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Controlled/Living Radical Polymerization in the Undergraduate Laboratories.

1. Using ATRP to Prepare Block and Statistical Copolymers of *n*-Butyl Acrylate and Styrene

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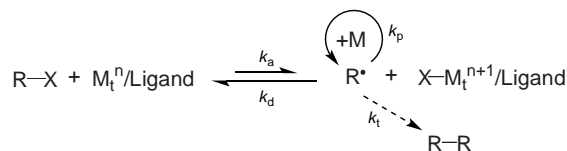
Background

Living polymerizations has become one of the most exciting and fast-paced areas of research in synthetic polymer chemistry (1, 2). Living anionic polymerization has found applications in industry ranging from surfactants to thermoplastics, but the conditions required for this type of chemistry are far more stringent than is amenable to most undergraduate laboratory courses. Recently, controlled/living radical polymerization has emerged as a more viable alternative to anionic polymerization, for several reasons. First, like conventional radical polymerizations, it can be performed under a fairly undemanding environment, often only requiring the removal of oxygen. Second, many more monomers can be polymerized via radical than ionic mechanisms, increasing the possible compositions of materials exponentially. Furthermore, the similar reactivity of radical chain ends almost regardless of the monomer structure increases the possible combinations of statistical copolymers that are accessible to radical polymerization.

There have been a number of reviews written on one such method of controlled/living polymerization, atom transfer radical polymerization (ATRP) (3–7). ATRP utilizes reversible halogen atom exchange between the propagating radical chain end and an inorganic catalyst to reduce the radical concentration and suppress the contribution of irreversible bimolecular termination, reactions that pervade conventional radical polymerization. This, combined with fast initiation from a small organic halide, R–X, with a sufficiently reactive C–X bond, leads to a polymer sample of fairly uniform molecular weight chains, which retain the halogen end group, X. We describe the uniformity of the polymer sample numerically with the polydispersity, which is the weight average molecular weight, M_w , divided by the number average molecular weight, M_n , and is typically less than 1.3 in these polymer samples as compared to 1.8 or more for conventional free radical polymerizations. Molecular weights can be predicted and controlled by the molar ratio of consumed monomer to initiator ($\Delta[M]/[I]_0$), assuming that initiation is quantitative (8).

The most commonly applied catalyst systems in ATRP include a transition metal compound, M_t^n , for example, Cu(I)X salt (where X = Cl or Br) complexed by bidentate or tridentate nitrogen ligands such as 2,2-dipyridyl-based ligands and

N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA), which is oxidized to Cu(II)X₂ upon homolytic cleavage of the carbon–halogen bond (Scheme 1) (9). The exchange equilibrium ($K_{eq} = k_a/k_d$, where k_a is the rate constant of activation of the polymer chain end and k_d is the rate constant of deactivation) necessarily favors the dormant organic halide species in order to maintain a low steady-state concentration of radical chain ends. It is the greatly reduced concentration of propagating radicals, [R•], that leads to a suppression of irreversible termination reactions (k_t) relative to propagation (k_p).



Scheme 1

ATRP has been applied successfully in an undergraduate synthetic organic lab under various conditions including the use of an additive to consume small amounts of air in the reaction vessel and thus eliminate the need for displacing oxygen with an inert gas (10). Discussed here are similar experiments conducted without additives under a nitrogen atmosphere. Both approaches are equally simple to apply; however, the method described here yields higher blocking efficiency and a lower amount of coupling product during the chain extension to prepare the ABA triblock copolymer.

In the lab described herein, poly(*n*-butyl acrylate) (p*n*BA, $T_g = -56^\circ\text{C}$) (11) was prepared from a difunctional initiator and the kinetics of the homopolymerization by ATRP were measured. This difunctional p*n*BA macroinitiator was then chain-extended with polystyrene (pS, $T_g = 100^\circ\text{C}$) (11) to prepare a thermoplastic elastomer. For comparison, a statistical copolymer of styrene and *n*-butyl acrylate of similar composition was also prepared by ATRP. Kinetic data for the homopolymerization were obtained from gas chromatography (GC), molecular weights were measured by size exclusion chromatography (SEC), and composition of the copolymers was determined using ¹H NMR (300 MHz).

