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Concurrent Chain and Stepwise Polymerizations for the Preparation of Block Copolymers in One Step

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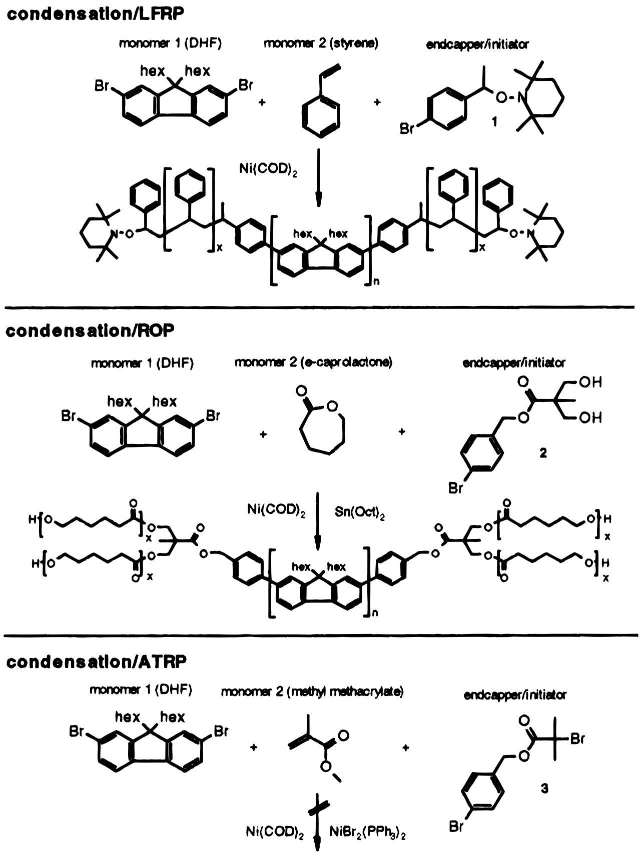
The control of polymer properties through the synthesis of block copolymers and complex macromolecular architectures is central to many areas of research and advanced technological applications.[1,2] Molecular structures such as AB or ABA-type block copolymers are important since many applications require a combination of desired properties in one material. Traditional strategies for the synthesis of block copolymers include the sequential polymerization of different monomer units using the same polymerization technique (i.e., anionic or cationic procedures) or the coupling of preformed reactively functionalized polymers. However, for some applications the desired block copolymer properties require the incorporation of highly dissimilar monomer systems, which in many cases can only be polymerized using fundamentally different chemistries. In this regard a number of consecutive polymerizations (e.g., cationic/radical, anionic/radical, and radical/ring opening from a double-headed initiator) have been reported.[3,4] The use of such initiators requires that one of the initiating units is chemically stable during the polymerization of the other. The utility of double-headed initiators was recently raised to a new level when the two different blocks were grown simultaneously.[4a] It was demonstrated that controlled living free radical processes such as nitroxide mediated (LFRP) and atom transfer radical polymerization (ATRP) were compatible with living ring-opening polymerization (ROP) of ϵ-caprolactone. This led to a variety of well-defined block copolymers. This technique has also been utilized in the concurrent polymerization of graft block copolymers through the use of new ABC monomers.[5] Although these polymerizations occur by different mechanisms, they are all chain reactions, which are kinetically similar. Here we report an expansion of the concurrent polymerization approach to include block copolymers where one of the blocks is prepared via a stepwise polycondensation technique.

We have previously described the Ni(0) mediated condensation polymerization of 2,7-dibromo-9,9-dialkylfluorenes and introduced in-situ end-capping not only as a method to control molecular weights but also as an approach for the introduction of reactive functionality at the polymer chain ends.[6] In order to combine a condensation polymerization with a controlled chain growth polymerization technique such as living free radical (LFRP) or living ring-opening polymerization (ROP) in a simultaneous process, new molecules that can serve both as end-cappers in the condensation and concurrently as an initiator have been developed. The end-capping moiety for the polycondensation is typically an aryl bromide while the selection of the initiator part is determined by the polymerizing comonomer. For the "living" component, we have studied ring opening (ROP), nitroxide mediated (LFRP), and atom transfer free radical polymerizations (ATRP). Each of these polymerization techniques utilizes available monomers such as lactones, lactides, styrenes, acrylates, etc., and represents "living"-type mechanisms which enable accurate control of molecular weight and narrow polydispersities.

Scheme 1



The end-capper **1** (1-(4′-bromophenyl)-1-(2″,2″,6″,6″-tetramethyl-1-piperidinyl-oxy)ethyl) was prepared under mild conditions by reaction of 4-bromostyrene with TEMPO in the presence of Jacobsen's catalyst {[*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato]manganese(III) chloride}.[7] The suitable end-capper/initiator for the ring-opening polymerization was prepared from 4-bromobenzyl bromide. Esterification with 2,2′-bis(hydroxymethyl)propionic acid (bis-MPA) yielded the diol functionalized ROP initiator **2**. The proper choice of bis-MPA derivatives allows the introduction of multiarm initiators with two, four, or more initiating sites.[8] The end-capper/initiator for the atom transfer polymerizations **3** was prepared from 4-bromobenzyl alcohol. Reaction with 2-bromoisobutyryl bromide led to the corresponding ATRP initiator.

