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# Controlled radical polymerization initiated by stable radical terminated polytetrahydrofuran

**Yusuf Yağcı*, Ayşegül Başkan Düz and Ayşen Önen**
*Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 80626, Turkey*
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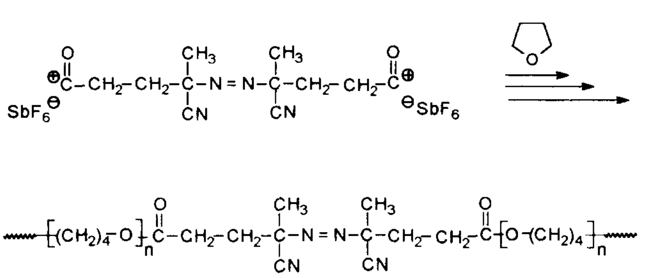
Block copolymers of tetrahydrofuran and styrene were prepared by using stable free radical polymerization (SFRP) of styrene with 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (TEMPO) terminated polytetrahydrofuran (PTHF). For this purpose azo containing PTHFs were prepared and reacted with TEMPO. © 1997 Elsevier Science Ltd.

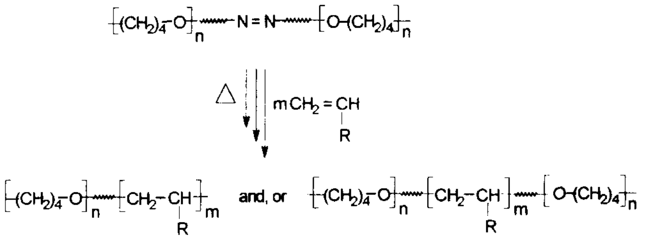
**(Keywords: cationic polymerization; stable free radical polymerization; TEMPO)**

## *Introduction*

Design and synthesis of materials with novel properties is becoming an increasingly important aspect of polymer chemistry[1]. Quite often desired properties are not attainable by the properties of a single homopolymer. Most notably, block copolymers consisting of several types of monomer sequences are of special interest because they combine the properties of the corresponding homopolymers without phase separation. In general, controlled block copolymerization is accomplished using living anionic and cationic polymerization techniques. However, major drawbacks of the ionic processes are the monomer selectivity and rigorous synthetic requirements. On the other hand, free radical polymerization is easy to perform, less susceptible to impurities and, more importantly, can be applied to most of the vinyl monomers. Recently, several reports[2–9] from the authors' laboratory dealt with the design and synthesis of block copolymers. In our work, free radical initiator moieties were incorporated into the polymer chains by means of various polymerization techniques. For example, living cationic polymerization of tetrahydrofuran[8] (THF) initiated by azooxocarbenium ions results in the formation of polymers with functionality in the main chain that is appropriate for the subsequent free radical block[3,8,9] copolymerization.

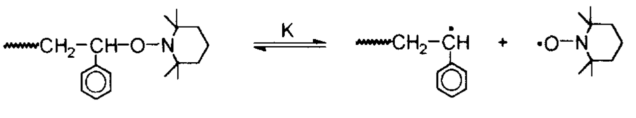


The azo-linked polytetrahydrofuran (PTHF) is then decomposed in the presence of a comonomer to give block copolymers.



While living conditions for the PTHF segment has been achieved, the free radical polymerization in the second step yielded block copolymers with broad polydispersities[7]. Moreover, the overall structure of block copolymers was found to be governed by the termination mode of the particular monomer involved, i.e. termination by disproportionation or combination yielded AB or ABA type block copolymers, respectively.

Recently, free radical polymerization by mediated nitroxide-stable free radicals (SFR), such as 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (TEMPO), was reported[10] to yield polymers with narrow polydispersities. This process is based on the simultaneous initiation and the reversible termination of the polymer radical with the SFR.



Although several successful block copolymerizations using SFR polymerization (SFRP) have been achieved[14,15], the initial radicals were derived from low molar-mass initiators and a second monomer was added either sequentially or by mixing with TEMPO-terminated polymer after precipitation and purification. The obtained block copolymers comprised sequences of monomers polymerizable only by free radical mechanism.

In this paper, we describe briefly our preliminary results on the SFRP initiated by cationically obtained polymeric initiator possessing TEMPO, terminal groups.

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* To whom correspondence should be addressed

## *Experimental*

*Materials.* Tetrahydrofuran (THF) was dried over potassium hydroxide, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use. Styrene (St) and toluene were purified by conventional drying and distillation procedures. $AgSbF_6$, 4,4′-azobis(4-cyanopentanoic acid) and 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (TEMPO) (Aldrich) were used without further purification.

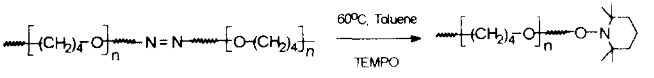
*Preparation of polytetrahydrofuran terminated with TEMPO.* PTHF was prepared by the polymerization of THF initiated by azo-oxocarbenium salt according to the described procedure[3]. Respective solutions of obtained PTHF containing excess TEMPO in toluene were made oxygen free with a nitrogen flow. At the end of heating in a thermostated bath at 60°C for 72 h, solutions were poured into cold methanol and purified by reprecipitation from THF into cold methanol, the precipitated polymer was filtered off and dried *in vacuo*.

