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ABC BCD Polymerization: A Self-Condensing Vinyl and Cyclic Ester Polymerization by Combination Free-Radical and Ring-Opening Techniques

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ABSTRACT: The sequential and concurrent polymerizations of an ABC monomer (γ-(ϵ-caprolactone) 2-bromo-2-dimethylpropionate) with a BCD monomer (2-hydroxyethyl methacrylate) are introduced. This novel polymerization method is a versatile concept to branched copolymers. The two monomers that polymerize by different chemistries, ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP), bear initiating centers that are for the type of chemistry that is on the opposite monomer. In this way, a branched copolymer is realized without going through a traditional multistep procedure. The branching density can be altered simply by the addition of the appropriate AB (ϵ-caprolactone) and/or CD (methyl methacrylate) monomers.

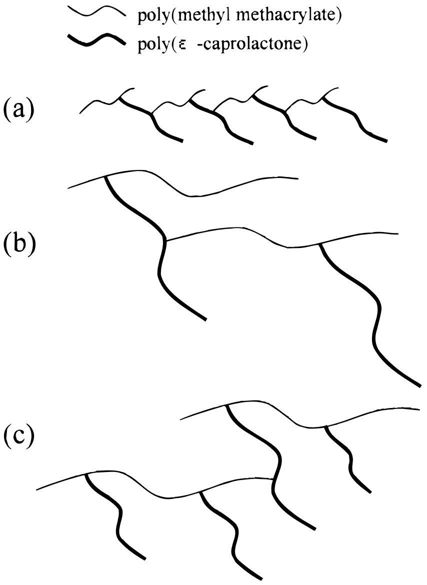
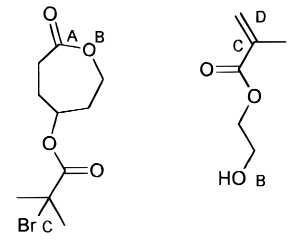


Figure 1. Variations in the molecular architecture, realized simply by using different ratios of the four participating monomers (**1**, **2**, ϵ-CL, MMA), i.e., (a) 1:1:5:5, (b) 1:1:20:20, and (c) 1:2:20:20.

Chart 1



1 (ABC) **2** (BCD)

In this paper, we detail a novel one-step polymerization technique to branched copolymers based on the combination of "living" ring-opening and controlled radical polymerization. This work is built upon several recent developments in controlled polymerizations.[1,2] First, Fréchet et al.[1a] showed that vinyl monomers which contain a pendent-initiating moiety (AB* monomers) will self-polymerize to produce highly branched polymers. This new synthetic route to branched macromolecules, denoted as "self-condensing vinyl polymerizations", was further developed by Hawker et al.,[1b] Gaynor et al.,[1c] Lu et al.,[1d] and others by using different controlled radical polymerization techniques. Second, the concept of simultaneous "living" polymerizations to produce block and graft copolymers in one step using ring opening, controlled, and living radical as well as other polymerization methods was concurrently demonstrated by Sogah et al.[2a] and us.[2b−d] Our new approach, denoted ABC BCD polymerization, combines these two general concepts as a route to branched copolymers. Here, we introduce the sequential and concurrent polymerizations of an ABC monomer (**1**) with a BCD monomer (**2**) as a new and versatile concept to branched copolymers. The γ-(ϵ-caprolactone) 2-bromo-2-dimethylpropionate (**1**) serves as a monomer (AB functionality) for ring-opening polymerization (ROP), and the activated alkyl bromide moiety serves as an initiator (C functionality) for atom transfer radical polymerization (ATRP) of vinyl monomers, once properly activated (Chart 1). The synthesis of **1** has been previously reported.[2c] The other monomer, 2-hydroxyethyl methacrylate (**2**), contains an initiating site for ROP (B functionality) and a vinyl group (CD functionality) that will polymerize by ATRP. Different from self-condensing vinyl polymerizations, where one vinyl monomer containing an initiating site (AB*) is used to prepare highly branched structures, our system employs two monomers (ABC and BCD) that polymerize by different chemistries (AB or CD) to produce branched copolymers (Scheme 1).[3] The initiating center for each type of chemistry resides on the opposite monomer, precluding the possibility of self-polymerization of a given monomer, and ensures copolymerization and branching. What is particularly interesting about this approach is that the molecular architecture can be altered simply by adding unfunctionalized comonomers (AB and/or CD) and/or varying the ratios of the monomers (Figure 1). Furthermore, these branched copolymers will have a block structure and a molecular architecture analogous to starburst[3], dendrigraft,[4] and dendrimerlike star[5] block