The polymerizations were concurrently performed in one pot. An initiator/end-capper, two different monomers, and either one or two catalysts were mixed in suitable order (Scheme 1). Increasing the temperature started the respective polymerizations. This approach was successfully applied to the preparation of ϵ-capro-

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Table 1. Characteristics of the Prepared Block Copolymers

polymer (entry) method	monomer ratio	M_w/M_n (GPC)	M_n (GPC)	molar ratio (^{1}H NMR)
PCL/PDHF (1) ROP/cond	CL/DHF 10/1.25	2.39	17 000	PCL/PDHF 10/0.8
PCL/PDHF (2) ROP/cond	CL/DHF 10.5/1	1.80	25 000	PCL/PDHF 10/3.5
PCL/PDHF (3) ROP/cond	CL/DHF 10/0.4	1.65	31 600	PCL/PDHF 10/0.3
PS/PDHF (4) LFRP/cond		1.52	36 000	PS/PDHF 70/30
PMMA/PDHF (5) ATRP + cond[a]		1.64	83 000 [b]	PMMA/PDHF 93/7

[a] This polymer was prepared in a stepwise approach. [b] PDHF 3800.

lactone/di-*n*-hexylfluorene (DHF) block copolymers. In this case, one-step synthesis of block copolymers requires two separate catalysts, Ni(COD)$_2$/2,2′-bipyridyl and Sn(Oct)$_2$. Fortunately, the two catalysts are compatible, and the polymerization reactions are each highly chemoselective and yield narrowly dispersed block copolymers. In a further demonstration of versatility of the one-pot procedure, the aryl−aryl condensation reaction and nitroxide mediated living free radical polymerization (LFRP) have been combined. In this case, styrene is used as both a monomer and solvent. Attempts to combine ATRP with aryl−aryl coupling in a simultaneous procedure were somewhat more complicated since the ATRP initiators (α-haloesters) appear to be unstable under the conditions of the condensation polymerization. In this case, ^{1}H NMR spectroscopy studies revealed that some dehalogenation of the ATRP initiator occurs, which corresponds well with observations made by Masters et al.[9] This difficulty can be circumvented by the initial synthesis of a telechelic polymer containing alcohol functionalities (e.g., end-capping with either 4-bromobenzyl alcohol or the 4-bromobenzyl ester of bis-MPA, **2**). Subsequent reaction with 2-bromoisobutyryl bromide leads to the corresponding ATRP macroinitiators. Polymerization of methyl methacrylate (MMA) from the bis(2-bromo-2-methyl)propionic ester derived from the 4-arm macromolecular initiator catalyzed by bis(triphenylphosphine)nickel dibromide yielded the corresponding DHF/MMA block copolymer (Table 1, entry 5).[10]

The nature of the prepared block copolymers was studied by a combination of analytical techniques, including size exclusion chromatography (SEC) and ^{1}H and ^{13}C NMR spectroscopy. The SEC traces in all cases were monomodal with relatively narrow molecular weight distributions (Figure 1 and Table 1). This, in combination with the high conversions (>95%), clearly suggests the formation of block structures. To confirm that the two polymer blocks were indeed covalently bonded to each other, an end-capped DHF homopolymer containing the ROP end-capper/initiator was prepared as a model compound. Examination of the ^{1}H NMR spectra of the model compound and the PCL/DHF block polymers respectively showed unique resonances for the methylene and the benzyl protons of the bis-MPA unit for the two polymers (Figure 2). The chemical shifts observed correspond well with earlier observations using bis-MPA as an “initiator” for ROP.[11] In addition, the PCL part of the block copolymer (M_n = 28 600, M_w/M_n = 1.80) was selectively hydrolyzed by HCl (1 M) in dioxane, which resulted in a DHF homopolymer containing the bis-MPA end-cappers. The ^{1}H NMR spectrum from the polymer remaining after hydrolysis corresponds exactly with the spectrum of the model compound. The remaining polymer from the hydrolysis had a M_n of 13 900 and a polydispersity of 2.57 according to SEC analysis. Although the hydrodynamic volumes for the block copolymer (flexible) and the remaining DHF homopolymer (rigid) should be different, this clearly suggests that the poly(caprolactone) was initiated from the end-capper/DHF block. Furthermore, no bromide-bound aromatic carbons could be detected in the block copolymer by ^{13}C NMR spectroscopy, indicating that all the DHF blocks were indeed attached to the end-capper/PCL block. However, the concentration of these carbons could be fairly low and may not be detectable under the analysis conditions. For this reason, 2-bromo-9,9-di-*n*-hexylfluorene monomer in a 2 wt % concentration (relative to block copolymer) was added to the sample. In this case, a clear signal for the bromide bound carbon appeared at 121.3 ppm, clearly distinguishable from the aromatic carbon atoms in the polymer. This result is consistent with earlier MALDI-TOF studies on well-defined DHF oligomers produced by end-capping polymerization which showed that two end-capping groups were incorporated into each oligomer chain.[6] These results, in combination with the data from SEC and ^{1}H NMR spectroscopy, clearly suggest

