Simultaneous Dual Living Polymerizations: A Novel One-Step Approach to Block and Graft Copolymers**

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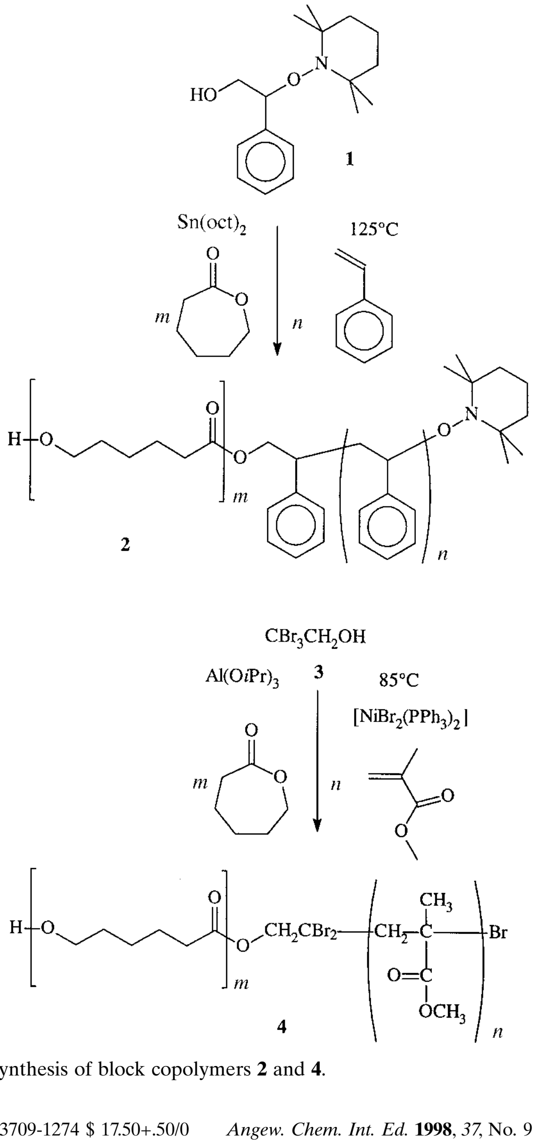
The need to control the polymer properties in an increasingly precise manner explains why the synthesis of block copolymers of well-defined macromolecular architecture is a continuing theme of research in polymer chemistry. Since its discovery by Szwarc et al.[1] in 1956, living polymerization remains the main tool for polymer chemists to efficiently control length, composition, and architecture of polymer chains.[2] The last two decades have witnessed the emergence of new "living" (controlled) polymerization reactions based on radical chemistry.[3] While not strictly living polymerizations, these new procedures have many of the attributes of traditional living polymerizations such as living anionic or cationic procedures. Among them, stable free radical polymerization (SFRP) and atom transfer radical polymerization (ATRP) are the most successful methods which allow molecular weight, polydispersity, and chain-end functionality to be controlled accurately. The renewed interest in the ring-opening polymerization (ROP) of lactones and lactides is justified by the capability of organometallic compounds to synthesize aliphatic polyesters of high molecular weight. For instance, ROP mediated by aluminum alkoxide has proved to be a living polymerization[4] and leads to the controlled synthesis of oligomers and block copolymers with functional groups at the chain ends.[5]

The traditional synthesis of block copolymers relies upon the sequential polymerization of corresponding comonomers by the same chemistry (e.g. anionic polymerization). Although this strategy may be successful, its extension to comonomers which do not polymerize by the same chemistry is usually a challenge. In this case, two strategies have been proposed: the coupling of preformed polymers with functional groups at the chain ends and the use of a macromolecular initiator for the polymerization of the second monomer. The second strategy usually requires a sequence of transformation reactions to convert the propagation center of the first block into an initiating site for the polymerization of the second monomer. Whichever method is used, two polymerization steps cannot be avoided.

Here we propose a new strategy for the one-step synthesis of block copolymers. It involves the use of an asymmetric difunctional initiator that is able to start the simultaneous polymerization of two comonomers by different polymerization chemistries in such a way that this initiator remains attached to each type of growing chain. We previously reported the successful synthesis of diblock copolymers by a sequential two-step method without any transformation or activation of intermediates.[6] The implementation of this one-step synthesis is not straightforward: The two catalysts must be compatible and tolerate each other as well as the monomers, the reaction temperature must remain constant, and the kinetics must be closely controlled. "Living" radical polymerization and ROP by coordination and insertion can, at least in principle, meet these requirements (Scheme 1).