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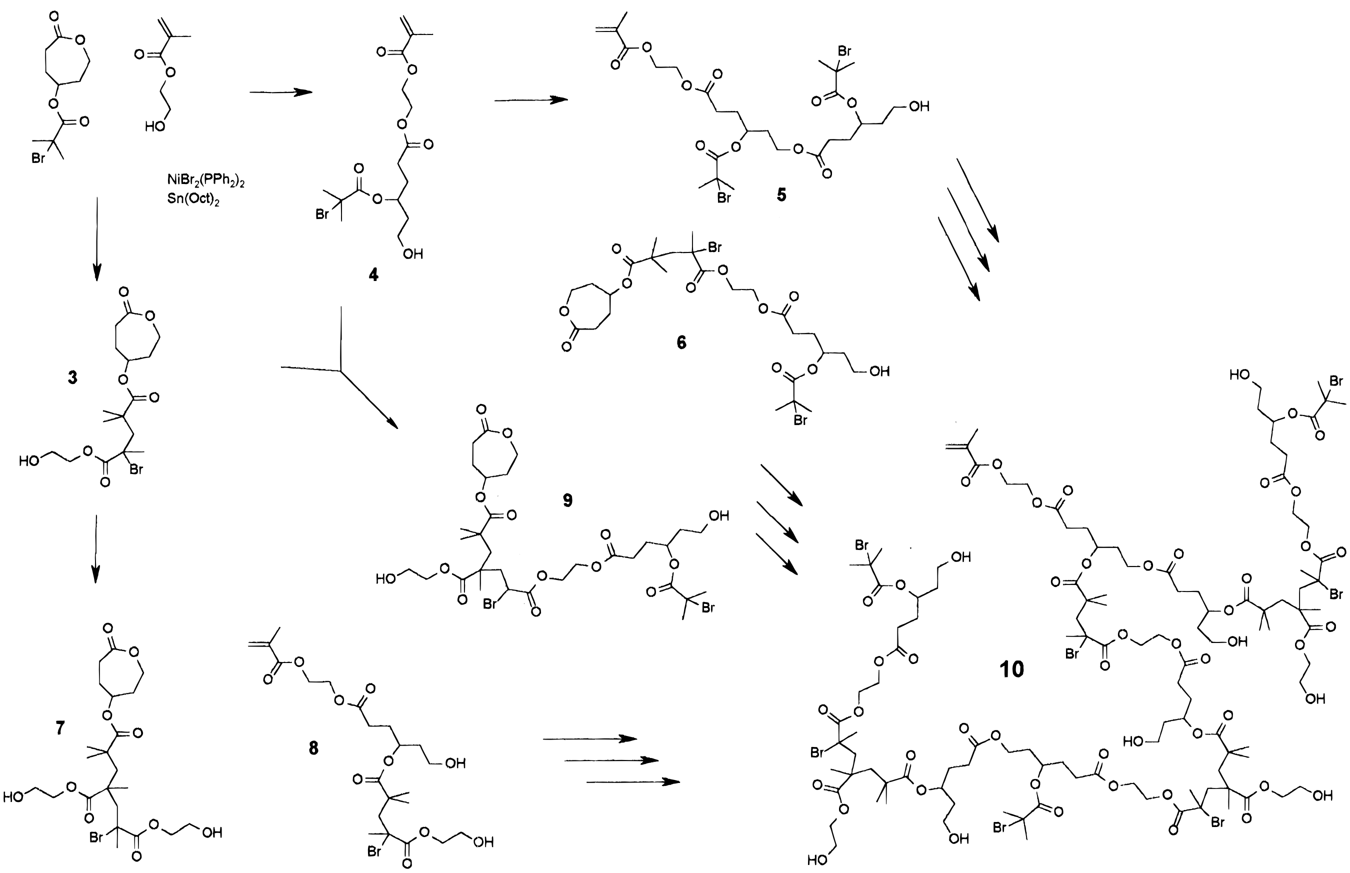
Scheme 1



