# USE OF ATOM TRANSFER RADICAL COUPLING REACTIONS FOR THE SYNTHESIS OF VARIOUS MACROMOLECULAR STRUCTURES

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Introduction

In the past decade, the development of controlled/living radical polymerizations (CRP) [1, 2] has allowed the synthesis of (co)polymers not only with a predetermined degree of polymerization and narrow molecular weight distribution but also with high functionality and desired microstructure. Among the various controlled radical polymerization routes, atom transfer radical polymerization (ATRP) seemed to be the most versatile because of its simplicity and applicability to many vinyl monomers [3–5]. ATRP leads to the formation at one or both chain ends of halogen atoms due to the fast deactivation process. The coupling of bromine terminated polystyrenes was initially investigated by Fukuda *et al.* [6]. Their synthetic utility was first recognized by us. We proposed a novel route for directly obtaining *α,ω*-telechelics by combining ATRP with atom transfer radical coupling (ATRC) processes[7]. Bi-functional polystyrene telechelics, with double the molecular weight of the starting materials, were prepared by coupling of mono-functional polymers in atom transfer radical generation conditions, in the absence of monomer, using CuBr as catalyst, tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) as ligand, Cu(0) as reducing agent and toluene as solvent (Scheme 1). We have also studied the combination of ATRP and atom transfer radical cross-coupling (ATRCC) [8], and reversible ATRP and ATRC processes [9] as potential routes to prepare telechelic polymers. Following our work, other groups also reported successful synthesis of telechelics by ATRC of different halide-terminated polymers prepared by ATRP [10–13].
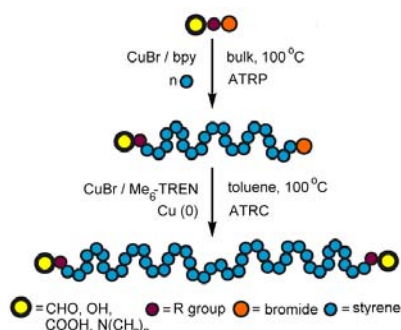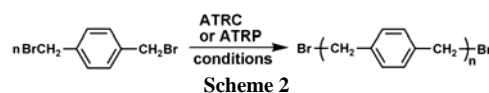

Scheme 1

Recently *p*-dibromo xylene, a typical ATRP bifunctional initiator, was polymerized in ATRC conditions, yielding poly(*p*-xylylene)[14]. However, the resulting polymer was poorly characterized because of its limited solubility. In order to confirm the success of the reaction by conventional characterization methods such as ^{1}H NMR spectroscopy and GPC, a more soluble product, poly(methyl methacrylate-*b*-*p*-phenylene-ethylene), was also synthesized by adding poly(methyl methacrylate) with an activated bromine atom at the chain end obtained by ATRP to the polymerization feed.

Moreover, polyrecombination reactions were also shown to be a potential route for the synthesis of polymers that can not be prepared by free radical polymerization. By this way, certain condensation polymers and perfectly alternating copolymers can also be readily obtained from the structurally designed monomers.

In this presentation, the use and limitations of ATRC reactions including polyrecombination reactions for the preparation of telecehelic polymers, polycondensates and alternating copolymers will be discussed.

Results and Discussion

Since the radicals are generated from the initiator in the first step of ATRP reaction, it seemed appropriate to use any bifunctional ATRP initiator as a monomer in ATRC or even ATRP (without adding Cu(0)) conditions. In this way a large number of already reported compounds can be polymerized by polyrecombination reactions. One of the drawbacks of ATRP relates to the limitation of the method to certain monomers, i.e., vinyl monomers and their derivatives. This could be overcome by our method, polyrecombination by ATRC, which can furnish new polymers from a wide range of classes. The fastest way to verify this assumption was, in a first stage, to polymerize a simple and traditional and commercially available ATRP bifunctional initiator, *p*-dibromoxylene, (Scheme 2).
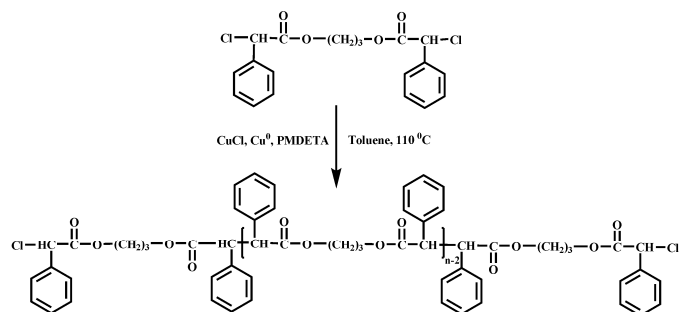

