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SmI$_2$/Sm-Based γ-Buyrolactone−ϵ-Caprolactone Copolymers: Microstructural Characterization Using One- and Two-Dimensional NMR Spectroscopy

Seema Agarwal* and Xiulan Xie

Philipps-Universität Marburg, Fachbereich Chemie, Institut für Physikalische Chemie,
Kernchemie und Makromolekulare Chemie und Wissenschaftliches Zentrum für
Materialwissenschaften, Hans-Meerwein Strasse, D-35032, Marburg, Germany

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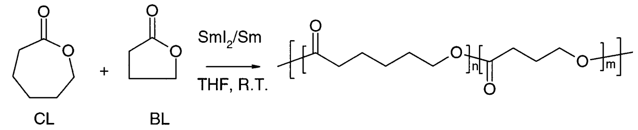
ABSTRACT: Copolymers containing nonhomopolymerizable γ-butyrolactone (BL) and ϵ-caprolactone (CL) units of different compositions were synthesized by the ring-opening polymerization method using the SmI$_2$/Sm initiator system. A maximum of 33 mol % of BL was incorporated into polycaprolactone (PCL) backbone. The microstructure of these copolymers was analyzed by one- and two-dimensional NMR spectroscopies. The overlapped methylene proton signals of CL and BL were resolved using 2D ^{1}H−^{13}C heteronuclear multibond correlation (HMBC) and homonuclear ^{1}H−^{1}H total correlation spectroscopy (TOCSY) techniques. The triad sequence distribution centered at the carbonyl carbon and methylene carbon of CL and BL has been obtained from ^{13}C NMR spectroscopy. Further, 1D and 2D NMR spectroscopic techniques were used to confirm the change of microstructure from PCL blocks separated by discrete BL units to random copolymer structure having BL−BL units with increase in the mole percent of BL units in the copolymer.

Introduction

Aliphatic polyesters such as polycaprolactone (PCL) have vast commercial medical and pharmaceutical application as homopolymers or copolymers. Generally, copolymerization of PCL is carried out for modifying its physical properties and for tuning its degradability behavior. Although the copolymerization behavior of CL with other comonomers like β-butyrolactone, valerolactone (VL), glycolide, and L-lactide[1−5] and nonhomopolymerizable cyclic monomers like γ-butyrolactone (BL)[6−9] and ethylene carbonate (EC)[10] using different catalysts is available, but most of the reports have mentioned the configurational and compositional assignments of the comonomeric units in the polymer based on 1D ^{1}H and ^{13}C NMR techniques. The knowledge of microstructure is essential to understand the macroscopic characterization of the polymers as it directly affects the physicochemical and thermal properties. Penczek et al.[6,7] studies using ^{13}C NMR on copolymers of CL with BL indicate pseudoperiodic or random copolymer structure with a maximum of 43 mol % incorporation of BL units. The copolymerization was initiated with aluminum isopropoxide trimer [Al(O^{i}Pr)$_3$]$_3$. Nakayama et al.[8] have reported the same copolymerization behavior (formation of stastical copolymers with 26 mol % of BL units) using ^{1}H and ^{13}C NMR spectroscopic techniques in the presence of tetraphenyl tin initiator. The recent research focus is on the ring-opening coplymerisations using lanthanide catalysts. The literature reveals that the structure and nature of the catalyst has an effect on the microstructure of the resulting copolymer and also on the maximum percent of the comonomers incorporated. Wakatsuki et al.[9] have reported the formation of CL−BL copolymers using Sm(II) aryloxides, in which the BL units all exist in an isolated form and CL units all in blocks with 22 mol % incorporation of BL units.