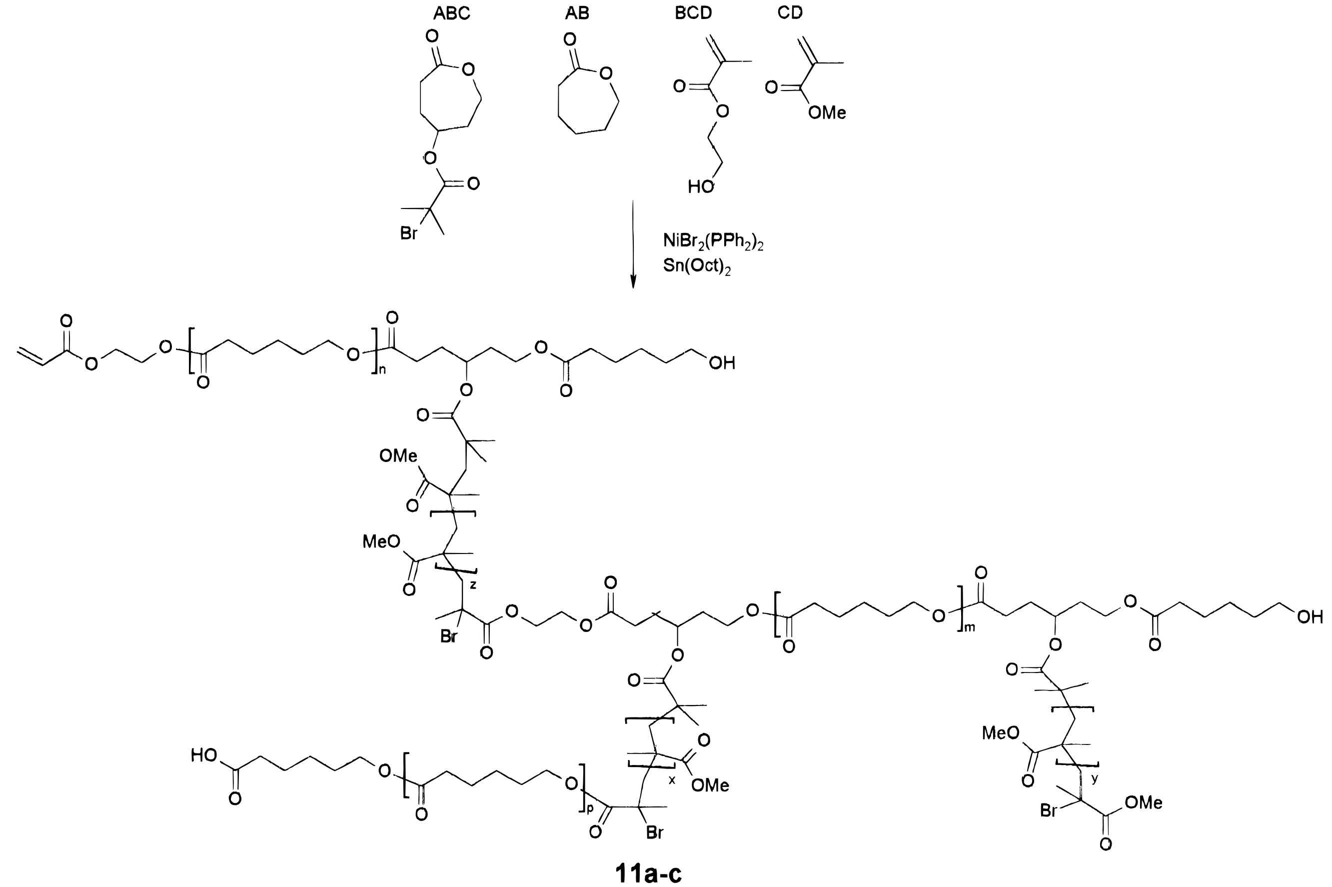
copolymers prepared by successive grafting procedures or to hyperbranched block copolymers[6] prepared from macromonomers yet, prepared by a single-step process.

The implementation of the single-step approach to branched copolymers is complex and requires that the two catalysts be compatible and tolerate each other and the monomer mixture. We have previously demonstrated that controlled radical and ring-opening polymerization meet these requirements.[2b,c] The use of either $Al(O^iPr)_3$ or $Sn(Oct)_2$ as the ROP catalyst has been shown to be compatible with many controlled radical polymerization conditions.[2c] Likewise, several ATRP catalysts were exercised including $CuCl(2,2'\text{-bipyridyl})_2$ complex, $FeBr_2/(PPh_3)_2$ complex, and $NiBr_2(PPh_3)_2$. The catalyst-to-monomer concentration in the self-condensing vinyl polymerization of 4-(chloromethyl)styrene using ATRP was reported to be critical in controlling the content of linear-to-branch species formed because of the unequal reactivity of the primary and secondary benzylic halide reactive sites.[1g] This is simplified in the ABC BCD polymerization because both the initiating and the propagating moieties are identical. Moreover, Gaynor et al.[1c] proposed that high catalyst concentrations led to an enhanced rate of radical–radical coupling, promoting network formation.

