Mono- and Dinitroxide Styrene Polymerization Initiators

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The successful preparation of block copolymers requires utilization of polymerization processes which allow control of termination. Typically, anionic polymerization is used to prepare styrene-containing block copolymers because it results in truly living polymers which can be terminated at will. However, anionic polymerization is costly to conduct on an industrial scale because of the need for highly purified monomers and solvents.[1] Free radical polymerization of styrene, on the other hand, has a multitude of termination processes which make it very difficult to control polymer chain architecture.[2] However, free radical polymerization is very forgiving with regard to monomer purity, thus making it the most heavily utilized chemistry for polymer production. In fact, worldwide over 75% of all vinyl polymers are produced using free radical chemistry.

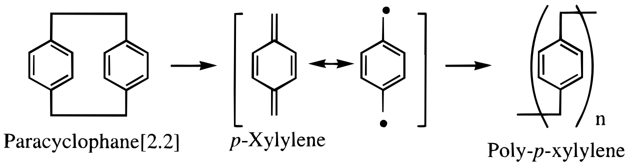
Vinyl block copolymers (e.g., styrene-*b*-isoprene) generally arise from anionic polymerization chemistry and therefore are more costly materials than typical free radically produced homopolymers (e.g., polystyrene and polyethylene). The high cost of these materials is the key factor that has limited their market growth. If free radical chemistry could be used to make these block copolymers, the cost of manufacture could be reduced, thus increasing sales volume. However, before free radical chemistry can be used to make block copolymers, a technique must be developed which allows control of termination processes.

Currently, the most studied approach for controlling the termination step during free radical polymerization is by the addition of stable free radicals (SFR) to the polymerization feed. The SFR most widely utilized are nitroxyl radicals. When the nitroxyl radical is coupled with certain carbon atoms, the bond formed is labile and dissociates upon heating, allowing monomer to insert between the carbon and nitroxyl radical pair. This process appears to eliminate most of the other termination processes and offers the ability to control the polymer architecture. The addition of nitroxyl radicals to control termination processes has been referred to as nitroxide-mediated radical polymerization (NMRP) and has received considerable attention over the past three years.[3−15]

In this paper, we compare styrene polymerization initiated/mediated with mono- and difunctional nitroxide compounds and also report on our efforts to prepare block copolymers using NMRP.

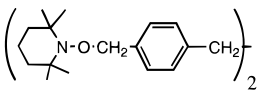
Results and Discussion. Synthesis of nitroxide initiators has been generally accomplished by the trapping of carbon-centered radicals by nitroxyl radicals. The carbon radicals that are trapped are generally formed by electron transfer, H abstraction, or vinyl addition. We have found it quite difficult to generate dinitroxides by these methods and thus have been exploring other routes to synthesize dinitroxyl initiators. We began by reviewing previous reports of diradical reaction intermediates and then attempted to trap the intermediates using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).

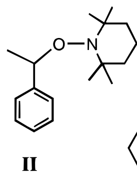
Scheme 1. Mechanism of Formation of Poly(*p*-xylylene)

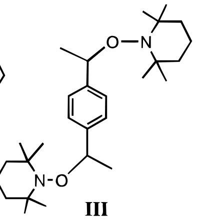


Polymerization of *p*-xylylene has been known for over 40 years and has been shown to proceed via a diradical intermediate (Scheme 1). We pyrolyzed paracyclophane[2.2] at 600 °C and condensed the resulting *p*-xylylene vapor in toluene/TEMPO solution at −78 °C. Upon warming the solution slowly to room temperature, the solution lightened in color from orange to yellow, indicating that the TEMPO concentration had decreased. No polymer formed. The solution was concentrated by rotary evaporation and then poured into acetonitrile. Upon allowing the mixture to stand, the product crystallized as a white solid in high yield. The crystals were collected and characterized by NMR and mass spectroscopy and were found surprisingly to be the dinitroxide of *p*-xylylene dimer (**I**) rather than the monomer. Since it is well known that TEMPO traps carbon-centered radicals at diffusion-controlled rates,[17] it is surprising that the dimer diradical rather than the monomer diradical species was trapped.

Previously, we reported the preparation of a monofunctional NMRP initiator (**II**) by H-atom abstraction from ethylbenzene.[13] The procedure involved simply refluxing excess ethylbenzene (overnight) containing a small amount of di-*tert*-butyl peroxide and TEMPO and then rotoevaporating to remove the excess ethylbenzene. The crude oil which remained was purified by column chromatography, affording pure **II** in about 50% yield based upon di-*tert*-butyl peroxide. We applied a similar procedure to prepare dinitroxide compound **III** by double H-atom abstraction from *p*-diethylbenzene in the presence of TEMPO. Abstraction of two H-atoms from the same molecule requires that an excess of di-*tert*-butyl peroxide be used relative to the diethylbenzene substrate. Heating of *p*-diethylbenzene in the absence of solvent at 110 °C using a large excess of di-*tert*-butyl peroxide afforded the desired dinitroxide. Hammouch and Catala recently prepared another dinitroxide of *p*-diethylbenzene by electron transfer to α,α′-dichloro-1,4-diethylbenzene in the presence of di-*tert*-butylnitroxyl.[14]


I


II


III

Initiation of NMRP of styrene at 135 °C in evacuated glass ampules using **I**, **II**, or **III** at equimolar concentration of nitroxide functionality gave quite different results. **I** is almost inert in the polymerization, resulting in very little difference vs the polymerization control without nitroxide (no added initiator; i.e., autoinitiated). The inability of **I** to have a significant effect on styrene