Scheme 1. Synthesis of block copolymers **2** and **4**.

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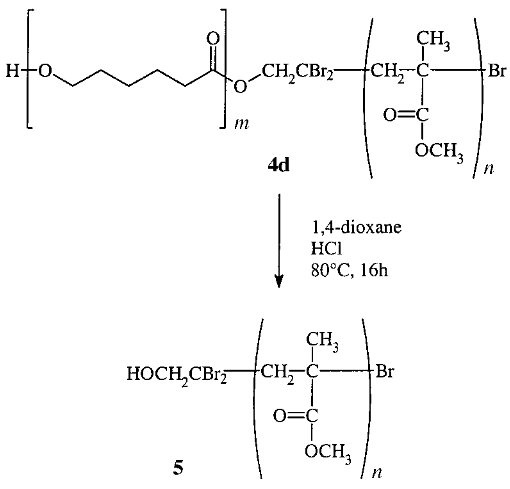
Initiator **1** contains a single primary alcohol functionality, which is the initiation center for the living ROP of cyclic lactones, as well as a secondary benzyl group linked to an alkoxyamine; the benzyl group is an efficient initiator for the nitroxide-mediated "living" free radical polymerization of styrene. Polymerization of a mixture of styrene (S) and ε-caprolactone (CL) initiated by **1** in the presence of Sn(oct)$_2$ as ROP catalyst produces the block copolymer PS-b-PCL (**2**; "P" = poly). Analysis of the molecular weight M_n of **2** at various levels of conversion reveals a linear relationship, which agrees with the "living" or controlled nature of both polymerization processes. In the same way, 2,2,2-tribromoethanol (**3**) contains a single primary alcohol functionality and an activated bromoalkyl group, which is an efficient initiator for the ATRP. Thus, polymerization of a mixture of methyl methacrylate (MMA) and ε-caprolactone initiated by **3** in the presence of Al(O*i*Pr)$_3$ as ROP catalyst and [NiBr$_2$(PPh$_3$)$_2$] as ATRP catalyst[7] leads to the formation of the block copolymer PMMA-b-PCL (**4**). The characteristics of the copolymers are shown in Table 1. Particularly noteworthy are the unusually high conversions (70–90%) for these polymerizations, even though they are performed without any added solvent in an unusual dual-monomer bulk procedure. Interestingly, under both sets of reaction conditions, the ROP occurs at a much faster rate than the "living" free radical polymerization, which results in a reduced molar fraction of caprolactone in the product upon increasing the reaction time or the number of conversions. For example, the mole fraction of caprolactone in **4** decreases from 85 to 61 to 48% on increasing the reaction time from 1 to 4 to 20 hours, while a concomitant increase in the conversion from 55 to 80 to 95% is observed. The molecular-weight distributions are somewhat broader (1.5–2.3) than for most living polymerizations, possibly owing to inadequate kinetic control and occurrence of side reactions, particularly polyester transesterifications. The extent of the transesterifications is decreased by the addition of pyridine when the ROP catalyst is an aluminum alkoxide.[8] This is confirmed by a narrower molecular-weight distribution in the case of polymers **4d** and **4e** (Table 1). The most important observation is the relatively good agreement between the molecular weights calculated from the monomer-to-initiator molar ratio and the experimental values. Even though the molecular weights are not absolute values (calibration of size-exclusion chromatography (SEC) with PMMA or PS standards), they are in the range of the expected values. ^{1}H and ^{13}C NMR and IR spectra of the block copolymers show signals typical for the different blocks, and SEC analysis shows unimodal molecular-weight distributions. The dynamic mechanical thermal analysis (DMTA) of block copolymer **2** also shows two glass-transition temperatures, one each for the caprolactone block and the polystyrene block. To conclusively confirm the formation of the block copolymer, **4d** was hydrolyzed with HCl to poly(methyl methacrylate) (**5**, Scheme 2). The ^{1}H NMR and IR spectra clearly show the total disappearance of the poly(caprolactone) block and, as expected, a complete shift of the SEC trace to lower molecular weights. The experimental molecular weight of **5** ($M_n = 7000$ g mol^{-1}) is in good agreement with the theoretical molecular weight ($M_n = 6000$ g mol^{-1}), and the polydispersity is low (PDI = 1.2). This observation confirms the reliability of the synthetic strategy and the production of only negligible amounts of homopolymers.

