

## Chapter 12

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

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The use and limitations of Atom Transfer Radical Coupling (ATRC) reactions including polyrecombination reactions for the preparation of telechelic polymers, segmented block copolymers, and polycondensates are presented. Specifically, the preparation of telechelic polymers with hydroxyl, aldehyde, amino and carboxylic functionalities, poly(*p*-xylylene) and its block copolymers, and polyesters via ATRC process is described. The method pertains to the generation of biradicals at high concentration from polymers prepared by ATRP or specially designed bifunctional ATRP initiators. The possibility of using silane radical atom abstraction (SRAA) reactions, that can be performed photochemically in the absence of metal catalysts, as an alternative process to ATRC is also discussed.

In the past decade, the development of controlled/living radical polymerizations (CRP)<sup>1, 2</sup> 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 route because of its

simplicity and applicability to many vinyl monomers<sup>3-5</sup>. ATRP leads to the formation of halogen atoms at one or both chain ends due to the fast deactivation process. The coupling of bromine terminated polystyrenes was initially investigated by Fukuda *et al.*<sup>6</sup> Their synthetic utility was first recognized by us. We proposed a novel route for directly obtaining  $\alpha$ ,  $\omega$ -telechelics by combining ATRP with atom transfer radical coupling (ATRC) processes<sup>7</sup>. We have also studied the combination of ATRP and atom transfer radical cross-coupling (ATRCC)<sup>8</sup>, and reverse ATRP and ATRC processes<sup>9</sup> 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<sup>10-13</sup>. Recently, *p*-dibromo xylene, a typical ATRP bifunctional initiator, was polymerized in ATRC conditions, yielding poly(*p*-xylylene)<sup>14</sup>. 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.

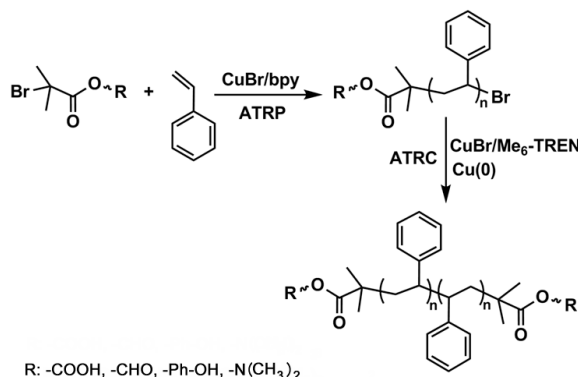
In this chapter, the use and limitations of ATRC reactions including polyrecombination reactions for the preparation of telechelic polymers, segmented block copolymers and polycondensates are discussed.

## Preparation of Telechelic Polymers

Telechelic polymers having a variety of functional groups are prepared by a wide range of polymerization methods, namely anionic<sup>15</sup>, cationic<sup>16</sup>, ring opening<sup>17,18</sup>, group transfer<sup>19,20</sup>, free radical<sup>21,22</sup>, metathesis<sup>23-30</sup> and step-growth<sup>31</sup> polymerization, and chain scission<sup>31</sup> processes. Among them living ionic polymerization methods are usually preferred since they allow the preparation of well-defined telechelics with better control of functionality, molecular weight and polydispersity. On the other hand, ionic techniques have serious limitations because of the requirement of high purity monomer and solvents, and monomer selectivity. Telechelics can also be prepared under classical free radical polymerization conditions by using a large amount of functional initiator<sup>32-37</sup> or performing the copolymerization of olefinic monomers with suitable heterocyclic monomers.<sup>38-40</sup> However, nonfunctionalized end group formation is unavoidable due to the mutual side reactions of the free radical process. Therefore, the overall structure of telechelics was not controlled or well-defined. Recent developments in CRP provide possibility to synthesize well-defined telechelic polymers also with radical routes. For example, the polymer produced by ATRP preserve the terminal halogen atom(s) and can be successfully converted into various end groups through appropriate transformation, especially nucleophilic substitution<sup>41</sup>, free radical reaction or electrophilic addition catalyzed by Lewis acids.