In the concurrent polymerizations, the $NiBr_2(PPh_3)_2$ catalyst concentration was held constant relative to the amount of **1** (30 mol %) and $Sn(Oct)_2$ was used in catalytic amounts to activate the ATRP and ROP, respectively, using bulk conditions (85–100 °C). This general polymerization procedure was applied to the ABC/BCD monomer combination with and without additional AB (ϵ-caprolactone (ϵ-CL)) and CD (methyl methacrylate (MMA)) monomers. Although the mechanism for molecular weight attainment for each block is either by ring-opening or free-radical polymerizations, where molecular weight increases linearly with monomer conversion, the overall ABC BCD polymerization kinetics is believed to proceed by a stepwise coupling similar to a condensation polymerization.[1,7] Monitoring these polymerizations at various stages with size-exclusion chromatography (SEC) showed only dimers **(3** and **4)**, trimers (**5**–**8**), tetramers (**9**), etc., during the early-to-moderate polymerization times, whereas the evolution of oligomers and polymer was not observed until high conversions were obtained (72–100 h; Scheme 1). These data are consistent with earlier observations on analogous systems.[1] Scheme 1 shows only a selection of the many possible oligomers. The branched copolymers were isolated by precipitation into hexane or methanol in 85–90% yield. The concurrent polymerization of **1** and **2** yielded a polymer (**10**) with a number-average molecular weight of 5000, by SEC relative to a polystyrene standard, and a polydispersity of 2.20 (Scheme 1). The molecular weight is comparable to those reported for self-condensing vinyl polymerizations and is relative to polystyrene standards.[1b,c]

The concurrent polymerization of **1** and **2** was also surveyed with the addition of ϵ-CL and MMA with the objective of altering the branching density. This may reduce steric hindrance and enhance the propagation rate (Scheme 2). The four monomers **1**, **2**, ϵ-CL, and MMA were surveyed in the molar composition of 1:1:10:10 (**11a**), which should produce a symmetric copolymer with an average of one branching junction for every 10 repeating units of monomers, assuming quantitative monomer-to-polymer conversion (Figure la). This polymerization generated a copolymer with a M_n of 15 000

Scheme 2



11a-c

Table 1. ABC BCD Dual Polymerizations: Characteristics of Block Copolymers

sample entry	target				incorporated				M_n (SEC), g/mol	M_w/M_n
	ABC	BCD	AB	CD	ABC	BCD	PMMA comp. (average DP)	PLC comp. (average DP)		
11a	0.10	0.10	1.00	1.00	0.05	0.12	1.2 (16)	1.0 (9)	15 000	2.30
11b	0.05	0.05	1.00	1.00	0.037	0.05	1.0 (30)	1.1 (18)	30 000	3.28
11c	0.05	0.10	1.00	1.00	0.06	0.20	1.1 (22)	1.0 (9)	15 300	2.51

(SEC) and a broad and multimodal molecular weight distribution ($M_w/M_n = 2.30$) (Table 1). The broad dispersity, characteristic of a "self-condensing" polymerization, is similar to other reports[1,7] and has been described in detail by Müller et al.[7a–c,e] The structure and the molar composition of the branched copolymers was studied in detail by ^{1}H NMR spectroscopy (Figure 2) and, surprisingly, significant information on the copolymerization process was revealed. The overall composition of poly(methyl methacrylate) (PMMA) to poly(ϵ-caprolactone) (PCL) was found to be 1.2:1, which is close to the target value of 1:1.[8] The PCL block had an average degree of polymerization (DP) of 9 (target 10) and contained 5% of **1** (target 10%) (Table 1).[9] ^{1}H NMR spectroscopy showed that each of the alkyl bromide units (**1**) incorporated in the PCL blocks had initiated polymerization of MMA/**2** (Figure 4c). The PMMA block was found to have an average DP of 16 (target 10).[10] The higher DP of the MMA block can be explained by the lower than expected incorporation of **1** in the PCL block. The concentration of **2** in the PMMA block was found to be 12%, which corresponds well with the target value of 10%, and commensurate with this data is the accurate control of the PCL block.[11] To investigate the MMA block in more detail, the PCL was hydrolyzed by HCl (1 M) in dioxane.[2d,5e] Figure 3 shows the SEC traces of the branched copolymer **11a** and the PMMA block **12** remaining after the hydrolysis. The remaining PMMA block had a M_n of 1900 (SEC) and a polydispersity of 1.23, which clearly shows that the nickel-catalyzed radical polymerization is unexpectedly well controlled.

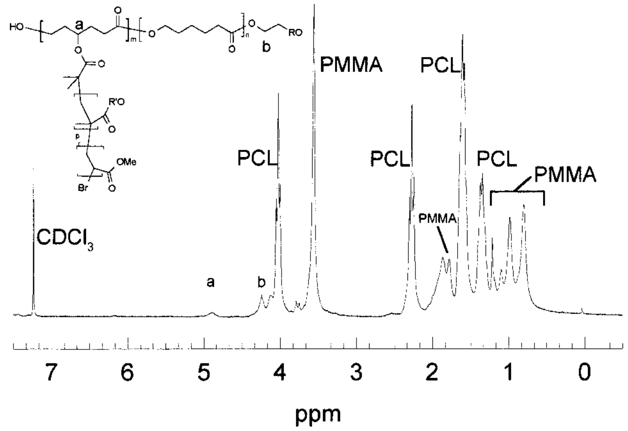


Figure 2. ^{1}H NMR spectrum of the branched copolymer **11a**.