Table 1. Synthesis of block copolymers PS-b-PCL (**2**) and PMMA-b-PCL (**4**).

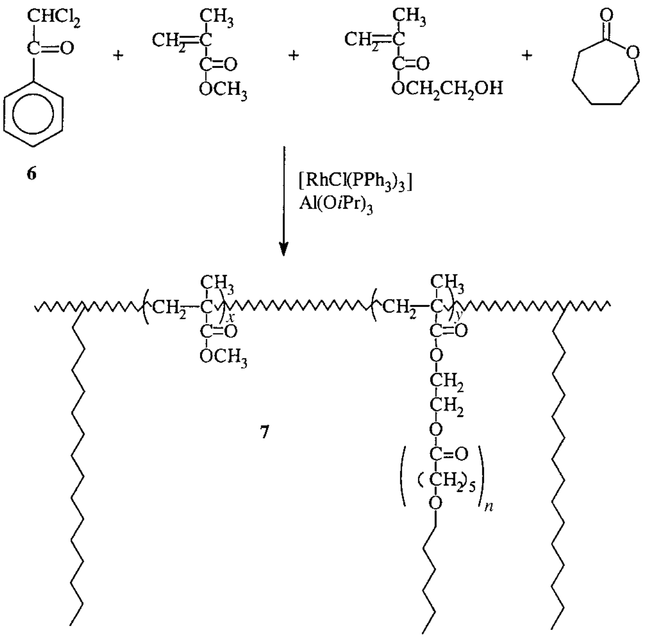
Polymer	T [°C]	t [h]	f_{CL}[a]	F_{CL}[b]	Yield [%]	$M_{n(theor)}$[c]	$M_{n(SEC)}$[d]	M_w/M_n
2a	125	12	0.5	0.67	70	6000	6300	1.6
2b	125	24	0.5	0.60	75	12000	14000	1.7
2c	125	24	0.33	0.38	85	18000	17000	1.4
2d	125	24	0.25	0.26	85	24000	21000	1.5
4a	75	20	0.47	0.48	95	20000	20000	2.3
4b	75	1	0.47	0.85	55	10000	25000	1.3
4c	75	4	0.47	0.61	80	16000	24000	1.9
4d[e]	75	4	0.47	0.63	85	17700	26000	1.4
4e[e]	75	4	0.47	0.67	87	8700	11000	1.4
4f	60	13	0.47	0.70	75	7500	13000	1.7
4g	60	13	0.47	0.70	75	15000	26000	1.7

[a] Molar ratio of ε-caprolactone in the feed: $f_{CL} = [CL]_0([CL]_0 + [MMA\ or\ S]_0)^{-1}$. [b] Molar ratio of ε-caprolactone in the copolymer as measured by ^{1}H NMR spectroscopy. [c] Theoretical molecular weight = $\{[CL]([initiator] \times 114)^{-1})\} + \{[MMA\ or\ S]([initiator] \times 100)^{-1}\} + MW_{INIT}$. [d] $M_{n(SEC)}$ with use of PS (**2a**–**2d**) or PMMA (**4a**–**4g**) as standards. [e] Addition of three equivalents of pyridine (with respect to Al(O*i*Pr)$_3$).



Scheme 2. Hydrolysis of **4d**.

Interestingly, the "one-step" approach can be extended to the synthesis of graft copolymers. This strategy is illustrated in Scheme 3 for the particular case of the simultaneous "living" radical copolymerization of MMA and 2-hydroxyethyl methacrylate (HEMA), initiated by 2,2-dichloroacetophenone (**6**) and catalyzed by [RhCl(PPh$_3$)$_3$], and the ROP of ε-caprolactone promoted by the hydroxyl groups from the HEMA units and Al(O*i*Pr)$_3$ as ROP catalyst. As an example of this one-step production of graft copolymers, polymerization of a 1:0.1:1 mixture of MMA, HEMA, and ε-caprolactone initiated by **6** gave the expected poly(MMA-g-CL) copolymer (**7**) after 18 hours at 50 °C. The polymer was isolated in 73% yield after purification by precipitation in heptane, and the presence of PMMA and PCL was confirmed by ^{1}H NMR spectroscopy. As with the block copolymers, the poly(caprolactone) grafts were hydrolyzed to analyze the molecular parameters of the backbone. ^{1}H NMR spectroscopy clearly



Scheme 3. Synthesis of graft polymer **7**.

shows the disappearance of the resonances for ε-caprolactone. Size-exclusion chromatography of the isolated backbone polymer reveals a molecular weight M_n of 30000, which is in agreement with that expected from the monomer-to-initiator molar ratio, while the polydispersity was quite low (M_w/M_n = 1.25).