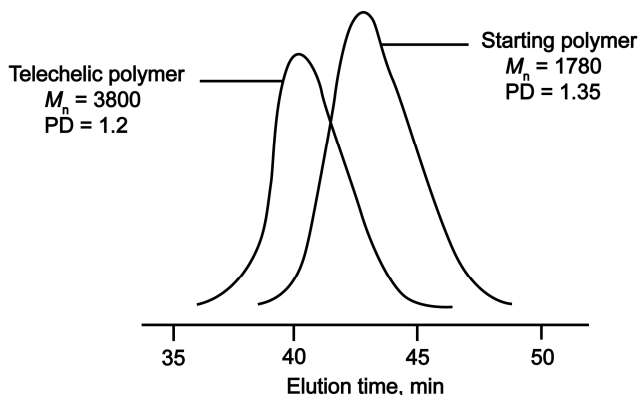
## Preparation of Telechelic Polymers by ATRC

Recently, an alternative route for obtaining directly  $\alpha,\omega$ -telechelics via combination of ATRP and ATRC processes have been proposed<sup>7</sup>. The ATRP initiators having aldehyde, tertiary amine, phenolic and carboxyl groups were used for the styrene polymerization to yield a polymer with the desired chain end at the  $\alpha$ -position. Then, bifunctional polystyrene telechelics, with double 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<sub>6</sub>TREN) as ligand, Cu(0) as reducing agent and toluene as solvent. The overall process is depicted in Scheme 1.



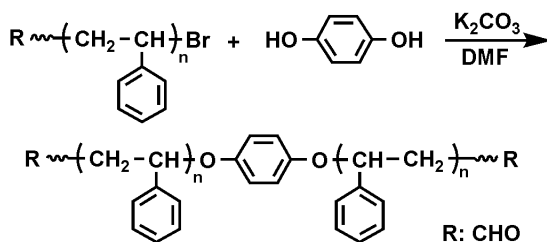
**Scheme 1.** Synthesis of  $\alpha,\omega$ -telechelics via combination of ATRP and ATRC processes.

ATRC, is based on the application of Cu(0) to an ATRP system, leading to the reduction of any Cu(II) in the reaction medium to form Cu(I). The increase of Cu(I) in the reaction medium dramatically shifts the equilibrium between active and dormant species to the side of the active radical species. So the high concentration of radicals presents in the system favor the recombination reactions between two macroradicals. This method was performed to obtain telechelic polymer from monotelechelic polystyrene and results showed that it is very effective way with high efficiency in a short reaction time. Figure 1 shows  $\alpha,\omega$ -telechelic polymer with double molecular weights as compared with the mono functional polystyrene obtained by ATRP using aldehyde functional initiator.



**Figure 1.** Gel Permeation Chromatography (GPC) traces of mono-aldehyde functional starting polymer and  $\alpha,\omega$ -telechelic polymer obtained by ATRC.

The direct coupling of monofunctional polymers prepared by ATRP can also be realized by etherification reaction with low-molar mass dialcohols. Typically, the preparation of aldehyde functional  $\alpha,\omega$ -telechelic polymers by classic etherification is demonstrated on the example hydroquinone as the coupling agent (Scheme 2).



**Scheme 2.** Synthesis of  $\alpha,\omega$ -telechelic polymer by etherification.

The comparison of coupling by ATRC and condensation processes are collected in Table 1. Although quantitative coupling efficiency was attained in both cases, ATRC is more convenient method for obtaining  $\alpha,\omega$ -telechelics, due to the shorter reaction time and easier reaction conditions. Moreover, the condensation coupling is more sensitive to the reaction stoichiometry which can be influenced by the experimental errors such as weighing, molecular weight determination, and transferring the components into a reaction vessel. In fact, these factors may be the reason for the relatively higher polydispersity observed in the condensation process.

**Table 1. Coupling of Mono-aldehyde Functional Polymer by ATRC and Classical Etherification.**

Run	Method	Polymer Conc. (mmol L <sup>-1</sup> )	Time (min)	$M_{n,NMR}^d$ (g mol <sup>-1</sup> )	$M_{n,GPC}^e$ (g mol <sup>-1</sup> )	$M_w/M_n^e$
1 <sup>a</sup>	ATRC <sup>c</sup>	15	1440	3750	3800	1.20
2 <sup>b</sup>	ATRC <sup>c</sup>	15	45	3900	4200	1.21
3 <sup>a</sup>	Etherification	305	4320	3770	3600	1.35

<sup>a</sup> Starting aldehyde functional polystyrene;  $M_{n,theo}$ :1740,  $M_{n,NMR}$ : 1830,  $M_{n,GPC}$ :1780,  $M_w/M_n$ :1.35.