Copolymers having two other molar compositions (1:1:20:20 **(11b)** and 1:2:20:20 (**11c**)) were also prepared,

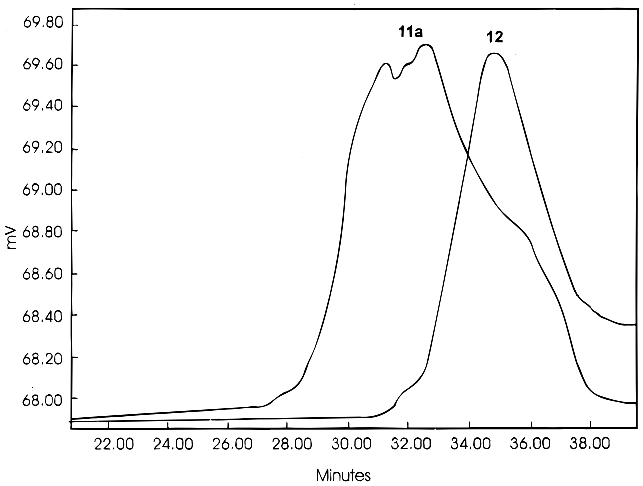


Figure 3. SEC traces of the branched copolymer **11a** and the PMMA block **12** remaining after hydrolysis of the PCL.

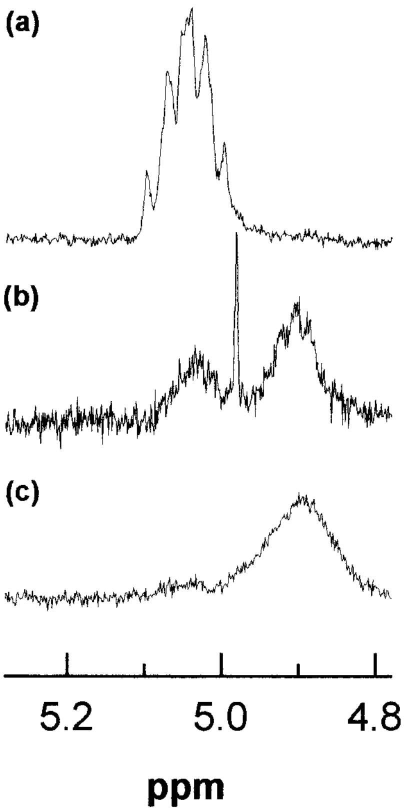


Figure 4. ^{1}H NMR spectra showing the α-methine ester signals before (δ = 4.90) and after (δ = 5.00) atom transfer radical initiation, i.e., (a) macromonomer **13**, (b) branched copolymer **15b**, and (c) branched copolymer **11a**.

with the objective of showing the versatility and simplicity in varying the architecture. For instance, the composition 1:1:20:20 should give a symmetric block copolymer with an average of one branching juncture for every 20 repeating units (Figure lb), while a 1:2:20:20 composition should give an asymmetric block copolymer with two shorter CL blocks initiated from each MMA block and only one MMA block from every CL block (Figure 1c). These polymerizations gave high molecular weight polymers (M_w = 30 000; 15 300) with broad polydispersities (3.28; 2.51). The polymer with the composition 1:1:20:20 was found to have a molar composition of PCL to PMMA of 1:1.1, which correlates very well with the target value of 1:1. Moreover, the CL block had a DP of 18 (target 20) and contained 3.7% **1**, which correlates. well with the target value (5%). All of the pendent alkyl bromides **1** in the CL blocks initiated the polymerization of MMA/**2** with an average DP of 30 (target 20). Again, the higher than expected DP of the MMA block correlates well with the lower than expected concentration of **1** in the CL block. The concentration of **2** in the MMA block was found to be 5% (^{1}H NMR), which is identical with the target value. Clearly, this synthetic route provides an efficient and simple route to highly branched and defined copolymers.

The modest molecular weights might be explained by the compact molecular structure, typical of hyperbranched polymers.[12] This is partially supported by the higher molecular weights obtained by SEC for the less branched polymers. In addition, it is important to note that, in such “step-growth” type polymerizations, high conversions are required to facilitate molecular weight. We have previously reported that the monomer-to-polymer conversion and molecular weight distribution are somewhat compromised in copolymers prepared by the simultaneous living polymerization procedure.[2b,c] Therefore, the modest molecular weights of the branched copolymers are probably a result of the nonquantitative conversions (85−90%) in these one-step syntheses. Furthermore, nonquantitative conversion may be one possible explanation for the low incorporation of **1** into the CL block, which may occur as a consequence of a lower rate of polymerization for this monomer relative to CL.[2c,6] Finally, some metal catalysts have been reported to cause elimination of alkyl bromides.[2d,13] In this case, a methacrylate would form that would participate in the polymerization process which may explain the higher than expected molecular weights of the MMA blocks.