Scheme 1



Previously, we have reported the enhanced reactivity of the SmI$_2$/Sm system for ROP of caprolactone, valerolactone (VL), and L-lactide[11,12] as compared to the polymerization of lactones using only SmI$_2$, which is reported only at reflux with very low yield and multimodal GPC curves.[13] Recently, we have reported SmI$_2$/Sm-based copolymerization and microstructure characterization of CL and ethylene carbonate (EC) polymers using 2D NMR techniques.[10a] In the present paper, SmI$_2$/Sm-based room temperature (20 °C) copolymerization of BL and CL (Scheme 1) and the microstructural characterization of the resulting copolymers using one- and two-dimensional NMR spectroscopies like ^{1}H, ^{13}C, ^{1}H−^{13}C HMBC (heteronuclear multiple-bond correlation), and ^{1}H−^{1}H TOCSY (total correlation spectroscopy) techniques are given. The reassignment of some of the triad peaks in ^{13}C NMR spectrum of previously reported BL−CL (pseudo) random copolymers is also given.

Experimental Part

Materials. 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). SmI$_2$ was prepared as 0.1 M solution in THF by reacting 10 mmol of Sm (Aldrich, 40 mesh) with 5 mmol of diiodoethane.[14]

Experimental Techniques. Molecular weights of the polymers were determined by GPC using the Knauer system equipped with two columns PSS−SDV (linear, 10 μL, 60 × 0.8) and a differential refractive index detector using THF as eluent at a flow rate of 0.83 mL/min.

^{1}H (400.13 MHz) and ^{13}C (100.21 MHz) were recorded on Bruker DRX-400 spectrometer. Neat CDCl$_3$ was used, and ^{1}H

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* Corresponding author: e-mail seema@chemie.uni-marburg.de.

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Table 1. SmI_2/Sm-Based Copolymerization of BL with CL at Room Temperature (20 °C)[a]

run	BL (mmol)	yield[b] (%)	$M_n \times 10^{-4}$	M_w/M_n	polymer composition BL (mol %)[c]
1	2.90	88	5.79	1.54	12
2	5.81	80	5.00	1.64	18
3	8.72	76	4.47	2.01	23
4	11.62	59	3.91	1.75	27
5	23.25	38	2.88	1.64	33

[a] 0.2 mmol of SmI_2 and 8.77 mmol of CL were used in each experiment, and time of polymerization was 48 h. [b] Based on total monomer content (CL + BL) in the feed. [c] Calculated from ^1H NMR.

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 the -gs-HMBC[15] pulse sequence. 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, and the number of increments for t_1 was 256. The number of scans of eight was used for HMBC experiment, and dummy scans of four was used for the experiments. A relaxation delay of 1 s was used for all 1D experiments and 2 s for all 2D experiments. A typical experiment time was about 3.0 h for HMBC. The $^1H-^1H$ TOCSY[16] was recorded on a Bruker DRX-400 spectrometer. The composite pulse MLEV-17 was used for spin-lock, with 90° pulse length of 40 μs and transmitter attenuation of 12 dB, corresponding to an effective lock field of ca. 7000 Hz. Total mixing time was set to be 210 ms: 76 MLEV-17 cycles (205 ms) plus two trim pulses of 2.5 ms each. TOCSY data were acquired with 1024 points in t_2, and the number of increments for t_1 was 128, with eight scans for each and eight dummy scans. The TPPI scheme was used to distinguish positive and negative frequencies in F_1, and data were processed in phase-sensitive mode in both dimensions. A typical experiment time was about 0.5 h.

A Typical Procedure for Copolymerization Reactions. In general, all copolymerization reactions were carried out under dry conditions in an argon atmosphere due to air and moisture sensitivity of SmI_2. In a typical copolymerization reaction, 8.77 mmol of CL and 11.62 mmol of BL (run 4, Table 1) were taken in a predried Schlenk tube under argon. SmI_2 (0.1 M, 2 mL) was added by a syringe, and reaction contents were stirred at room temperature. The color of the solution remained blue. The reaction was stopped after 48 h by precipitation into 200 mL of methanol containing a few drops of HCl. The polymer obtained was purified by filtration, drying, and 2-fold reprecipitation from THF/methanol−HCl. A similar procedure was used for other polymerization reactions except changing the amount of BL in the feed. The detailed reaction conditions are given in Table 1.