This laboratory was designed to introduce upper-level undergraduates to the general principles of controlled/living radical polymerization and material synthesis. The structure of the experiment is intentionally modular, enabling the

application of different sections to different types of courses. An organic synthesis course may stress the kinetics of homopolymerization in controlled versus conventional systems or the difference in reactivities of two monomers that are polymerized simultaneously and the resulting effects on the composition distribution along the polymer chain. A polymer laboratory course or a course designed for engineering students may choose to focus on the types of materials prepared and investigation of their mechanical or thermal properties. This could exclude the use of GC and NMR in investigating the kinetics and chemical composition of the polymers. The characterization of polymeric products by SEC is relevant to both types of undergraduate laboratory.

Experimental Procedure

Depending on the objectives of the course and the allotted time for the experiment, there are several ways in which the work can be accomplished. As a team project, 3–4 students can work on separate stages of the whole experiment; one student can measure kinetics of free radical and controlled/living radical polymerization, one student can perform chain extension and statistical copolymerization to prepare the two material samples, and another student can be involved in material characterization. Several pieces of the whole experiment can be very effective in demonstrating synthetic polymer chemistry in 3–4 three-hour lab periods.

All reagents used in the experiment are available commercially. Inhibitors were *not* removed from the monomers and all reagents were used as received from Aldrich or ACROS chemicals.

On the first day, homopolymerization(s) of *n*-butyl acrylate (*n*BA) should be carried out using ATRP or a conventional radical initiator such as 2,2'-azobisisobutyronitrile (AIBN). If the focus of the lab is to be material synthesis, kinetics need not be measured. If the focus is organic synthesis, 5 or 6 kinetic samples from each reaction are sufficient to analyze the progress of the reactions. Students should calculate the molar concentrations and ratios of all of the reagents used in ATRP to obtain theoretical molecular weights of the polymer at various conversions (measured by GC). A commercially available difunctional initiator is used for the ATRP of *n*BA, enabling an ABA triblock copolymer, poly(styrene-*b*-*n*-butyl acrylate-*b*-styrene), to be prepared on the second day by chain-extending in two directions. The homopolymerization reaction mixture should not be exposed to air and should be stored at <0 °C to reduce the contribution of further polymerization.

On the second day, the chain extension of the homopolymer, *p**n*BA, prepared by ATRP should be carried out with styrene (S) as well as the statistical copolymerization of S and *n*BA. The molar ratios of the two monomers in the chain extension are chosen in such a way that the optimal ratio of 3:1 *n*BA:S is obtained at significantly less than quantitative conversion. This avoids the large contribution of coupling products, which may occur at high conversions of styrene under these conditions (i.e., high radical concentrations). Although there is some gradient character to the statistical copolymer due to the different reactivity ratios of S and *n*BA, there is no observable difference in the properties of the polymers obtained from growing the chain in one direction

as opposed to two. Hence, use of the significantly cheaper monofunctional initiator, methyl 2-bromopropionate, is recommended.

On the third day, the catalyst should be removed from the polymers prepared by ATRP and all samples should be isolated by precipitation and dried. The kinetic samples should be analyzed using GC and SEC (however, this can carry into the fourth day if necessary). Finally, material characterization may require less than one class period if ¹H NMR to determine compositions of the copolymers is sufficient; otherwise more time to measure thermal properties (*T*_g), or mechanical properties is necessary. Students should at least be able to qualitatively observe the differences between the block and statistical copolymers. It should be kept in mind how much material will be necessary to carry out the final experiments, so that large enough samples are obtained from the synthesis. Yields from the precipitation of poly(*n*-butyl acrylate) can be quite low (<50%) if students are careless or pressed for time.