<sup>b</sup> Starting aldehyde functional polystyrene;  $M_{n,theo}$ :2000,  $M_{n,NMR}$ : 2100,  $M_{n,GPC}$ :1970,  $M_w/M_n$ :1.38.

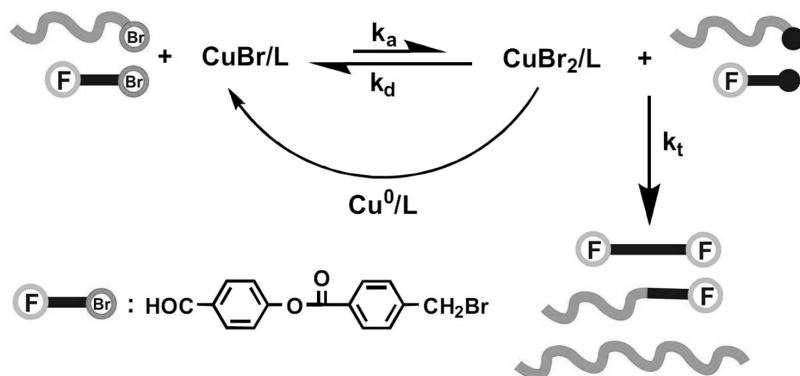
<sup>c</sup> Atom Transfer Radical Coupling Conditions: [Cu<sub>0</sub>]: 75 x 10<sup>-3</sup> M; [CuBr<sub>2</sub>]: 15 x 10<sup>-3</sup> M; [Me<sub>6</sub>TREN]: 30 x 10<sup>-3</sup> M; solvent: toluene; temperature: 110 °C.

<sup>d</sup> Determined by <sup>1</sup>H NMR spectra.

<sup>e</sup> Determined by GPC based on polystyrene standards.

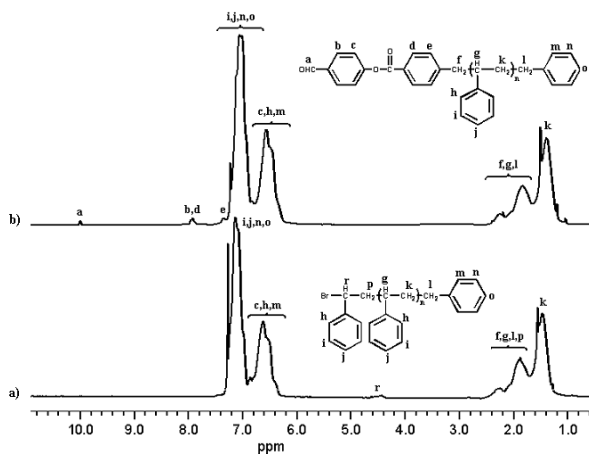
### Preparation of Telechelic Polymers by ATRCC

Preparation of telechelic polymers by ATRCC was also demonstrated<sup>8</sup>. The concept is based on the activation of the dormant species at the chain ends of polystyrene (PS-Br) prepared by ATRP and also functional ATRP initiator (*F*-R-Br) in the absence of a monomer. Depending on the number of functionality of the polymer used in the system, ATRCC yields ω-polystyrene and α,ω-polystyrene telechelics. However, at least in principle, not only the desired functional polymers but also various side products may be formed due to the self coupling reactions of macroradicals generated from PS-Br, and low-molecular weight radicals from *F*-R-Br. The possible reactions of the model system are depicted in Scheme 3.