Scheme 2

The polymers prepared, are insoluble in common organic solvents which therefore make them difficult to characterize using traditional NMR spectroscopic techniques. In order to obtain a more convenient material that can be analyzed, an experiment was performed in the presence of 5 mol % poly(methyl methacrylate) PMMA. As the PMMA was obtained by ATRP, one end contains an activated Br atom. In this connection it should be pointed out that the polymeric halide end groups are structurally different than those of the benzylic halides of the monomer. The first reason of choosing PMMA as reaction partner for *p*-dibromoxylene is the copolymer ^{1}H NMR spectrum is free of signals in the regions where PPX should give peaks and the second is the experiment also tests the efficiency of other type of activated bromines that are usually used in initiating ATRP for such polyrecombination reactions. So, principally, it was expected that besides the homopolymer, poly(xylylene), a copolymer, PMMA-polyxylylene should be formed as depicted in Scheme 3.
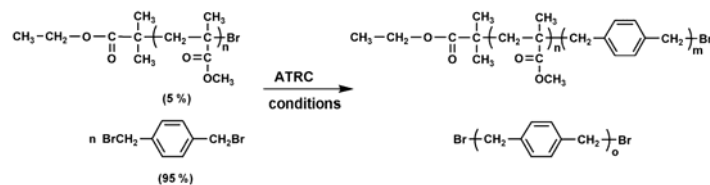
Scheme 3

This demonstrated not only the success of the synthesis of poly(p-xylylene), but also the activity of other type of activated bromine atoms in ATRC. In fact, the strategy described here opens a new pathway for the possibility for using of any potential ATRP bifunctional initiator as monomer, leading to new or already known polymers from very different classes.

Following this strategy, new polyester was synthesized by using ATRC reaction (Scheme 4). For this purpose, a bifunctional ATRP initiator was designed and synthesized as a monomer, and its polymerization was performed (Table 1). In this case, one mol of CuCl was introduced for every mol of monomer in order to facilitate successful coupling.

Scheme 4

Table 1 illustrates results of polyrecombination reaction of this monomer at fixed concentration of monomer and catalyst with different reaction times. As can be seen, although certain chain growth is achieved, the polydispersity of the resulting polymers quite high. It is also noted that higher molecular weigh polymers were formed at the early stages of the polymerization.

Table 1. **Synthesis of Polyester by ATRC Reactions**.

Run	Time (h)	Conversion, %	$M_{n,NMR}$[b]	$M_{n,GPC}$[a]	M_w/M_n[a]
1	24	30	6772	11437	3.29
2	48	33	4978	14214	2.65
3	96	35	4721	7844	2.80

Polymerization conditions; $[M]_0$ = 265 mM, $[M]_0$ / $[Cu^o]_o$ / $[CuCl]_o$ / $[L]_o$ = 1/2/1/1 in toluene at 110 °C. PMDETA used as a ligand.
[a] Determined by GPC based on polystyrene standards.
[b] Determined by ^{1}H NMR spectra.