Hazards

All the reactions in this experiment should be carried out in well-ventilated fume hoods. All chemicals should be handled in fume hoods and protective clothing, including lab coats, protective gloves, and eyewear, should be worn.

Liquid waste should be collected and labeled as halogenated organic waste containing copper salts, although only trace amounts of either of these two species are present in the liquid waste. Initiation from the organic halides is near quantitative, incorporating the halogens into the polymers, which can be disposed of as solid waste. The copper salts (along with the triamine ligand) are reduced to ppm quantities in the liquid wastes by use of an ion-exchange resin and filtration through alumina, transferring the heavy metal salts into solid waste as well.

Both of the monomers used in this experiment, styrene and *n*-butyl acrylate, are flammable, toxic irritants. Styrene is a suspected carcinogen and *n*-butyl acrylate is a suspected teratogen. The ligand, pentamethyldiethylenetriamine, is combustible, flammable, and toxic and is readily absorbed through the skin and lungs; but it is used in small quantities and should only be handled in syringes. The use of needles and syringes was closely monitored to ensure their return and proper disposal.

Results

The controlled polymerization of acrylates by ATRP has been investigated previously (9, 12, 13). The conditions have been optimized here to accommodate the lack of purification of the starting materials including the presence of inhibitors in the monomers and Cu(II) impurities in the CuBr, which slow the rate of reaction. Conditions were also modified to enable a yield of moderately high conversion polymers (~80%) in the three-hour class period while retaining a high degree of functionality for chain extension with S. The temperature should not be raised to accelerate the reaction because the equilibrium constant, *K*_{eq}, will be enhanced. This would lead to a higher radical concentration, larger contributions of irreversible termination reactions, and an

Table 1. Typical Data for Isolated Macroinitiator, *p*nBA, and Copolymers of Styrene and *n*-Butyl Acrylate

Sample	Styrene (mol %)	M_n	M_w/M_n
<i>p</i> nBA	0	24,600	1.10
<i>p</i> (S- <i>b</i> - <i>n</i> BA- <i>b</i> -S)*	40	36,800	1.18
<i>p</i> (S-co- <i>n</i> BA)	38	16,600	1.13

increased loss of end groups, which will reduce the functionality of the macroinitiator. The loss of end-group functionality leads to an increase in the amount of homopolymer, *p*nBA, present in the block copolymer, as evidenced by an increase in the bimodality of the SEC trace due to residual low-molecular-weight polymer. This will affect the overall properties of the polymer sample. Conversely, if an increase in bimodality is observed in the SEC trace owing to a high-molecular-weight coupling product, this will also have a significant effect on the physical properties of the material, but is the result of radical-radical coupling of polystyrene chain ends.

Typical kinetic results for the ATRP of *n*BA are plotted in Figures 1 and 2. These plots clearly demonstrate the differences between conventional and controlled/living radical polymerizations. The linear progression of molecular weights indicates a constant concentration of growing chains, which differentiates controlled from uncontrolled processes. By plotting the theoretical molecular weights based on the conversion measurements, $\Delta[M]/[I]_0$, along with molecular weights obtained from SEC, it is clear that molecular weights can be predicted and controlled by the ratio $[M]_0/[I]_0$. The polydispersities are also a clear indication of the differences in the two methods; typical conventional radical polymerization yields polydispersities (M_w/M_n) > 1.8, whereas in the case of ATRP, $M_w/M_n < 1.3$.

The typical molecular weight data for a set of isolated (co)polymers are listed in Table 1. Comparison of the SEC traces for both the *p*nBA macroinitiator and the ABA-triblock copolymer provides a qualitative indication of the end-group functionality of the macroinitiator (Fig. 3). As discussed above, different forms of bimodality in the block copolymer may be observed.