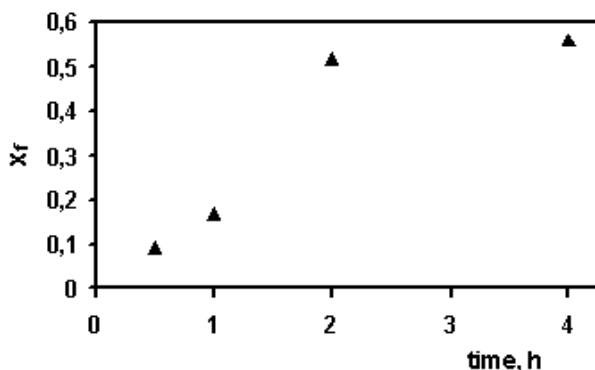
*Scheme 3. General reactions of ATRCC process.*

The chain end functionality was investigated by  $^1\text{H}$  NMR analysis. Figure 2 represents the  $^1\text{H}$  NMR spectra recorded for PS-Br prepared by ATRP and its coupling product in the presence of **F-R-Br**. The signal at 4.38 ppm was attributed for  $-\text{CH}(\text{Ph})\text{Br}$  (Figure 2a). When the spectrum of the coupling product was investigated (Figure 2b), the characteristic chemical shift for aldehyde proton was detected at 10.01 ppm. The aromatic protons of the initiator near the carbonyl groups appeared at 7.94 ppm. The other aromatic protons of the initiator were noted at around 7.34 ppm. It should be pointed out that the signal of the proton (r) located in the  $\alpha$ -position of the bromine end functionality disappeared after the reaction, confirming the efficient coupling reaction of PS-Br chains. However, the number of the styrene repeating units of the coupling product, which was estimated from the peak area integration of aromatic region (6.58 ppm), showed not only functional polymer formation (56 %) but also coupling of the macroradicals (44 %) occurred during ATRCC reaction. Protons originating from the self coupling reaction of PS-Br ( $-\text{CH}-\text{CH}-$ ) were located in 2–2.5 ppm region and overlapped with the other  $\text{CH}_2$  and  $\text{CH}$  protons of the polystyrene chains. Notably, low molar mass coupling products (**F-R-F**) were removed during the precipitation.



**Figure 2.**  $^1\text{H}$  NMR spectra of PS-Br ( $M_n$ : 2132,  $M_w/M_n$ : 1.2) (a) and its coupling product (b).

We have investigated the effect of various parameters such as catalyst concentration,  $[\text{PS-Br}]/[\text{F-R-Br}]$  ratio, PS-Br concentration, and time dependence on the ATRCC system. It has also been observed that under these experimental conditions the highest functionalization is achieved after 2h and then the composition of reaction mixture does not change significantly with time (Figure 3).



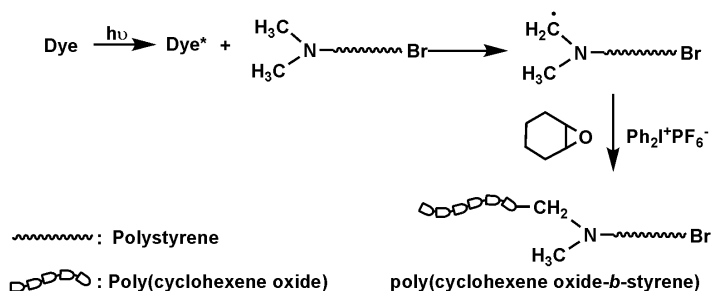
**Figure 3.** Variation of coupling efficiency in time for ATRCC using PMDETA as a ligand.  $[PS-Br]_0 / [F-R-Br]_0 / [Cu^0]_0 / [CuBr]_0 / [L]_0$ : 1/15/15.6/3.1/22.5,  $[PS-Br]_0$ : 1.37 mmol L<sup>-1</sup>.

Further investigations regarding the effect of molecular structure of bromo end group on the coupling process were performed. In the system under consideration, PS-Br and *F*-R-Br possess structurally different end groups and consequently produce radicals with different stability and reactivity which may contribute to different equilibrium constants. In order to achieve similar reactivity between structurally different end groups Matyjaszewski proposed to introduce small amount of St in the ATRC<sup>13</sup>. Following the same strategy, styrene monomer was added to obtain structurally similar chain ends in ATRCC. As a result, styrene-terminated radicals are simultaneously formed from both this polymerization and initial PS-Br. This experiment was carried out in toluene at 110 °C with  $[PS-Br]_0 / [St] / [F-R-Br]_0 / [Cu]_0 / [CuBr]_0 / [L]_0$  = 1/10/15/15.6/3.1/22.5. Under these conditions the highest functionalization (85 %) with  $M_n$ : 3039 with 1.33 polydispersity was achieved. The increase of molecular weight of the resulting telechelic from the initial value ( $M_n$ : 2495) is due to the addition of short styrene unit and also functional initiator.

Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for preparation of condensation polymers, block and graft copolymers. Moreover, star and hyper-branched or dendric polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. Among them, the use of telechelics as the building blocks of polycondesates may be more common. For example, hydroxy-telechelic polymers are used for the preparation of polyurethanes or polyesters. Besides ATRC, these polymers can be synthesized by ATRP followed by end group transformation such as end-capping with allyl alcohol<sup>42</sup>. Also, the combination of ATRP and click chemistry is an interesting and promising strategy to synthesize various end functionalized polymers. Recently,  $\alpha,\omega$ -dihydroxy telechelic polystyrene was synthesized by combination of ATRP and subsequent modification via click reactions<sup>43</sup>. Furthermore, step-growth click coupling of telechelic polymers was performed by using  $\alpha$ -alkyne- $\omega$ -azido-terminated polystyrene and  $\alpha,\omega$ -diazido-terminated polystyrene was

polymerized with propargyl ether at room temperature to yield higher molecular weight polystyrene<sup>44</sup>.

Other important use of telechelic polymers is preparation of block copolymers. Depending on the type of telechelics (heterotelechelic or telechelic), AB and ABA type block copolymer can be obtained, respectively. Moreover, different polymerization modes can be easily combined by using telechelics<sup>45</sup>. Typically, appropriately functionalized telechelics can be used as initiators for photoinitiated free radical and cationic polymerizations. Scheme 4 depicts the general reactions for the combination of ATRP and photoinduced radical promoted cationic polymerization by using *N,N* dimethylaniline functional polystyrene. Macroradical generation in visible region was achieved via a visible light initiating system which involves a xanthene dye (erythrosin B), an aromatic *N,N*-dimethylamino group and diphenyliodonium hexafluorophosphate as the sensitizer, radical source and oxidant, respectively.



**Scheme 4.** Synthesis of block copolymer by combination of ATRP and Free Radical Promoted Cationic Polymerization.

## Preparation of Polycondansates

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 or new compounds can be polymerized by polyrecombination reactions<sup>14</sup>. 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 5).



**Scheme 5.** Synthesis of poly(*p*-xylylene) by polyrecombination in ATRC or ATRP conditions



Conditions and results of polyrecombination reaction of *p*-dibromoxylene in ATRC and ATRP conditions were collected in Table 2. First experiment was performed under typical ATRC condition at 110 °C for 20 h. Although the precipitate was extracted with toluene and THF, soluble polymer fraction or unreacted monomer could not be separated. At lower temperature and concentration, unreacted monomer was recuperated from the solution and the yield was calculated as 15%. Also, ATRP condition is efficient for this polyrecombination even at relatively low monomer and catalyst concentration.

**Table 2. Conditions of polyrecombination reaction of *p*-dibromoxylene in ATRC conditions**

Run	[M] (mol L <sup>-1</sup> )	[M]/[Cu <sup>0</sup> ]/ [CuBr]/[PMDETA]	Time (h)	Temperature (°C)	Yield <sup>a</sup> (%)
1	0.19	2/4/2/2	20	110	100
2	0.10	2/1/1/1	2	90	15
3	0.08	2/0/0.5/0.5 <sup>b</sup>	16	80	37
4	0.15	2/1/0.5/0.5 <sup>c</sup>	72	110	16.3 <sup>d</sup>

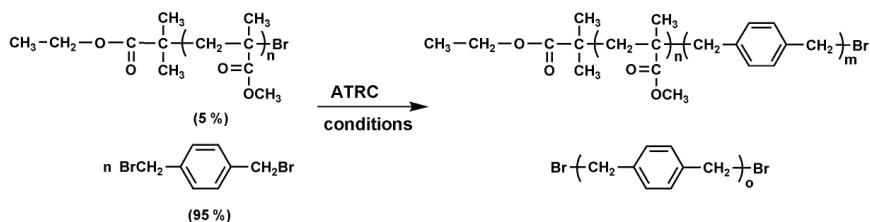
<sup>a</sup>Calculated gravimetrically from the unreacted monomer recuperated from reaction solution and extractions of insoluble part.