A one-step approach based on dual simultaneous living polymerizations has been demonstrated to be a viable technique for the synthesis of a wide range of block and graft copolymers. The main advantages of this methodology are the bulk conditions used for the polymerization and the fact that only one step is required, making it very attractive from an industrial and academic point of view. Future work will concentrate on developing procedures for reducing the polydispersity of the block copolymers, which are broader than those obtained by traditional anionic procedures, as well as extending the method to other monomer and monomer combinations.

Experimental Section

Starting materials: 2,2,2-Tribromoethanol (97%), [$NiBr_2(PPh_3)_2$] (99%), [$RhCl(PPh_3)_3$] (99%), pyridine (99%), and 2,2-dichloroacetophenone (99%) were purchased from Aldrich and used as received. Triphenylphosphane (Aldrich) was purified by recrystallisation in methanol. Methyl methacrylate (MMA, 99% Aldrich), styrene (S, 99% Aldrich), and ε-caprolactone (CL, 99% Janssen) were dried over CaH_2 for 24 h and distilled under high vacuum before use. 2-Hydroxyethyl methacrylate (HEMA, Aldrich) was dried over molecular sieves and distilled just before the reaction. THF and toluene were dried by heating under reflux over sodium benzophenone and degassed by bubbling nitrogen for 15 min just before use. Al(O*i*Pr)$_3$ (Aldrich, sublimed twice) was dissolved in dry toluene and titrated by complexometry with a standard solution of EDTA. Pyridine was dried over KOH and distilled just before use.

PS-b-PCL (**2**): In a typical experiment a 100-mL round-bottom flask that had been previously dried with a flame was charged with styrene (6.2 g, 62 mmol), CL (6.2 g, 54.3 mmol), and 1-phenyl-1*O*-(2,2′,6,6′-tetramethylpyperidin-1-yl)ethane-1,2-diol (0.2 g, 0.72 mmol) and heated to 120 °C under nitrogen. Sn(oct)$_2$ (0.004 g, 0.1 mmol) was added, and the reaction allowed to proceed for 12–24 h. Finally, the reaction mixture was dissolved in THF, and the block copolymer precipitated into cold methanol, filtered, and dried to provide a white powder.

PMMA-b-PCL (**4**): In a typical experiment [$NiBr_2(PPh_3)_2$] (0.074 g, 0.1 mmol) was introduced into a Schlenk tube that had been previously dried with a flame and purged with nitrogen. The tube was then closed with a three-way stopcock, and a cycle of evacuation and filling with nitrogen was repeated three times. Then MMA (1 g, 1 mmol) and CL (1 g, 0.88 mmol) were added with a syringe. Finally, a previously prepared solution of CBr_3CH_2OH (0.1 mmol) and Al(O*i*Pr)$_3$ (0.017 mmol) was added. The isopropyl alcohol contaminant of aluminum alkoxide was previously removed by azeotropic distillation with toluene. The reaction mixture was heated at 75 °C under N_2. After the appropriate reaction time, the reaction mixture was dissolved in THF, and the reaction ended with a small excess of HCl (0.1 M). The copolymer was precipitated by dropwise addition to cold heptane, filtered, and dried at 50 °C until a constant weight was obtained.

PMMA-g-PCL (**7**): In a typical experiment [$RhCl(PPh_3)_3$] (0.109 g, 0.12 mmol) and PPh_3 (0.217 g, 0.83 mmol) were introduced under nitrogen into a 100-mL round-bottom flask that had been previously dried with a flame and purged with nitrogen. Then MMA (3.56 g, 35.5 mmol), HEMA (0.41 g, 3.18 mmol), and CL (4.12 g, 36.1 mmol) were successively added with a syringe. Finally, 2,2-chloroacetophenone (0.23 mmol) and Al(O*i*Pr)$_3$ (0.15 mmol) were added, and the reaction mixture was heated at 50 °C . After 18 h the mixture was diluted with THF, and the graft copolymer precipitated into cold heptane (yield: 5.50 g, 73%).

General procedure for hydrolysis: the block copolymer (1 g) was dissolved in 1,4-dioxane/37% HCl (95/5, 30 mL). Hydrolysis was carried out at 85 °C for 16 h. The product was isolated by precipitation in cold methanol (yield: 0.30 g, 75%).

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