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Summary: We report the synthesis of well-defined block copolymers by covalent coupling of hydroxy end-functionalized polymers. Using the high volatility of the coupling agent phosgene as compared to the solvent, very high conversion (up to 96%) is obtained in a one-pot reaction with as little as 10^{-5} moles of each of the reacting polymers, even

without prior purification of the as-received reagents. This has potential as an alternative to the currently practiced method of sequential living polymerization of constituent monomers, with the added advantage of direct knowledge and control over the length distribution of each block.

Coupling of end-functionalized polymers using phosgene to form block copolymers of controlled composition.

Precise Block-Copolymers by Efficient Coupling of End-Functionalized Polymers Using Phosgene^a

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Introduction

Ever increasing efforts are being directed towards investigations of the self-assembling characteristics and potential applications of block copolymers.^[1] Block copolymers are most often synthesized by the sequential incorporation of monomers by living/controlled polymerization techniques. One remaining problem is the difficulty associated with control and evaluation of the length distribution of the second (and later) block, even as liquid chromatography under critical conditions emerges as a possible analytical tool.^[2] The living/controlled polymerization techniques have also provided a facile synthesis of end-functionalized homopolymers, either by chain growth from functionalized initiators or by terminating growing chains with suitable

functionalized units.^[3] Coupling of these end-functionalized homopolymers can provide an alternative technique for the formation of blocks of high-molecular-weight copolymer synthesis, while retaining information and control over the length distribution of the individual blocks. Such coupling of the dissolved polymeric chains at the involved low molar concentrations requires a very efficient reaction, and is particularly successful for direct coupling of preformed *living* blocks under very stringent purity considerations.^[4] Condensation reactions of α,ω -difunctional oligomers, sometimes with the aid of difunctional coupling agents (such as bisoxazolines, diepoxides, diisocyanates, dianhydrides, and phosgene), have been widely described for chain extension as well as for the synthesis of multiblock copolymers.^[5] However, such reactions do not demand quantitative coupling, and lead to polymers of wide molecular weight distribution (MWD) even when starting with oligomers of narrow MWD. While targeting di/triblock copolymers from such reactions of end-functionalized homopolymers, the limitation with regards to

^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

obtaining high conversions is often handled by using a large excess of one homopolymer to drive high incorporation of the limiting homopolymer into the block copolymer, e.g., in the context of reactive compatibilization.^[6] Extraction processes can subsequently be used to remove the excess unreacted homopolymer. The requirement of a large excess of one homopolymer is somewhat alleviated by using difunctional coupling agents to enhance the activity of one constituent homopolymer. Such in-situ activation is also desirable to avoid deterioration of the minute amount of moisture sensitive end-functionality of the constituent homopolymers during handling. Self-coupling between molecules of the same homopolymer during such activation is possible and must be minimized. This can be achieved by using an excess of the coupling agent, though the activated homopolymer must be separated from the excess coupling agent before addition of the second homopolymer. However, this separation, and redissolution of this activated homopolymer for the subsequent polymer-polymer coupling, both result in substantial loss of the very reactive end-functionality, thereby limiting the copolymer yield.^[7] Here, the formation of block copolymers by a very efficient *one-pot* coupling reaction of even small quantities of high-molecular-weight end-functionalized polymers is described. It utilizes a unique characteristic of phosgene among coupling agents, its high volatility (bp = 8.2 °C, vapor pressure = 1 180 mmHg at 20 °C),^b which permits easy *on line* removal of its large excess used to avoid self coupling of the constituent homopolymer.

Experimental Part

Hydroxy-terminated polystyrene (HT-PS) and hydroxy-terminated polybutadiene (HT-PB) were obtained from Polymer Source Inc. HT-PS has a number-average molecular weight, $\bar{M}_n$, of 8 251, and a polydispersity index, $\bar{M}_w/\bar{M}_n$, of 1.062 (obtained by size exclusion chromatography (SEC) in tetrahydrofuran at 40 °C using polystyrene calibration). HT-PB has $\bar{M}_n = 9\,255$ and $\bar{M}_w/\bar{M}_n = 1.005$ (obtained from matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS)). Phosgene solution (20% in toluene, Fluka), pyridine (99+%, Acros), toluene (anhydrous, 99.8%, Aldrich), tetrahydrofuran (THF, AR stabilized with BHT, Biosolve), heptane (HPLC grade, Biosolve), dichloromethane stabilized with amylene (HPLC grade, Biosolve), and molecular sieves (pore diameter 3 Å, Fluka) were used as received. A Drierite gas-drying unit was obtained from

Aldrich. Standard polystyrene (S-PS, $\bar{M}_n = 11\,600$, $\bar{M}_w/\bar{M}_n = 1.03$) was obtained from Polymer Laboratories Ltd.