Results and Discussion

Copolymerization of CL and BL was 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. We have already proved the enhanced reactivity of this SmI_2/Sm system for homopolymerization of CL and LA as well as for the copolymerization of CL with ethylene carbonate (EC)[10a,11,12] as compared to the reported studies using SmI_2.[13] BL was found to be nonhomopolymerizable using the same initiator; i.e., no traces of high molecular weight, methanol-insoluble fraction were obtained. Various copolymer samples were prepared by changing the amount of BL in the feed. High molecular weight polymers with moderate polydispersity and unimodal GPC curves were obtained (Table 1). There was a decrease in the yield of the polymer obtained on increasing the BL content in the feed. Also, there was a decrease in the molecular weight of the polymers with an increase in the BL content in the copolymer. This could be due to the increase in the effective initiator concentration as the actual amount of the monomer reacted decreases with the increase in the BL content. The same trend was observed for tetraphenyltin-catalyzed ring-opening copolymerization of CL and butyrolactone.[8]

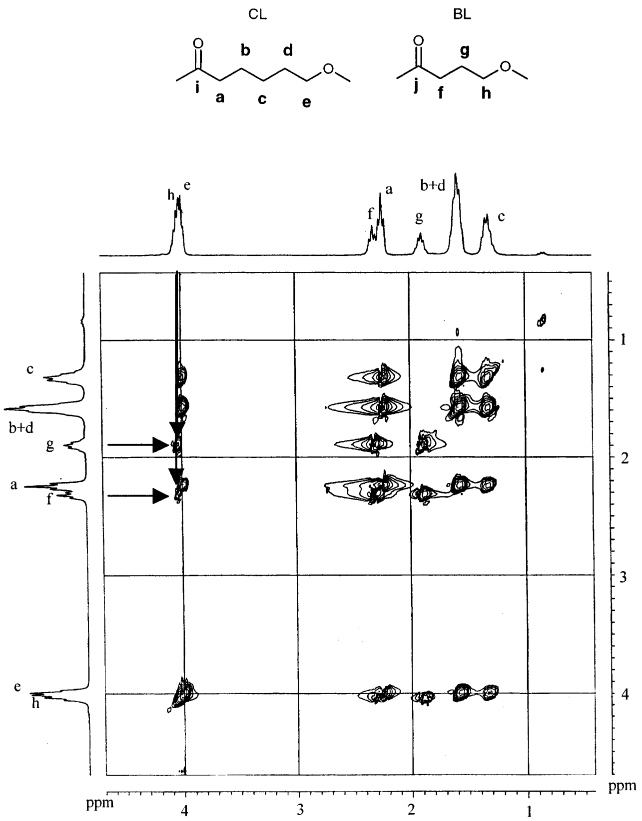


Figure 1. $^1H-^1H$ TOCSY NMR spectrum of run 3.

Microstructural characterization of the polymers obtained was done using one- and two-dimensional NMR spectroscopic techniques. The peaks in the ^1H NMR spectra of copolymers were assigned according to the literature.[9] PCL signals were obtained at ppm 3.99 ($-C\mathbf{H}_2OC(O)-$), 2.24 ($-C(O)C\mathbf{H}_2-$), 1.58 ($-C\mathbf{H}_2CH_2OC(O)- + -C(O)CH_2C\mathbf{H}_2-$), and 1.31 ($-C(O)CH_2CH_2C\mathbf{H}_2-$) whereas BL signals were present at ppm 1.70 ($-C(O)CH_2C\mathbf{H}_2CH_2O-$), 2.12 ($-C(O)C\mathbf{H}_2CH_2CH_2O-$), and 4.05 ($-C(O)CH_2CH_2C\mathbf{H}_2O-$). In most of the copolymer samples, the signals around 4 ppm for CL proton ($-C\mathbf{H}_2OC(O)-$) and BL proton ($-C(O)CH_2CH_2C\mathbf{H}_2O-$) were not separated well and were observed as one peak with multiplets. This multiplet is resolved for correct peak assignments using 2D homonuclear TOCSY and heteronuclear HMBC NMR techniques. The detailed $^1H-^1H$ correlation peaks for the representative sample (run 3) are given in Figure 1. The overlapping peaks for the protons e and h of CL and BL, respectively, in the ^1H NMR spectrum give two sets of clearly distinguishable correlation peaks (one with g and f of the BL unit and another with a, b, c, and d of the CL unit) in the $^1H-^1H$ TOCSY NMR spectrum. This shows the presence of BL proton h ($-C(O)CH_2CH_2C\mathbf{H}_2O-$) downfield to that of CL proton e ($-C\mathbf{H}_2OC(O)-$). Also in the $^1H-^{13}C$ HMBC NMR spectrum (Figure 2, run 3) four correlation peaks are observed correlating the methylene proton (down-