The polymer formation was investigated by ^{1}H NMR analysis. Figure 2 represents the ^{1}H NMR spectra recorded for bifunctional monomer and its coupling product. The signal at 5.30 ppm was attributed for chloride end of monomer (Figure 2a). When the spectrum of the coupling product was investigated (Figure 2b), the characteristic chemical shift for chloride chain end of polymer was detected at 5.27 ppm and Ph-C*H*-C*H*-Ph protons (d) of the linkage appeared at 4.94 ppm. The aromatic protons of the polymer were noted between 6.95-7.42 ppm. The aliphatic protons (b') of the polymer near the ester groups appeared at 3.51–4.28 ppm. The other aliphatic protons (c') of the polymer were noted between 1.07-1.84 ppm. The number average molecular weight (M_{nNMR}) were calculated using the values of the integrals of characteristic end peaks (a') for polymer in comparison with the integrals of aliphatic protons (b') of polymer.
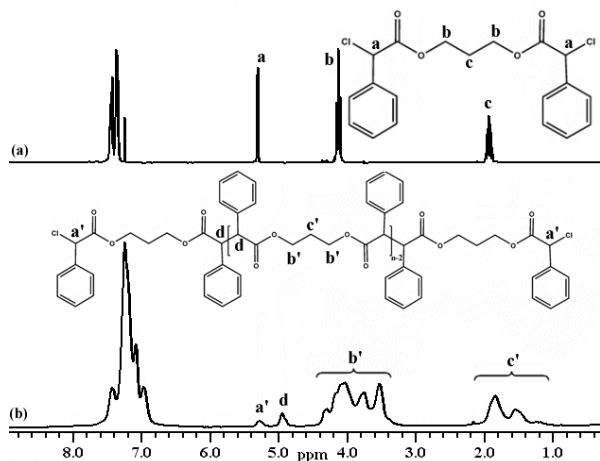
Figure 2. ^{1}H NMR spectrum of bifunctional monomer (a) and its coupling product (b).

Recently, a new methodology called as silane radical atom abstraction (SRAA) was introduced by Tillman and coworkers[15] as a metal-free alternative route for coupling of polymer radicals. They used the high bromophilicity of silane radicals in the generation of polymer radicals in the presence of a nitroxide trap[16]. It was independently demonstrated by Fouassier e*t al*[17] that silane radicals can also be generated from the reactions of photoexcited Type II phoptoinitiators such as benzophenone, camphorquinone, Eosin and isopropylthioxantone. It seemed appropriate to combine the two processes for the coupling approach. Taking the advantage of high reactivity of triplet benzophenone, silane radicals were generated photochemically. The resulting radicals abstract bromine from the polymer chain ends to form macroradicals capable of undergoing coupling reactions in a usual manner. The overall process is presented in Scheme 5. Experimentally, bromine terminated polystyrene (PS_n-Br) was irradiated at 350 nm in the presence of benzophenone and tristrimethylsillyl ($(TMS)_3$Si-H) at room temperature. Although a significant increase in the molecular weights was observed, it

appears some side reactions are also occurring beside the coupling reaction. At this point, further studies are necessary to optimize such photoinduced coupling reactions.
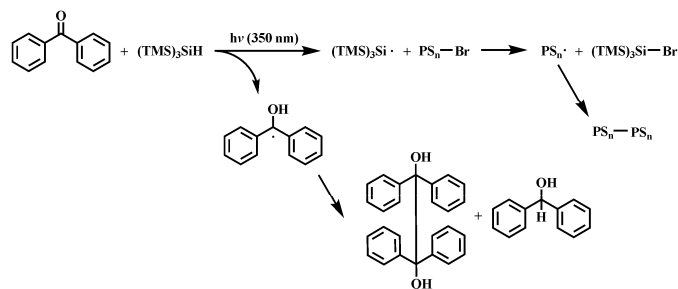
Scheme 5

Conclusion

It has been demonstrated that ATRC reactions are useful for preparing various macromolecular structures such as telechelics and certain polycondensates. The method pertains to the generation of biradicals from polymers prepared by ATRP or specially designed bifunctional ATRP initiators, respectively at high concentration. The radical generation process is not only limited metal catalyzed atom transfer reactions. Silane radical atom abstraction reactions can also be used for the formation of reactive radicals. Aromatic carbonyl assisted photoinduced reactions seemed to a promising alternative route for silane radical generation since it can be performed at room temperature and does not require metal catalysts.
Further studies in this line are now in progress.

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