For the coupling of HT-PS with HT-PS, a three-necked round bottom flask (50 mL) was charged with HT-PS (0.092 g, 0.0112 mmol) and toluene (5 mL), stirred with a magnetic stirrer, and purged for 30 min with argon gas that was predried by passing through a Drierite unit. Phosgene solution in toluene (0.2 mL, 0.38 mmol phosgene) was added under rapid stirring. The escaping phosgene and HCl were neutralized by passing the outgoing gases through aqueous NaOH solution. After reaction for 5 min, excess phosgene was removed by bubbling with argon for 10 min. To this mixture was added a solution (0.023 mL) of pyridine (1.2 mol · L⁻¹) in toluene that was predried by storing over molecular sieves. HT-PS (0.092 g, 0.0112 mmol), predried under high vacuum (0.01 mbar) overnight in a 50 mL flask and stored under argon, was now added (at time $t=0$) under argon purge. Samples were withdrawn for SEC analysis at desired intervals. At the desired time, the reaction mixture was concentrated by argon flow to evaporate the solvent and to reduce the reaction mixture volume to 0.5 mL in 1 h. Further pyridine solution (0.023 mL) was added. After overnight reaction, the final sample was collected for SEC analysis.

The synthesis of the PS-*b*-PB block copolymer was carried out as in the preceding section, but starting with HT-PB (0.103 g, 0.0112 mmol) as the first polymer for phosgenation, while HT-PS (0.092 g, 0.0112 mmol) was added as the second polymer, and evaporation of the solvent was started immediately thereafter.

Size exclusion chromatography (SEC) measurements were carried out using a Waters GPC equipped with a Waters 510 pump, a Waters 410 differential refractometer (40 °C), a Waters WISP 712 autoinjector (50 µL injection volume), a PLgel (5 µm particles) 50 × 7.5 mm² guard column and two PLgel mixed-C (5 µm particles) 300 × 7.5 mm² columns (40 °C). THF (Biosolve, stabilized with BHT) was used as eluent at a flow rate of 1 mL · min⁻¹, dilute polymer solutions of 1 mg · mL⁻¹ were prepared, and a 50 µL solution was injected for analysis. Calibration was performed using polystyrene (PS) standards (Polymer Laboratories, 580 to 7.1 × 10⁶ g · mol⁻¹). Data acquisition and processing were performed using Waters Millennium 32 (v32) software.

For samples with partial conversion of CT-PS and HT-PS into the coupled product, the corresponding bimodal distribution in the chromatograms was resolved using the software PeakFit, by deconvolution into two gaussian peaks corresponding to the reactants and the coupled product. The peak areas were then obtained by the respective peak integration, and used for calculation of the conversion.

Gradient polymer elution chromatography (GPEC) was used to examine the copolymer content in the coupling product and was carried out on an HP 1100 liquid chromatograph (Agilent Technologies), equipped with a degasser, a quaternary pump, autosampler, column oven, and an evaporative light scattering detector (ELSD) ($\lambda = 250$ nm, flow 1.6 mL · min⁻¹, temperature 60 °C). A Zorbax SB-CN column (150 × 4.6 mm², $d_p = 5$ µm, Agilent Technologies) was used. Polymer samples (1 µL of a 5.9 mg · mL⁻¹ solution in THF) were injected, and a heptane/THF gradient was run from 95:5 to 2:80 (v/v) in 15 min, then to 0:100 (v/v) in 2 min. Calibration was performed

^b In comparison, an alternative coupling agent such as dimethyldichlorosilane (DMDCS) has a bp of 70 °C, and a vapor pressure of 130 mmHg at 20 °C. Therefore, the use of excess (and subsequent removal) of DMDCS is not a possibility. Cho et al.^[8] have pointed out several limitations of coupling with DMDCS even in living systems, as yields can be as low as 44% as a result of the formation of at least three species.

Figure 1. a) SEC curves of samples withdrawn at $t = 0, 10, 30$ min, 1, 2, 3, and 4 h during coupling of HT-PS with in-situ prepared CT-PS. Initial concentration of each polymer ($C_0 = 2.24 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, pyridine concentration $= 5.57 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$). The arrows point to the curves for increasing time of reaction. Resolution of the bimodal curves into two Gaussian peaks (reactants and product) permits calculation of conversion (x) as function of reaction time (t). b) Kinetic data in triplo (symbols). Second order kinetic fit $\frac{x}{1-x} = yC_0kt$ is included as a continuous line. Slope $= 0.00649 \text{ min}^{-1}$.

with the HT-PS, HT-PB, and PS-*b*-PB samples (PS₉₄₀₀-b-PB₉₀₀₀ from Polymer Source Inc.). Chromatograms were analyzed using HP Chemstation (Hewlett Packard) software.