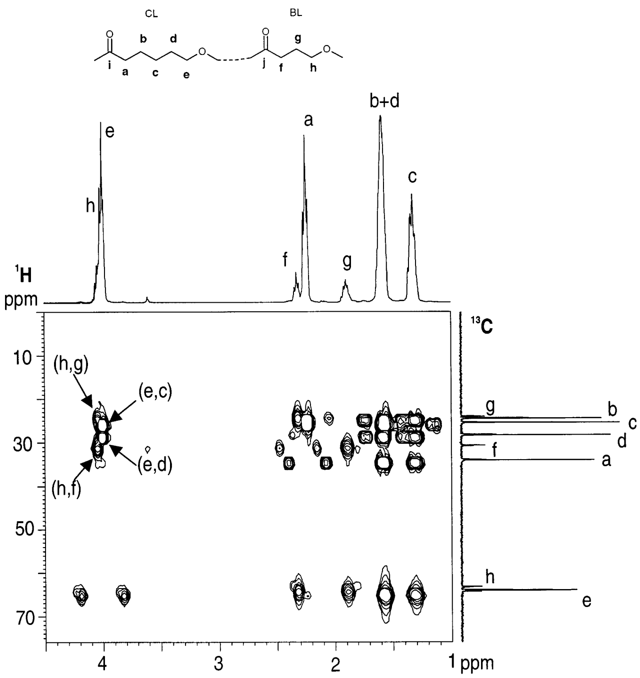


Figure 2. A part of ^{1}H−^{13}C HMBC NMR spectrum of run 3 in the regions 1−4.5 and 0−70 ppm.