<sup>b</sup>ATRP conditions

<sup>c</sup>M is a mixture 95/5 *p*-dibromoxylene/PMMA-Br (molar ratio).

<sup>d</sup>In soluble fraction

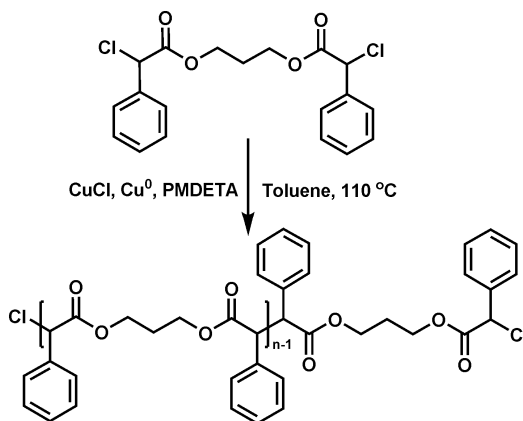
The polymers prepared, are insoluble in common organic solvents which therefore make them difficult to characterize using traditional NMR spectroscopic techniques. In order to obtain a more convenient material that can be analyzed, an experiment was performed in the presence of 5 mol % poly(methyl methacrylate) PMMA (Run 4 in Table 2). 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 <sup>1</sup>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 6. At the end of the reaction, insoluble homopolymer (16.3 %) was separated from the mixture.



*Scheme 6. Synthesis of poly(methyl methacrylate - b- p-xylylene) in ATRC conditions.*

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.

Accordingly, new polyester was synthesized by using ATRC reaction (Scheme 7). For this purpose, a bifunctional ATRP initiator namely propane-1,3-diyl bis(2-chloro-2-phenylacetate) (PDBCP) was designed and synthesized as a monomer, and its polymerization was performed (Table 3). In this case, one mol of CuCl was introduced for every mol of monomer in order to facilitate successful coupling.



*Scheme 7. Polyrecombination of PDBCP in the ATRC conditions.*

Table 3 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 is quite high. It is also noted that higher molecular weight polymers were formed at the early stages of the polymerization.

**Table 3. Synthesis of polyester by ATRC reactions.**

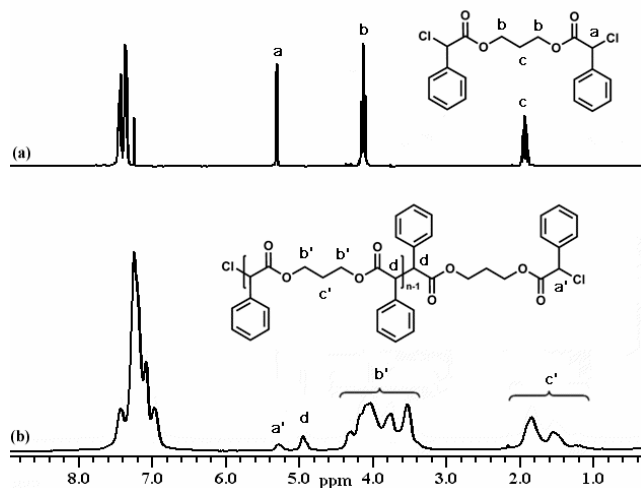
Run	Time (h)	Conversion (%)	$M_{n,NMR}^b$	$M_{n,GPC}^a$	$M_w/M_n^a$
1	24	30	6770	11440	3.29
2	48	33	4980	14210	2.65
3	96	35	4720	7840	2.80

Polymerization conditions;  $[M]_0 = 265$  mM,  $[M]_0 / [Cu^0]_0 / [CuCl]_0 / [L]_0 = 1/2/1/1$  in toluene at 110 °C. PMDETA used as a ligand.

<sup>a</sup> Determined by GPC based on polystyrene standards.

<sup>b</sup> Determined by  $^1H$  NMR spectra.