To obtain further insight into the feasibility of the ABC/BCD polymerization approach to branched copolymers and to increase the understanding of the polymerization process, a sequential route to the target copolymers was employed to separate the two polymer-forming reactions and characterize the molecular weight and end groups (Scheme 3). First, a lactone functional AB$_x$ macromonomer **14** was prepared by polymerizing **2** and MMA using **1** as the initiator in the presence of 0.2 mol % $NiBr_2(PPh_3)_2$ at 80 °C. The structure and the composition of the macromonomer (M_n = 3000 (SEC), 2500 (^{1}H NMR); DP = 22 (^{1}H NMR); M_w/M_n = 1.51) was confirmed by ^{1}H NMR (Table 2). The macromonomer had a 20% concentration of **2**, which was similar to the target (20%), and the lactone end group was clearly evident. The AB$_x$ macromonomer **14** was dissolved in CL and polymerized at 110 °C in the presence of $Sn(Oct)_2$. A very high molecular weight polymer **15a** was obtained (M_w = 125 000) with an expected broad polydispersity (8.15).[7] The yield was over 85%, and the composition of PCL/PMMA was 1.5:1, which is comparable to that expected from the polymerization feed (1:1), as measured by ^{1}H NMR spectroscopy. Although the initiation from the activated hydroxyl groups of the MMA block was almost quantitative (92% as measured by ^{1}H NMR spectroscopy), the CL blocks had an average DP (7.9) slightly larger than the target value (5). Moreover, the lactone end groups were no longer detectable. Prolonged reaction times (>20 h) resulted in a significant amount of gel, presumably because of high conversion of the $Sn(Oct)_2$-catalyzed ROP. The broad polydispersity further substantiated polymer growth by