If the copolymer samples are properly isolated, differential scanning calorimetry (DSC) should yield two glass transitions ($T_g = -56$ and 100 °C) for the block copolymer and one glass transition between those two values for the statistical copolymer. Qualitatively, students can observe that the statistical copolymer behaves like a soft plastic, whereas the block copolymer is a rubbery thermoplastic elastomer.

Supplemental Material

A complete description of this experiment and other supplemental materials are available in this issue of *JCE Online*.

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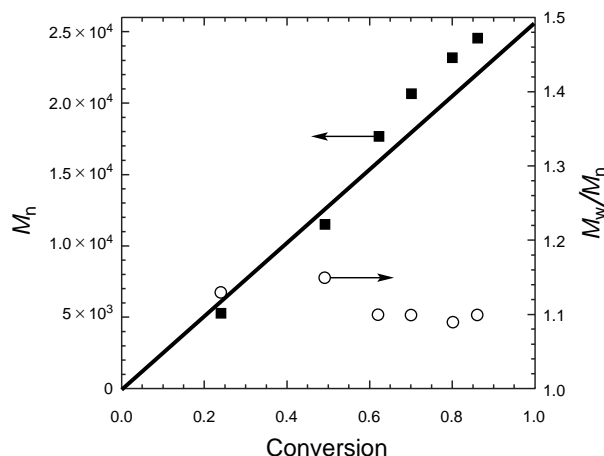


Figure 1. Molecular weight data for ATRP of *n*BA. $[M]_0/[I]_0$: $[CuBr(PMDETA)]_0 = 200:1:1$; ca. 20% acetone (v/v); $T = 80$ °C; (■) M_n , (○) M_w/M_n .

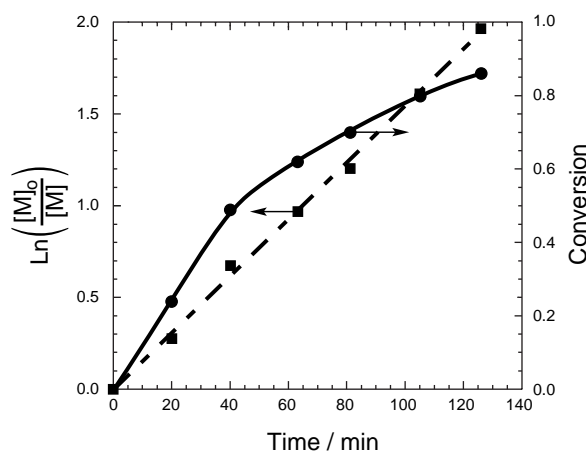


Figure 2. Semilogarithmic and linear plots of monomer conversion vs time for ATRP of *n*BA. $[M]_0/[I]_0$: $[CuBr(PMDETA)]_0 = 200:1:1$; ca. 20% acetone (v/v); $T = 80$ °C; (■) $\ln([M]_0/[M])$, (●) monomer conversion.

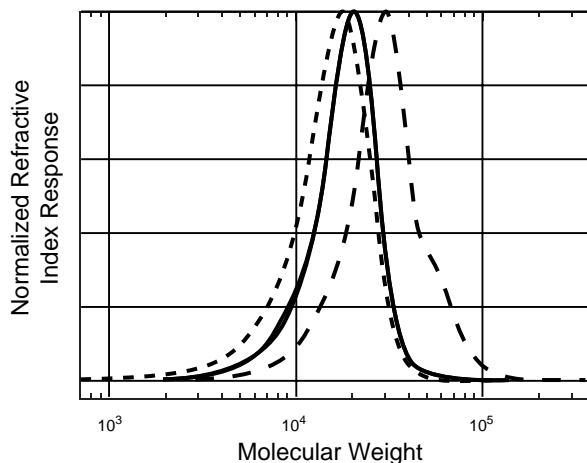


Figure 3. SEC traces of isolated polymer samples. Calibration vs polystyrene standards was used. Solid line: difunctional poly(*n*BA); dashed line: poly(S-*b*-*n*BA-*b*-S) Dotted line: poly(*n*BA-co-S).

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