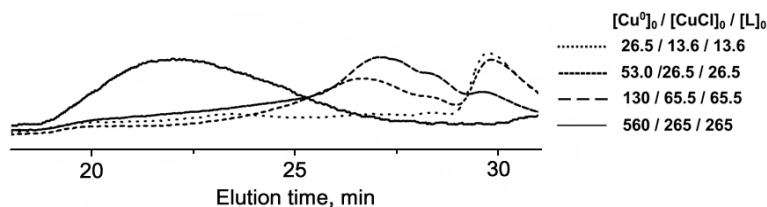
The polymer formation was investigated by  $^1H$  NMR analysis. Figure 4 represents the  $^1H$  NMR spectra recorded for bifunctional monomer and its coupling product. The signal at 5.30 ppm was attributed for chloride end of monomer (Figure 4a). When the spectrum of the coupling product was investigated (Figure 4b), the characteristic chemical shift for chloride chain end of polymer was detected at 5.27 ppm and Ph-CH-CH-Ph protons (d) of the linkage appeared at 4.94 ppm. The aromatic protons of the polymer were noted between at 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 ( $M_{n,NMR}$ ) 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 4.**  $^1H$  NMR spectrum of bifunctional monomer (a) and its coupling product (b).

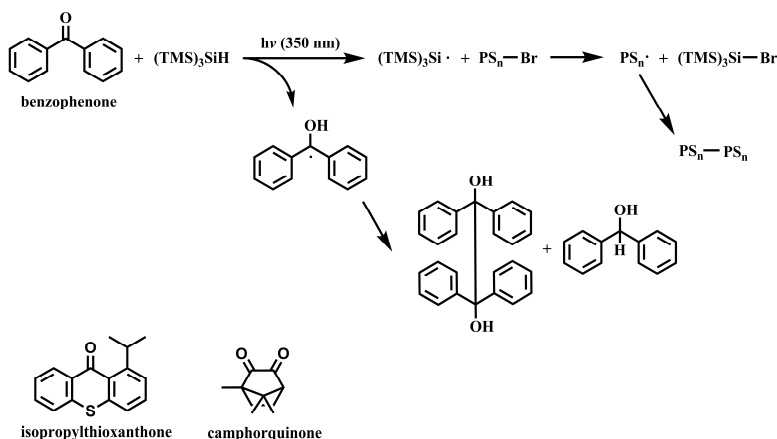
The effect of catalyst concentration at constant monomer concentration was investigated. Figure 5 shows the GPC traces of the polymers obtained with

different catalyst concentration. As can be seen, the GPC curves shifted to a higher molecular weight and the peak areas of the lower molecular weight regions decreased as the catalyst concentration increased. Because, the higher catalyst concentration leads to increase in concentration of active radicals, this manifests itself in more coupling probability.



**Figure 5.** GPC traces of the polymers obtained at constant monomer concentration ( $[M]_0 = 265 \text{ mmol L}^{-1}$ ) with different catalyst concentration ( $\text{mmol L}^{-1}$ ).

Recently, a new methodology called as silane radical atom abstraction (SRAA) was introduced by Tillman and coworkers<sup>46-48</sup> 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<sup>49</sup>. It was independently demonstrated by Fouassier *et al*<sup>50</sup> that silane radicals can also be generated from the reactions of photoexcited Type II photoinitiators 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, camphorquinone and isopropylthioxantone 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 8.



**Scheme 8.** Photoinduced coupling reaction of PS-Br in the presence of  $((\text{TMS})_3\text{Si-H})$ .

Experimentally, bromine terminated polystyrene (PS-Br) was irradiated at appropriate wavelengths depending on the absorption of the initiator in the presence of tris(trimethylsilyl)silane ((TMS)<sub>3</sub>Si-H) at room temperature and the results are summarized in Table 4. Although the highest coupling efficiency and a significant increase in the molecular weight (Figure 6) was observed with comphorquinone at visible region, it appears some side reactions are also occurring beside the coupling reaction.

