CH$_3$)C(O)$-$, 1) and EC peaks at 4.30 ppm (5 + 6) were observed. A negligible amount of decarboxylation of the EC units was noticed by the presence of a small peak (9) at 3.22 ppm (Figure 7). The EC content was determined from the ratio of the areas of the peaks of EC protons $-$C(O)OCH_{2-} (5) + $-$OCH_2CH$_{2-}$ (6) and that of PLA proton 1. In the EC$-$CL copolymers, a maximum of 19 mol % EC was obtained. As compared to this, incorporation of EC in the PLA polymer was much less (4.2%) (Table 1).

In the ^{13}C NMR spectrum of the EC$-$LA copolymer, the three strong signals at 170.3 ppm (9), 69.8 ppm (1), and 17.6 ppm (2) were identical with those of homo-PLA and are assigned to PLA units of the copolymer (Figure 8). Further, ^{13}C DEPT was used to differentiate between the resonance signals of PLA and EC units in the copolymer (Figure 8). The exact assignment of the signals in the region 63$-$73 ppm was not possible based on 1D NMR techniques.

From the 2D ^{1}H$-$^{13}C HMQC spectrum, the signals at 66.3, 63.6, and 72.3 ppm could be easily assigned to carbon atoms 5, 6 and 3, respectively (Figure 9).

A correlation of the protons at carbon 3 with both carbonyl carbons of the EC unit at 154.8 ppm and that of the PLA unit at 170.3 ppm was observed in the 2D ^{1}H$-$^{13}C HMBC spectrum (Figure 10). This information combined with the fact that no splitting of the carbonyl signal of the EC unit at 154.8 (11) ppm (Figure 8) was observed clearly shows carbon 3 as the linking PLA unit between PLA blocks and single EC units in the copolymer.

Conclusions

SmI_2 in the presence of excess Sm metal is proved to be a ring-opening copolymerization initiator for CL/LA and EC at room temperature and 50 °C, respectively, giving copolymers with moderate polydispersity index (1.3−1.6). The incorporation of 19 mol % EC into the PCL backbone by the ring-opening polymerization route is of interest as EC is non-homopolymerizable when present alone. The complete structural characterization of these copolymers and an insight into their micostructure, based on 1D spectroscopies such as ^1H, ^{13}C, and ^{13}C DEPT NMR and 2D $^1H-^{13}C$ HMQC, $^1H-^{13}C$ HMBC, and COSY NMR techniques is carried out for the first time to the best of our knowledge. The reassignment of previously reported peaks in the ^{13}C NMR spectrum of EC−CL copolymers is also reported.

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