field, h) of the BL unit with carbons g and f of BL and the methylene proton (e, upfield) of the CL unit with carbons c and d of CL. The copolymer composition was determined by taking the ratio of the intensities of the signals at 1.31 ppm (characterstic of PCL) and 1.70 ppm (characterstic of BL) in the ^{1}H NMR spectrum. There was an increase in the mole percent of BL in the copolymer with the increase in its amount in the feed. The copolymers with a maximum of 33 mol % of BL units in the copolymers were prepared. No attempts were made to optimize the reaction conditions for increasing the amount of incorporated BL in the copolymers. ^{13}C NMR of the polymer sample (run 3) is shown in Figure 3. One set of six strong signals at 173.4 (**i**), 64.0 (**e**), 33.9 (**a**), 28.2 (**d**), 25.3 (**c**), and 24.4 ppm (**b**) was identical with that of homo-PCL and was assinged to the PCL units of the copolymer, and the signals from BL were obtained at 172.7 (j), 63.4 (h), 30.6 (f), and 23.95 ppm (g). The peaks assigned are in accordance with the literature values.[9] The PCL signals for the carbons i, e, and a were split into a major and a minor peak. The BL peaks j, f, g, and h were also split into a major and minor. This shows the presence of diad homo and diad hetero sequences like CL−BL and BL−CL as marked in Figure 3. These diad homo and hetero sequences were not distinguishable in ^{1}H NMR spectra of the copolymers. No splitting of BL peaks was observed for run 1 (BL content 12 mol %) in the ^{13}C NMR spectrum, and it was negligibly small in run 2 (BL content 18 mol %). The nonsplitting of BL units in this sample shows their presence as discrete units, i.e., microstructure of the type CLCLCLBLCLCLCLCLBLCLCLCLCLBLCLCL-CLBLCLCLCL with the majority of CLCLCL type blocks separated by isolated BL units. ^{1}H−^{13}C HMBC NMR spectra of runs 3−5 clearly show four separate cross-peaks in the carbonyl carbon and methylene hydrogen region (Figure 4). The correlation of carbonyl carbon (2) of homo diad (CL**CL**) with methylene hydrogen (−C(O)OC**H**$_2$−) (1) of the neighboring CL unit gives a cross-peak N. The heterodiad sequence BL**CL** in the polymer chain is responsible for giving a cross-peak O by correlation of the carbonyl carbon of the CL unit (8, BL**CL**) with the methylene hydrogen (7) of the BL unit. Similarly, the carbonyl carbons (4 and 6) of BL are correlated to methylene hydrogens of the CL unit (cross-peak M) and that of the BL unit itself (cross-peak P), respectively, showing the presence and the chemical links between CL−CL, CL−BL, and BL−BL units. The peaks from the carbonyl carbon and methylene carbon of BL units (runs 3−5) further showed triad sensitivity in ^{13}C NMR. The detailed triad characterization of the peaks for the methylene carbon region is shown in Figure 5. Although in the present system the peaks centered at the methylene carbon of CL units do not show triad sensitivity under the experimental conditions, it is emphasized here that $\mathrm{CL\underline{CL}CL}$ triad in the methylene carbon region will be structurally closer to $\mathrm{BL\underline{CL}CL}$ rather than to the $\mathrm{CL\underline{CL}BL}$ triad. The dependence of ^{13}C chemical shift ($\delta(^{13}\mathrm{C})$) on microstructure and local conformation of polymers is reflected by the substituent effect on δ (^{13}C). It is shown by Tonelli[17] that

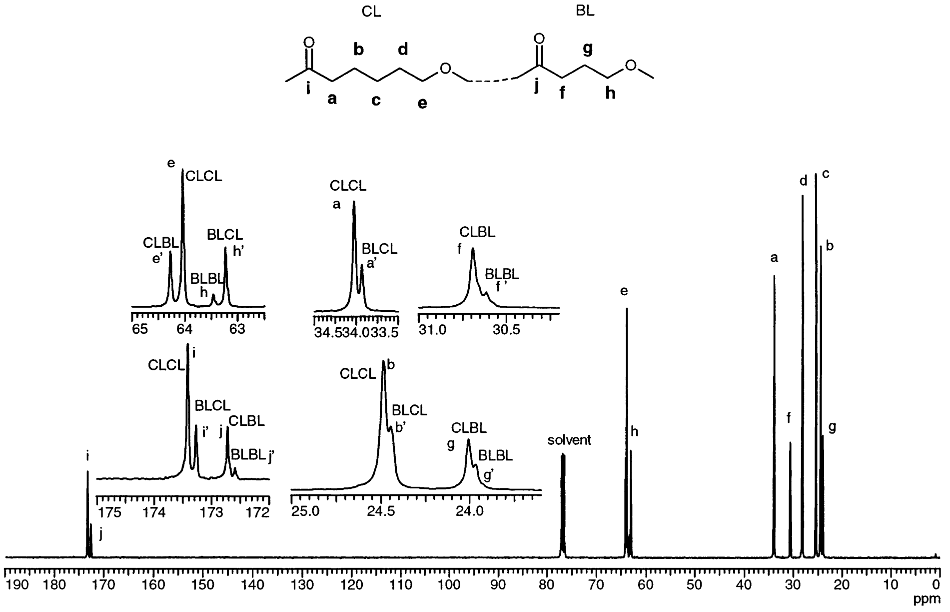


Figure 3. ^{13}C NMR spectrum of run 3 showing homo diad and hetero diad sequences.