**Table 4. Photoinduced coupling of polystyrene prepared by ATRP.**

Run	PS-Br (mol L <sup>-1</sup> )	Photoinitiator (mol L <sup>-1</sup> )	(TMS) <sub>3</sub> SiH (mol L <sup>-1</sup> )	Time (h)	λ (nm)	X <sub>c</sub>
1	0.083	BP (0.166)	0.498	2	350	0.14
2	0.042	ITX (0.083)	0.083	2	350	0.11
3	0.042	CQ (0.083)	0.083	1	430-490	0.57

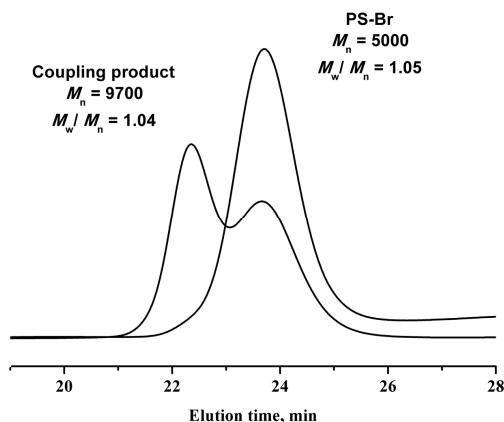
Solvent: Benzene/Hexane (2/3)

BP: Benzophenone, ITX: Isopropylthioxanthone, CQ: Camphorquinone

(TMS)<sub>3</sub>SiH : Tris(trimethylsilyl)silane

λ is irradiation wavelength.

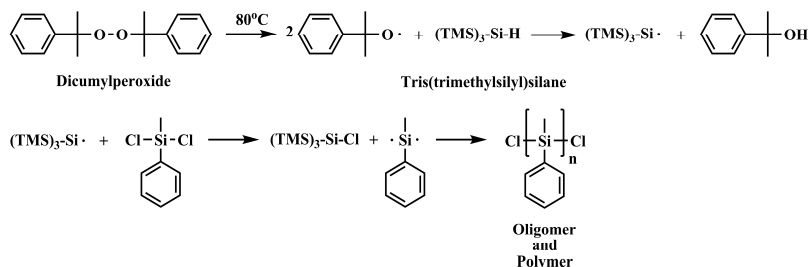
Coupling efficiencies (X<sub>c</sub>) were calculated from GPC.



**Figure 6. GPC overlays of PS-Br and Run 3.**

We have also used SRAA reactions for the polymerization of bifunctional monomers such as propane-1,3-diyl bis(2-chloro-2-phenylacetate) (PDBCP) and dichloromethylphenylsilane (DCMPS). As mentioned above this approach was

previously attempted via ATRC for polyester synthesis. The overall reactions for the case of DCMPS are presented in Scheme 9.



**Scheme 9.** Polyrecombination of DCMPS under SRAA conditions.

Silane radicals were generated *in situ* using SRAA method in the presence of dicumyl peroxide and subsequent coupling reactions of PDBCP and DCMPS gave rise to not only oligomers but also high molecular weight polymers. As shown in Table 5, for both monomers limited conversions were observed due to rapid consumption of the radicals at the beginning of the reaction. In order to provide permanent radical generation by extending life time of dicumyl peroxide the temperature was decreased to 65 °C (Run 4 in Table 5). Expectedly, molecular weight increased by decreasing temperature.

At this point, further studies are necessary to optimize such coupling reactions.

**Table 5. Results of the coupling reactions of bifunctional monomers using SRAA in the presence of dicumyl peroxide.**

Run	Monomer	Temperature (°C)	Time (h)	Conversion (%)	$M_{n, GPC}$ (g mol <sup>-1</sup> )	$M_w/M_n$
1	PDBCP <sup>a</sup>	80	20	7.5	1650	4.48
2	PDBCP	80	2	4.2	4500	4.8
3	DCMPS	80	2	5	64370 1650	1.49 1.01
4	PDBCP	65	20	2.3	53500 6280	1.54 3.76

PDBCP: propane-1,3-diyl bis(2-chloro-2-phenylacetate)

DCMPS: dichloromethylphenylsilane

<sup>a</sup> *tert*-Butyl hyponitrite was used as a persistent radical source instead of dicumyl peroxide.

In conclusion, it has been demonstrated that ATRC reactions are useful for preparing various macromolecular structures such as telechelics and certain polycondensates. The method preserves to the generation of biradicals at high concentration from polymers prepared by ATRP or specially designed bifunctional ATRP initiators. The radical generation process is not limited to the 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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