Results and Discussion

The potential of synthesizing well-defined block copolymers by coupling end-functionalized homopolymers with phosgene is examined. First, the end-functionality of one homopolymer ($R_n\text{-OH}$, dissolved in toluene) is modified with phosgene (solution in toluene) to form a highly reactive chloroformylated homopolymer (Equation (1)):

A large excess of phosgene is needed to avoid self-coupling, which leads to a homocarbonate ($R_n\text{O-CO-OR}_n$). Because of the high reactivity of and excess phosgene used here, a quantitative conversion can be expected even while using the as-received polymer and solvent without further purification. Water, the often present reactive impurity in the solvent and polymer, can be tolerated since its phosgenation products (HCl and CO_2) are volatile and, hence, do not interfere with the subsequent reaction. In addition, the excess coupling agent must be removed from the reaction mixture. This is easily achieved by bubbling with argon for several minutes, because of the high volatility of phosgene as compared to the solvent toluene. Phosgene is a very toxic compound and requires careful handling. This is facilitated by the commercial availability of phosgene as a 20% solution which can be safely dispensed with a syringe in a fume hood.^[9,10]

The subsequent step involves the addition of a stoichiometric amount of the second polymer ($S_n\text{-OH}$) to couple

with the chloroformylated polymer (Equation (2)):

High conversion also demands high purity of the reactants and the solvent medium, and this necessitates addition of the predried second polymer without additional solvent. The second order reaction between polymeric species proceeds slowly at the very low concentrations employed ($< 0.0025 \text{ mol} \cdot \text{L}^{-1}$), but the rate is easily enhanced by partial solvent evaporation. Pyridine is used as a catalyst and as a HCl scavenger, and needs to be replenished after solvent evaporation. The results of efforts to quantitatively couple hydroxy-terminated polystyrene (HT-PS) with two hydroxy-terminated polymers: polystyrene (HT-PS) and poly(1,4-butadiene) (HT-PB) are described below.

Figure 1(a) shows the size exclusion chromatography (SEC) plots of several samples withdrawn during the coupling reaction of stoichiometric amounts of HT-PS ($\bar{M}_n = 8251$, $\bar{M}_w/\bar{M}_n = 1.062$, Polymer Source, Canada) with chloroformate-terminated polystyrene (CT-PS, $1.12 \times 10^{-5} \text{ mol}$) that was prepared in-situ by phosgenation (Reaction (1)) from the same HT-PS in toluene (5 mL). The chromatograms display a bimodal distribution, with a peak at $M_p = 9100$ ($\log M_p = 3.95$), which corresponds to the reactants (HT-PS and CT-PS), and a peak at $M_p = 18000$ ($\log M_p = 4.25$), which corresponds to the coupled product (PS-*b*-PS). With increasing conversion of the reactants HT-PS and CT-PS into the coupled product with reaction time, a decrease in the reactant peak and an increase in the product peak is seen.

MALDI-TOF MS and GPEC reveals that only a fraction ($y = 0.91$) of the total initial HT-PS is hydroxy-

terminated,^c and hence active. Estimating the ratio (z) of the area of the product peak ($\log M_p = 4.25$) to the total area of the bimodal peak, the conversion ($x = z/y$) is defined as the fraction of the *active* HT-PS that undergoes coupling by Reaction (2). The second-order rate constant is deduced from the corresponding linear kinetic plot (Figure 1(b)), where $k = 0.053 \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$, which indicates that 99% conversion can be expected only at $t = 254 \text{ h}$. Hence, in an otherwise identical experiment, the reaction rate is enhanced at $t > 4 \text{ h}$ by concentrating the reaction mixture. This is achieved by solvent evaporation (argon bubbling over 1 h) to a reaction mixture volume of 0.5 mL followed by replenishment of pyridine (lost during toluene evaporation). After overnight reaction, the conversion is found to be 92%. In an experiment targeting high total conversion, the step involving evaporation of the solvent is carried out immediately after addition of HT-PS in the second step. The final conversion after overnight reaction is 96%. This indicates that a limited extent of side reaction(s) is present, and has a larger influence during a slower coupling reaction at high dilution. When pyridine is added in large excess (10 times), it accelerated the initial reaction,^d but had a deteriorating effect on the final conversion (88%), presumably because of side reactions or an influence on the polarity of the reaction medium.