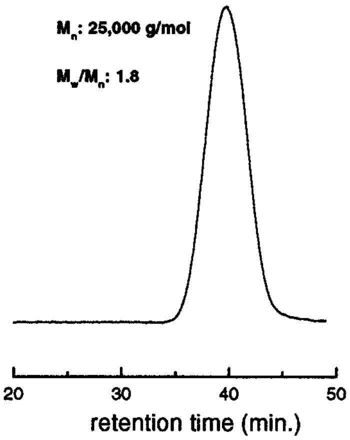

Figure 1. SEC trace of a PCL/PDHF block copolymer.

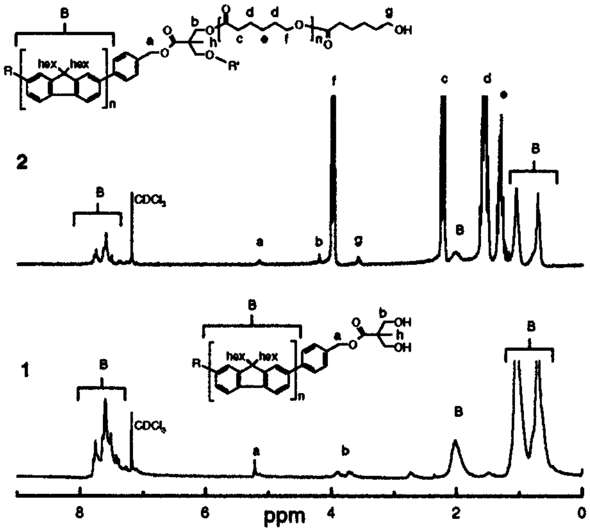

Figure 2. ^{1}H NMR spectra of the hydroxyl-functional PDHF model compound (**1**) and a PCL/PDHF block copolymer (**2**). The resonances of the methyl group of the bis-MPA (h) are hidden under the repeating units of PCL, while the DHF peaks (δ 7.3−7.8) overlay the aromatic protons of the benzyl groups.

that true block copolymers have been prepared. These results allow us also to conclude, within the detection limits of the analytical methods used, that no fluorene homopolymer should be present.

In addition, the quantitative disappearance of the bromide bound carbons, as observed by ^{13}C NMR spectroscopy, suggests that the block copolymers may have an ABA structure. To further investigate the actual structure (AB or ABA block copolymer), a series of PCL/PDHF block copolymers were prepared by the simultaneous growth approach. The length of the DHF block was maintained constant (i.e., a constant molar ratio of dibromide/monobromide was utilized), but the size of the PCL block was varied by changing the relative concentration of ϵ-caprolactone monomer in the polymerization mixture. Although the molecular weight was controllable for the polymers comprising short PCL segments (degree of polymerization (DP) < 20) (Table 1, entry 1), it was difficult to control the overall molecular weight for the block copolymers comprising larger PCL blocks (DP > 20) (Table 1, entry 3). We speculate that this may be due to a reduced rate of the condensation polymerization, as the PCL block grows longer at higher conversions. This can be explained by the different nature of the polycondensation reaction and the “living” ring-opening polymerization. The molecular weight of the PCL block increases linearly with conversion, whereas the PDHF block grows slowly and reaches high molecular weight only at high conversions ($>95\%$). Consequently, this may reduce the rate of the condensation polymerization and prevent the condensation polymerization from reaching high conversions. The critical points, where the rate of condensation is almost zero and consequently the conversion of the condensation reaction stops, may be dependent on the molecular weight of the ϵ-caprolactone block. This would rationalize the problem of controlling the overall molecular weight of the block copolymer.

In conclusion, we have demonstrated simultaneous condensation and chain polymerization to produce block copolymers in one step. This was possible through the introduction of new unimolecular compounds, which can simultaneously act both as an initiator for chain polymerizations and as an end-capper for condensation polymerizations. ^{1}H and ^{13}C NMR spectroscopy in combination with SEC were used to confirm the block structures. This provides a simple and yet novel synthetic method to combine ROP, LFRP, or ATRP with a condensation polymerization to yield interesting and useful block copolymers. It was concluded that the preparation of more well-defined ABA structures is hampered by kinetics and requires a stepwise strategy involving prior polymerization and end-capping of the DHF block. That block can then be used as a macroinitiator to afford the final ABA structure. A more detailed study of this approach will be reported separately.

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Supporting Information Available: Synthesis and characterization of the end-capping initiators as well as experimental procedures for the preparation of the block copolymers reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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