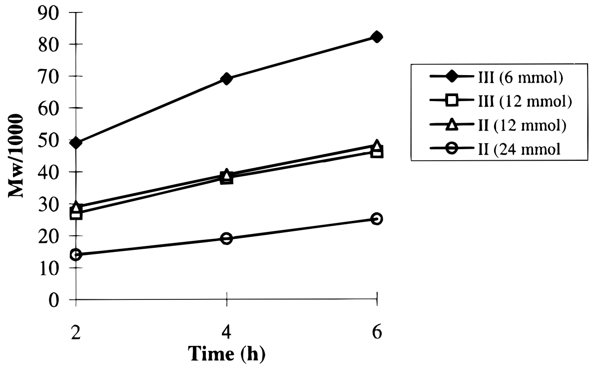


Figure 1. Comparison of mono- (**II**) and difunctional nitroxides (**III**) as NMRP initiators.

Table 1. Comparison of Mono- and Dinitroxides for Initiation of Styrene Polymerization

initiator	conc (mmol/L)	time (h)	conv (%)	M_w/1000	M_n/1000	M_w/M_n
II	12	2	30.4	28.9	23.6	1.22
II	12	4	49.3	39.2	31.5	1.24
II	12	6	60.6	48	37.4	1.28
II	24	2	28.3	14.2	11.6	1.22
II	24	4	44.4	19.4	15.9	1.22
II	24	6	69.4	24.7	20.2	1.22
III	6	2	30.2	49.3	38	1.30
III	6	4	45.5	68.9	50.4	1.37
III	6	6	60.6	81.8	56.4	1.45
III	12	2	32.4	27.4	22.8	1.20
III	12	4	45.6	37.7	30.1	1.25
III	12	6	59.3	46.1	35.1	1.31

polymerization indicates that a nitroxyl bonded to a primary benzylic carbon atom is not labile under styrene polymerization conditions. **II** and **III**, however, gave PS with much narrower polydispersity than the control (M_w/M_n of the control was 1.95). Also, at the same nitroxide functionality concentration, the difunctional nitroxide **III** gives about the same monomer conversion but leads to the formation of almost twice the molecular weight polystyrene as the monofunctional nitroxide **II** (Figure 1). This indicates that the polystyrene chain propagates from both active sites within the initiator. It is also interesting that the rate of polymerization is nearly independent of initiator concentration (Table 1). This is because the contribution of autoinitiation is inversely proportional to the concentration of nitroxide initiator. Since the two types of initiation are additive, the polymerization rate remains constant.

III (12 mmol/L) was dissolved in styrene and the solution heated in an evacuated glass ampule at 140 °C for 15 min, resulting in 5.8% conversion to polymer. The polymer was isolated by precipitation into methanol and was analyzed using gel permeation chromatography (GPC) ($M_w = 7600$ and $M_n = 5700$). The presence of TEMPO moieties attached to the polymer was confirmed by ^{13}C-NMR. The M_n of the polymer calculated using ^{13}C-NMR was 5000 (assuming a TEMPO on each chain end), confirming that the polystyrene possessed TEMPO functionality close to 2.

The telechelic polystyrene was then dissolved in *p*-methylstyrene (5% w/w) and the solutions sealed in evacuated glass ampules. Polymerization at 140 °C for 15 min resulted in the formation of a solution containing 12.6% by weight polymer. The polymer was isolated by precipitation from methanol and analyzed by GPC. Overlay of the GPC curves for the polystyrene from the first step and the polymer formed from the second step strongly suggests that a block copolymer was formed (Figure 2). The GPC curve of poly(*p*-methylstyrene) prepared under the same conditions without the addition of any initiator is also shown. Both the telechelic PS and block copolymer have lower molecular weight and narrower polydispersity than the autoinitiated poly(*p*-methylstyrene) control, indicating that the bulk of initiation is from the nitroxide rather than autoinitiation.

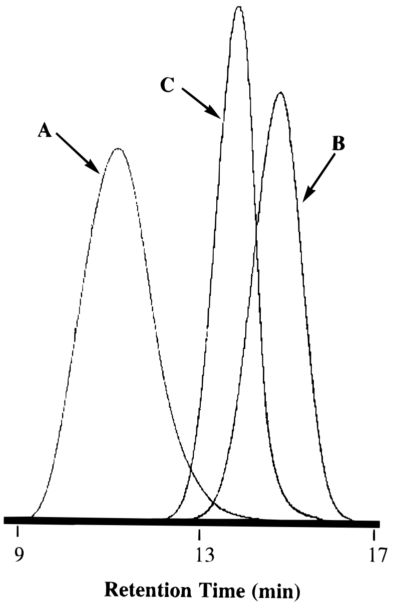


Figure 2. Overlay of (A) poly(*p*-methylstyrene) control, (B) telechelic PS made using **III**, and (C) A−B−A triblock polymer produced by initiating *p*-methylstyrene with the telechelic PS.

Conclusions. Benzylic nitroxides are not active initiators for NMRP unless the benzylic carbon is secondary. The use of a dinitroxide to initiate styrene polymerization results in the formation of telechelic polystyrene. Isolation of the telechelic polystyrene and its subsequent use to initiate NMRP of a second monomer leads to the formation of an A−B−A triblock copolymer.

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