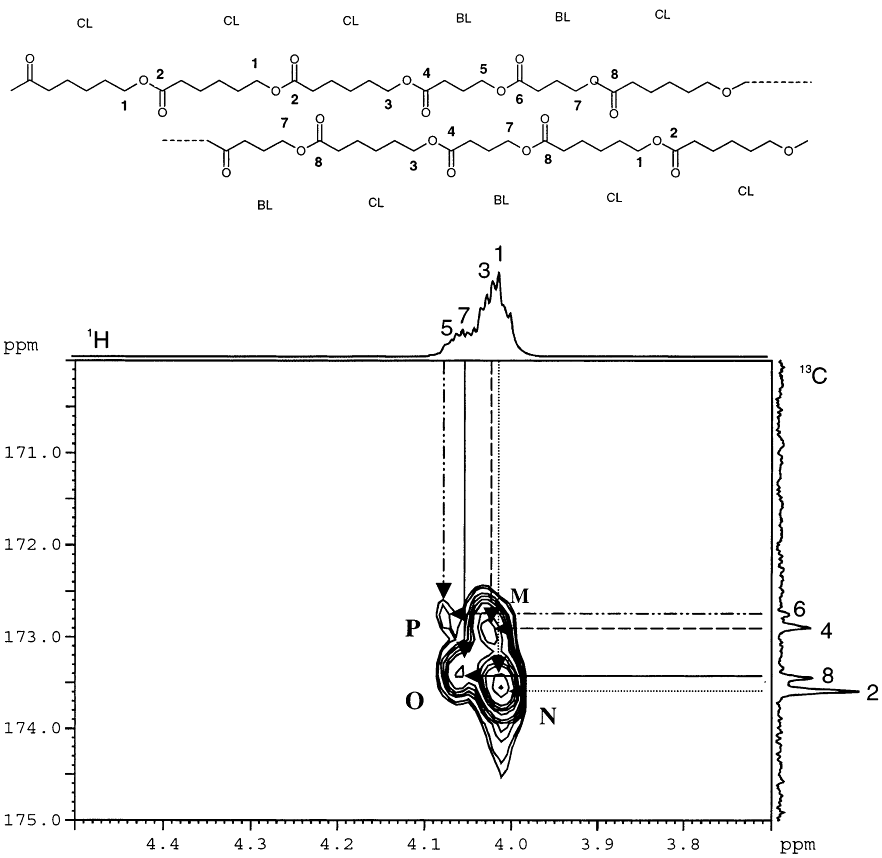


Figure 4. ^{1}H−^{13}C HMBC NMR spectrum of run 4 in the regions 3.6−4.6 and 170−175 ppm.

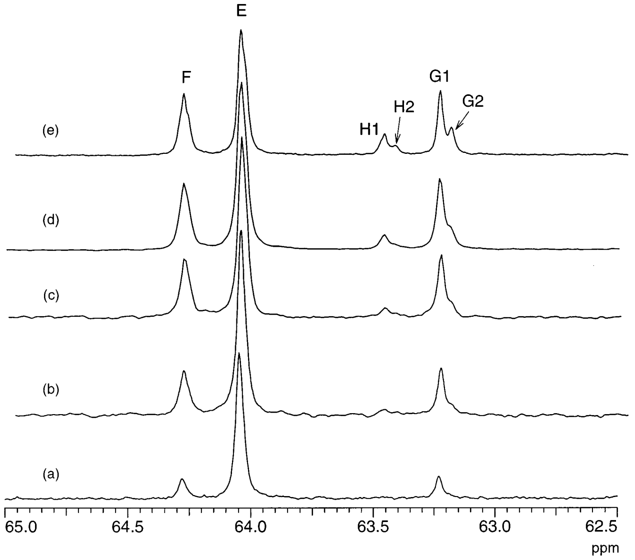
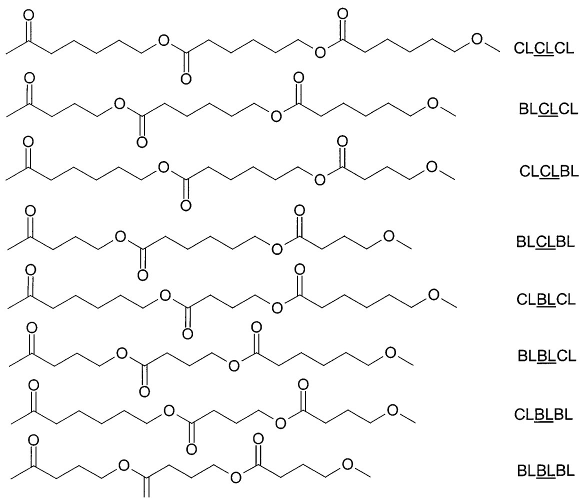