For coupling HT-PS with HT-PB, it is not possible to independently quantify the hydroxy end-functionality of the HT-PB ($\bar{M}_n = 9\,255$, $\bar{M}_w/\bar{M}_n = 1.005$, Polymer Source, Canada), so it is assumed to be the same as that for HT-PS, since the end-functionality is generated in the same manner, i.e., by termination of the anionic homopolymerization with ethylene oxide.

HT-PB ($1.12 \times 10^{-5} \text{ mol}$) is added to the in-situ prepared CT-PS ($1.12 \times 10^{-5} \text{ mol}$, end-functionality $y = 0.91$) in toluene (5 mL). The reaction mixture is concentrated by bubbling with argon over 1 h for solvent evaporation to a reaction mixture volume of 0.5 mL, followed by replenishment of pyridine. The SEC curve *a* (Figure 2) of the physical mixture of HT-PB and HT-PS (1:1 mole ratio) shows peaks at 14.9 and 15.7 min, which correspond to the two reactants. The SEC curve *b* (Figure 2) of the sample withdrawn at the end of the solvent evaporation procedure shows emergence of a peak at an elution time of 14.4 min, which corresponds to the coupled product (PS-*b*-PB), in addition to the peaks of the reactants

Figure 2. SEC curves (DRI response) of a stoichiometric physical mixture (curve *a*), and coupling reaction products at 1 h (curve *b*), 3 h (curve *c*), and overnight reaction (curve *d*). The peaks at 15.7, 14.9, and 14.4 min correspond to CT-PS (or HT-PS), HT-PB, and PS-*b*-PB, respectively. Curve (*e*) is obtained by subtracting a fraction of curve (*a*) from curve (*d*), so as to subtract the contribution of yet uncoupled reactants as judged from elimination of the 15.7 min peak in curve (*e*). Thus, the curve (*e*) corresponds to the PS-*b*-PB part in the product (curve *d*).

HT-PB and CT-PS also present in curve *a*. The SEC curve *c* of the sample withdrawn at 3 h shows further reduction of the CT-PS peak area, near merging of the HT-PB peak with the right-hand-side shoulder of the PS-*b*-PB peak, and an increase in the area of the PS-*b*-PB peak, which all correspond to the formation of the block copolymer from the two homopolymers. The SEC curve *d* of the sample obtained after allowing the reaction mixture to stand overnight shows an additional decrease in the CT-PS peak area, and a reduced right-hand-side shoulder in the PS-*b*-PB peak as compared to curve *c*. By trial and error, the fraction (q) of the stoichiometric physical mixture curve *a*, which, when subtracted from the final product curve *d*, resulted in the disappearance of the CT-PS peak (curve *e* thus representing the PS-*b*-PB fraction) is determined. This allows the conversion to be calculated as 97% based on the active end-groups.

GPEC is used to further confirm the formation of PS-*b*-PB in the overnight reaction product.^[12] A selection of HPLC column and solvent gradient allowed separation of the PS-*b*-PB block copolymer from the unreacted HT-PS and HT-PB homopolymers (Figure 3). The two homopolymers are also well separated, with a retention time difference of 5 min, which indicates that the selectivity of the selected gradient is high. The solid line in Figure 3 represents the chromatogram of the coupling product. The PS-*b*-PB peak, placed intermediate between the HT-PS and HT-PB peaks, is well resolved, and allows the area integration and conversion to be calculated as 95%. This is in good agreement with the conversion calculated from SEC.

^c See Supporting Information for details of MALDI-TOF and GPEC measurements and results towards the hydroxy-functionality of HT-PS. While the chromatographic technique allowed resolution/separation of the end-functionalized component for analytical purposes, and the literature^[11] describes preparative chromatography for 5–10 μg , we were unable to find a source for $\approx 1 \text{ g}$ quantity of the homopolymers of low polydispersity and 100% end-functionality.

^d See Supporting Information for conversion data for the case of low and high pyridine concentrations.

Figure 3. GPEC traces (ELSD signals) of the reactants HT-PS (dashed line) and HT-PB (dotted line), and the coupling reaction product (solid line).

Conclusion

A simple one-pot reaction for activating the end functionality of one polymer followed by a second-order reaction with another end-functionalized polymer provides quantitative coupling (conversion >95%), even without prior purification of the as received reagents. Block copolymers are, thus, easily synthesized while retaining direct information and control over the length distribution of each block. It opens up the possibility of a combinatorial approach to the synthesis of block copolymers of a wide range of molecular weights and compositions. A possible extension of our method to molecular weights much higher than about $10^4 \text{ g} \cdot \text{mol}^{-1}$ may require addressing the issues of a higher reaction time because of the lower concentration and diffusivity of end-groups, as well as a potentially lower maximum conversion as a result of the higher fractional contribution of the impurities in the reaction system.

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