Scheme 3

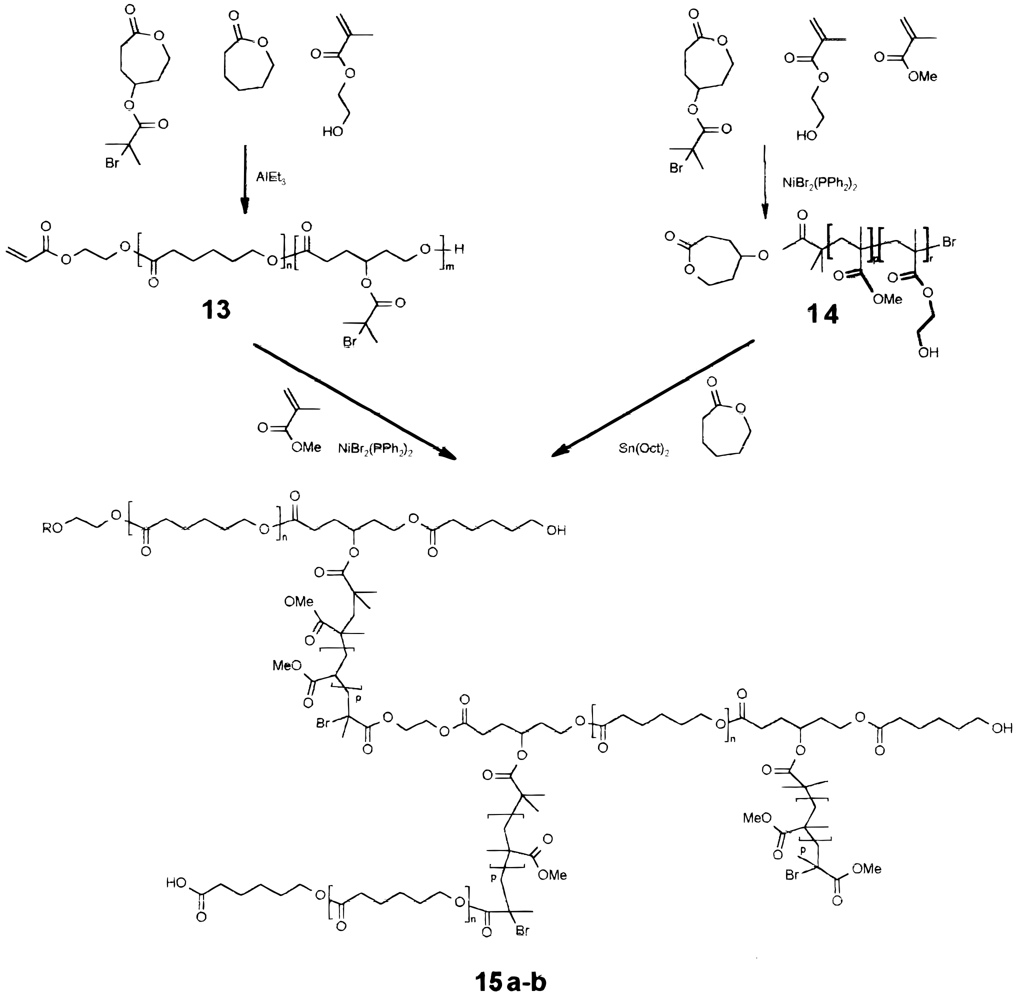


Table 2. ABC BCD Sequential Polymerizations: Characteristics of Block Copolymers

sample entry	AB$_x$ macromonomer					sample entry	block copolymer				
									composition (DP) yield		
	type	M_n(HNMR)	M_n(SEC)	M_w/M_n	DP		M_w(SEC)	M_w/M_n	PLC	PMMA	%
14	PMMA	2500	3000	1.51	22	**15a**	125 000	8.15	1.51 (8)	1.0	92
13	PCL	2400	6500	1.40	20	**15b**	208 000	6.22	1.00	1.2 (20)	92

a stepwise approach and that these polymers are significantly different than graft copolymers prepared from macromonomers or macroinitiators with polydispersities between 1.2 and 1.4.[2c,14]

Alternatively, the target branched copolymers were elaborated by a sequential route that first involves the preparation of a MMA-terminated PCL AB$_x$ macromonomer (**13**) containing pendent-activated alkyl bromides, followed by its cocondensation with methyl methacrylate (Scheme 3). This was accomplished by ROP of **1** and CL in toluene, initiated by **2** using AlEt$_3$ to form the active aluminum alkoxide. The molecular weight was comparable to that predicted from the monomer-to-initiator ratio (M_n = 2400 (^{1}H NMR), 6500 (SEC); DP = 20 (^{1}H NMR)), the polydispersity was narrow (M_w/M_n = 1.40), and the conversion was quantitative (Table 2). The macromonomer **13** had a 7% concentration of **1** (^{1}H NMR), which is similar to that charged (10%). Furthermore, ^{1}H NMR spectroscopy clearly shows the resonances associated with the MMA end groups and pendent alkyl bromides (Figure 5a). The AB$_x$ macromonomer (where x is 1 + 1.4 (7% of **1** × DP = 20)) was then dissolved in MMA and polymerized at 80 °C in the presence of NiBr$_2$(PPh$_3$)$_2$ (20 mol %). As before, a very high molecular weight polymer (**15b**; M_w = 208 000) with the expected broad polydispersity (M_w/M_n = 6.22) was obtained in 92% yield (Table 2). Figure 5 shows the ^{1}H NMR spectra of the macromonomer **13** and the branched copolymer **15b**, while Figure 6 shows the corresponding SEC traces. The composition (1:1.2) of the copolymer (PCL/PMMA) was comparable to that expected from the monomer feed (1:1) and consistent with the high conversion (Figure 5b). The MMA blocks had an average DP of 20 which is identical with the target value (20). However, only 75% of the activated alkyl bromides in the CL block had initiated the ATRP according to ^{1}H NMR spectroscopy (Figure 4).[11] To investigate the MMA block in detail, the PCL was hydrolyzed by HCl (1 M) in dioxane.[2d,5e] The remaining PMMA had a very narrow polydispersity of 1.19 and a number-average molecular weight of 1900 (SEC), which corresponds well with the average DP of 20, as measured by ^{1}H NMR spectroscopy, and the theoretically calculated DP of 20.