*Copolymerization of PTHF with St.* Appropriate solutions of the above obtained prepolymers and St in toluene were purged with nitrogen and heated to 125°C for 24 h. At the end of reaction, polymers were precipitated into methanol and dried.

*Analysis of polymers.* $^1H$ n.m.r. spectra were taken on a Bruker 200 instrument in $CDCl_3$, using tetramethylsilane as the internal standard. Gel permeation chromatography (g.p.c.) analyses were performed with a set up consisting of a Waters pump (model 600E) and three Ultrastyragel columns with porosities $10^4$, 500 and 100 Å, respectively. THF was used as eluent at a flow rate of 1 ml $min^{-1}$ and the detection was achieved with Waters differential refractometer (model 410). Molecular weights were calculated with the aid of polystyrene standards.

## *Results and discussion*

Synthetic conditions and molecular weights of PTHFs with labile azo groups are given in *Table 1*. For attaching TEMPO groups, these polymers were heated at 60°C for 72 h in the presence of excess TEMPO.



After purification by reprecipitation in cold methanol, the obtained PTHFs are expected to possess a TEMPO molecule at the chain end with essentially no free TEMPO. This was confirmed by block copolymerization experiments.

**Table 1** Synthesis[a] and molecular weights of azo-linked polytetrahydrofuran

| Run | ACPC (mol $l^{-1}$) | $AgSbF_6$ (mol $l^{-1}$) | Time (min) | Conversion (%) | $M_n^b$ (g $mol^{-1}$) |
|---|---|---|---|---|---|
| 1 | $7 \times 10^{-2}$ | $14 \times 10^{-2}$ | 20 | 14.7 | 14 000 |
| 2 | $3.5 \times 10^{-2}$ | $7 \times 10^{-2}$ | 20 | 12 | 31 000 |

ACPC: 4,4′-Azobis(4-cyanopentanoil chloride)

[a] Polymerizations were performed at 0°C in bulk THF

[b] Determined by g.p.c.

By the polymerization of bulk styrene with TEMPO terminated PTHFs at 125°C, the corresponding block copolymers were obtained quantitatively, according to the following reaction.

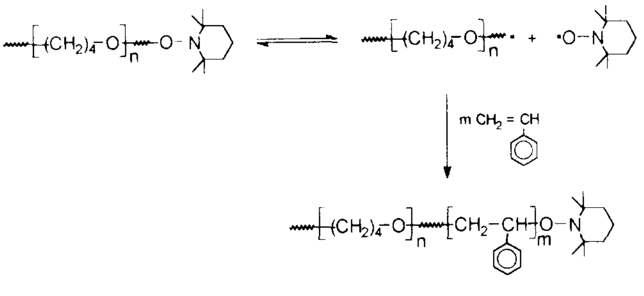


*Figure 1* shows the g.p.c. chromatograms of the precursor polymer and block copolymers recovered after the second heat treatment. As is clearly seen, there is no peak either of the precursor polymer after the reaction with TEMPO or the block copolymer indicating a high efficiency of processes. Furthermore, the polydispersity remains constant throughout both reaction steps. The mole composition of the block copolymer (18% THF, 82% St) determined by the ratio of aromatic protons of the PSt segment at 7–9 ppm to $-OCH_2$ protons of the PTHF segment at 3.4 ppm is close to the one determined by g.p.c. (22% THF, 78% St).

In this connection, it is noteworthy to mention the work of Steenbock *et al.*[16] who studied block copolymerization of methyl methacrylate (MMA) with PSt-TEMPO. These authors show that MMA cannot be polymerized by SFRP due to the irreversible termination resulting from proton transfer reaction between the propagating radical and TEMPO. For this reason our studies are limited to St as the free radical polymerizable monomer.

In conclusion, this communication clearly demonstrates a successful extension of SFRP to polymeric initiators obtained by cationic polymerization. It opens a

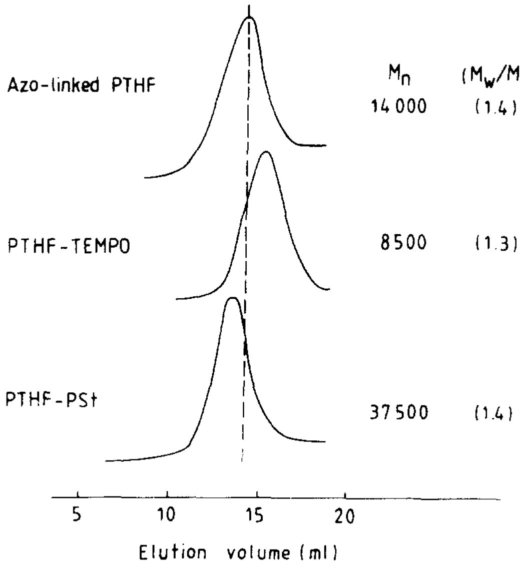


**Figure 1** G.p.c. traces for the precursor PTHF (Run 1), TEMPO terminated PTHF and PTHF-PSt block copolymer

large variety of synthetic possibilities to prepare well defined block copolymers with monomers of different chemical nature. Further studies are now in progress.

### *Acknowledgements*

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