Figure 5. ^{13}C NMR spectra of BL−CL copolymers with BL content: (a) 12, (b) 18, (c) 23, (d) 27, and (e) 33 mol % showing the methylene carbon region (E = $\mathrm{CL\underline{CL}CL}$ + $\mathrm{BL\underline{CL}CL}$; F = $\mathrm{CL\underline{CL}BL}$ + $\mathrm{BL\underline{CL}BL}$; G1 = $\mathrm{CL\underline{BL}CL}$; G2 = $\mathrm{BL\underline{BL}CL}$; H1 = $\mathrm{CL\underline{BL}BL}$; H2 = $\mathrm{BL\underline{BL}BL}$).

nonequivalence in δ(^{13}C) of the terminal isopropyl methyl carbons in branched alkanes is observable for those with an asymmetric center within five bonds to the methyl groups and decays to zero for a separation of six bonds. In $\mathrm{BL\underline{CL}CL}$ triads the methylene carbon of CL has a different center/chemical environment, i.e., methylene carbon of BL separated by seven bonds, and therefore, it is expected to show a single δ(^{13}C) as that of $\mathrm{CL\underline{CL}CL}$ or very close to it. As compared to this, in the triad $\mathrm{CL\underline{CL}BL}$ the methylene carbon of CL has a different center/chemical environment, i.e., carbonyl carbon of BL as its immediate neighbor (at a distance of one bond), and therefore is expected to appear at a different δ(^{13}C). With the same analogy, the methylene triad of BL units, $\mathrm{CL\underline{BL}CL}$, will be structurally more closer to $\mathrm{BL\underline{BL}CL}$ rather than to $\mathrm{CL\underline{BL}BL}$. This gives the peak assignments in the methylene carbon region as E $\mathrm{CL\underline{CL}CL}$ + $\mathrm{BL\underline{CL}CL}$; F $\mathrm{CL\underline{CL}BL}$ + $\mathrm{BL\underline{CL}BL}$; G1 $\mathrm{CL\underline{BL}CL}$; G2 $\mathrm{BL\underline{BL}CL}$; H1 $\mathrm{CL\underline{BL}BL}$; H2 $\mathrm{BL\underline{BL}BL}$ (Figure 5). The triad structures are shown in Scheme 2. Again, the peaks centered at the carbonyl carbon of the CL units do not show triad sensitivity in the present work, but the $\mathrm{CL\underline{CL}CL}$ triad will be structurally closer to $\mathrm{CL\underline{CL}BL}$ rather than to $\mathrm{BL\underline{CL}CL}$ and $\mathrm{BL\underline{CL}CL}$ will