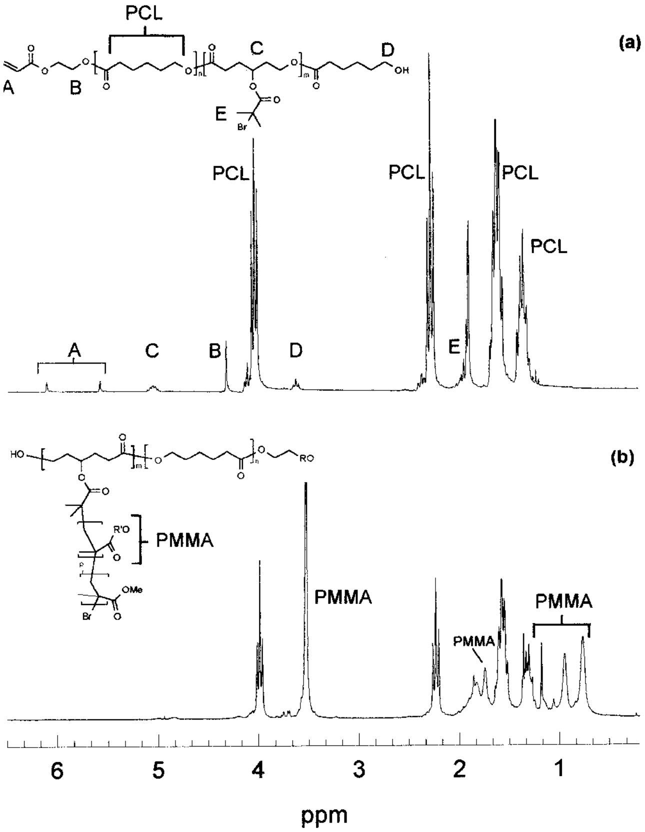


Figure 5. ^{1}H NMR spectra of the macromonomer **13** (a) and the branched copolymer **15a** (b).

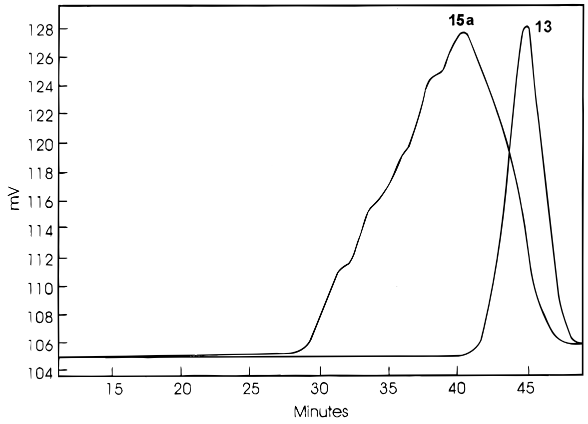


Figure 6. SEC traces of the branched copolymer **15a** and the macromonomer **13**.

The SEC data of the polymerizations performed sequentially indicate that very high molecular weight branched block copolymers with the expected broad polydispersities are possible by the ABC BCD polymerization approach. These data, in combination with careful NMR studies, have taught us about the control of the two different polymerizations (ROP and ATRP) involved. In addition, very effective characterization methods of the branched copolymers have been discovered through the use of these sequential model reactions.

In conclusion, we have introduced a new synthetic approach to branched copolymers, based on the novel combination of an ABC monomer and a BCD monomer. These two monomers that polymerize by different chemistries (ROP and ATRP) bear initiating centers for the opposite type of chemistry and polymerize concurrently in a one-step process. In this way, a branched copolymer is realized without going through a traditional multistep procedure. Considerable versatility in the macromolecular architecture is realized simply by the addition of the appropriate AB (CL) and/or CD (MMA) monomers and variation of the ratio of the two monomers. Another important and unique feature of this polymerization is that two populations of end groups, amenable toward numerous transformations, are realized. As a means of understanding the polymerization process and obtaining characterization handles, a sequential route to the branched copolymers was employed. This involved the synthesis and characterization of AB$_x$ macromonomers followed by the co-condensation with the opposite monomer(s). Due to the high conversions of the polymer-forming reactions, a high molecular weight copolymer was realized with the expected broad polydispersity. However, this ABC BCD polymerization technique needs to be optimized with respect to catalyst compatibility, solubility, polymerization kinetics, and possible homopolymer and intermolecular loop formation through the careful selection of monomers, initiators, catalysts, temperature, solvent, and reaction time. A combinatorial, or more precisely a high parallel, approach to this ABC BCD polymerization would facilitate the understanding and optimization of this new reaction.

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(8) The overall composition (PCL/PMMA) was determined by ^{1}H NMR spectroscopy, as the molar ratio of the integrated signal at $\delta = 4.10$ (t, 2H, $-\mathrm{C}\underline{\mathrm{H}}_2\mathrm{COO}-$) for PCL and the integrated signal at $\delta = 3.60$ (s, 3H, $-\mathrm{OC}\underline{\mathrm{H}}_3$) for PMMA.

(9) The DP's of the PCL blocks were calculated by a method previously reported.[5b]

(10) The DP's of the PMMA blocks were calculated by a method previously published: Heise, A.; Hedrick, J. L.; Trollsås, M.; Miller, R. D.; Frank, C. W. *Macromolecules* **1999**, *32*, 231 and references cited therein.

(11) The efficiency of the PMMA initiation was calculated as the molar ratio of the integrated signal at $\delta = 4.90$ (m, 1H, $-\mathrm{C}_2\underline{\mathrm{H}}\mathrm{COO}-$) for the branched polymer and the sum of the integrated areas for the signals at $\delta = 4.90$ and 5.00 (m, 1H, $-\mathrm{C}_2\underline{\mathrm{H}}\mathrm{COO}-$), as determined by ^{1}H NMR spectroscopy.

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