Scheme 2



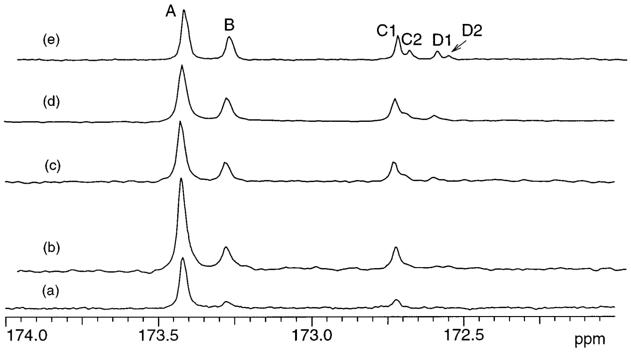


Figure 6. ^{13}C NMR spectra of BL−CL copolymers with BL content: (a) 12, (b) 18, (c) 23, (d) 27, and (e) 33 mol % showing carbonyl carbon region (A = CLCLCL + CLCLBL; B = BLCLCL + BLCLBL; C1 = CLBLCL; C2 = CLBLBL; D1 = BLBLCL; D2 = BLBLBL).

Table 2. Relative Proportions of Carbonyl Carbon Triad Sequences (A:B:C1:C2:D1:D2) in BL−CL Copolymers (A = CLCLCL + CLCLBL; B = BLCLCL + BLCLBL; C1 = CLBLCL; C2 = CLBLBL; D1 = BLBLCL; D2 = BLBLBL)

	relative proportion of carbonyl carbon triad sequences					
run	A	B	C1	C2	D1	D2
1	100	9.0	13.0			
2	100	25.0	24.0			
3	100	32.0	33.0[a]		3.0[b]	
4	100	42.0	41.0[a]		9.0[b]	
5	100	46.0	33.0	12	9.0	3.0

[a] CLBLCL + CLBLBL (C1 + C2). The peaks were not well resolved. [b] BLBLCL + BLBLBL (D1 + D2). The peaks were not well resolved.

be closer in structure to the BLCLBL triad. This gives the triad sequencing in the carbonyl carbon region as peak A CLCLCL + CLCLBL; B BLCLCL + BLCLBL; C$_1$ CLBLCL; C$_2$ CLBLBL; D$_1$ BLBLCL; D$_2$ BLBLBL (Figure 6). The respective relative proportion of these triads in different copolymers as determined from ^{13}C NMR spectra is shown in Table 2. The triad peak assignments in the carbonyl carbon region are in accordance with the literature,[6] but it is worthwhile mentioning here that splitted carbonyl and methylene carbon peaks showing triad sensitivity represent different triads for carbonyl carbon and methylene carbon regions as described above. Therefore, the present analysis gives reassignment of literature[6] triad peaks in the methylene carbon region of BL−CL copolymers.

The microstructure analysis shows a change of copolymer structure from PCL blocks with BL discrete units (CLBLCL) to random copolymer structure with PCL blocks with discrete BL units (CLBLCL), BL−BL units (BLBLCL, CLBLBL), and a very small amount of BLBLBL units with increase in the amount of BL content in the copolymer. Although homooligomerization of BL having units up to decamers is already reported,[6] the presence of BL−BL units was not observed in copolymers with low mole fraction of BL (run 1, Table 1) using the SmI$_2$/Sm system. Transesterification reactions and side reactions (combination of two propagating chains having BL end unit with −CH$_2$SmI and −CH$_2$I end groups) as mentioned in ref 12 in addition to a tendency to oligomerize could be the reasons for the formation of BL−BL units in the copolymers with 18−33 mol % BL.

Conclusions

SmI$_2$ in the presence of excess of Sm metal is proved to be a ring-opening copolymerization initiator for CL and BL at room temperature, giving high molecular weight copolymers with moderate polydispersity index (1.5−2.0). Microstructure characterization of copolymers showed the presence of isolated BL units separated by blocks of CL moieties for low content (12 mol %) of BL in the copolymer. The copolymers with BL content from 18 to 33 mol % showed random copolymer structure with very less amount of BLBLBL triads. The majority of BL units are present either as a discrete BL unit (CLBLCL triad) or as BLBLCL/CLBLBL triads. Reassignment of some of the triad sequences in ^{13}C NMR spectrum BL−CL copolymers is also done.

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