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Visible light-induced controlled/"living" radical polymerization of styrene

A. N. PATWA, N. S. TOMER[‡], R. P. SINGH*
National Chemical Laboratory, Organic Chemistry (Synthesis)[‡], and Polymer Chemistry Division, Pune-411008, India*
E-mail: singh@poly.ncl.res.in; www.ncl-india.org

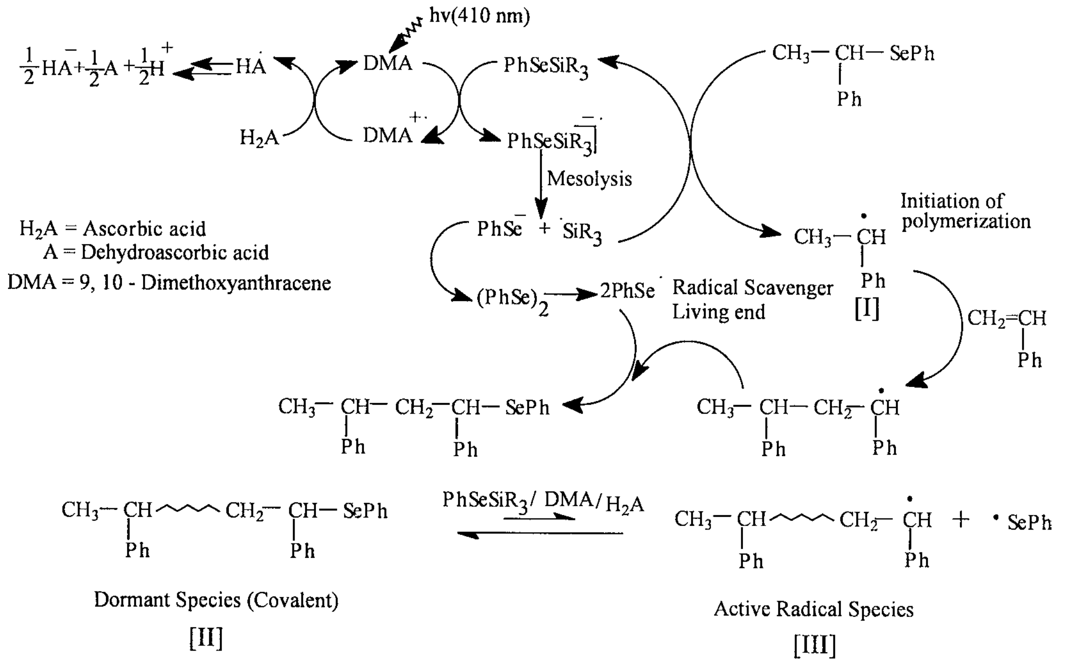
Well-defined polystyrene with low polydispersity index having methyl and phenylseleno (—SePh) groups at α- and ω-chain ends, respectively, was afforded via a controlled/"living" radical polymerization using a new initiating system: (1-phenylethyl)seleno benzene [1-PESePh]/tert.butyl diphenyl (phenylseleno) silane [$PhSeSiR_3$] and absorbing visible light at room temperature. A novel design initiating living radical polymerization in a catalytic fashion is described. The polymer yields and number average molecular weight (M_n) of the resulting polymer increased with reaction time. Further, a linear relationship was found for a plot of M_n versus polymer yield. These results indicate that this polymerization proceeds through a living radical mechanism.

Recently several remarkable methodologies [1–7] have been developed to design macromolecules via living radical polymerization. Among them, the iniferter method discovered by Otsu *et al.* [8–10] is an effective way to synthesize well-defined polymers [11, 12], which do not polymerize via an ionic mechanism. An iniferter is an initiator, which also functions as chain transfer and/or primary radical terminator.

Organoselenium compounds are useful for synthetic chemistry [13] and photochemistry [14, 15]. Kwon *et al.* [16, 17] reported that photo-polymerization in the presence of diphenyl diselenide afforded polystyrene carrying phenylseleno groups at both chain ends. The generation of $[PhSeSiR_3]^{\cdot -}$ was envisioned through one electron reductive processes involving 9,10-dimethoxyanthracene (DMA) as a light absorbing (>300 nm) electron donor and ascorbic acid (H_2A) as co-reductant [18] (Scheme I).

The objective of the present invention is to provide a narrow polydispersity polymer with photoinitiation at room temperature and providing controlled/"living" radical polymerization utilizing visible light thereby avoiding the use of free radical initiator. Here, we report a novel controlled/"living" radical polymerization by photo electron transfer (PET) process using 1-PESePh/$PhSeSiR_3$ as the initiating system having methyl (—CH_3) and phenylseleno (—SePh) group at α- and ω-chain ends, respectively, of the resulting polystyrene.

Polymerization of styrene was carried out by irradiation with a 400 W medium pressure mercury lamp



Scheme 1

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*Author to whom all correspondence should be addressed.

TABLE I Photo-polymerization of styrene at various monomer/initiator/catalyst mole ratios

S. no.	Monomer/Initiator/Catalyst (mole ratios)[a]	% Yield[b]	GPC Result M_n	M_w	M_w/M_n
1	500/2/1	10	2460	3300	1.34
2	700/4/1	15	2610	3986	1.52
3	1200/7/1	25	4168	6516	1.56
4	1600/10/1	33	5350	9180	1.60

[a] Monomer/initiator/catalyst were taken in mole ratios as mentioned, where $PhSeSiR_3$ (catalyst) = 0.0252 mmol, DMA = 0.0315 mmol, H_2A = 0.094 mmol and THF = 10^{-5} m^3.

[b] Yield obtained at 60 h. Irradiation time.

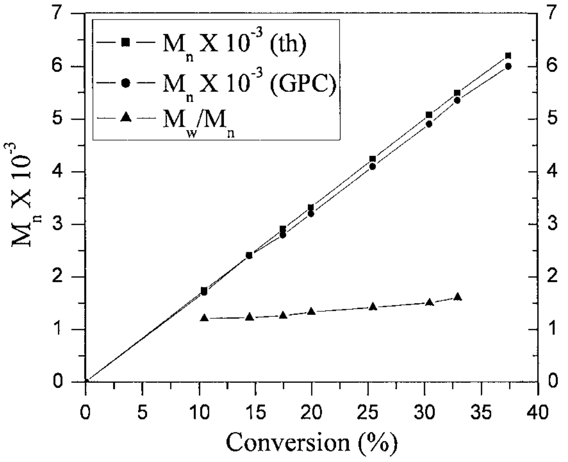


Figure 1 M_n-conversion and M_w/M_n-conversion relationship for photo-polymerization of styrene (monomer/initiator/catalyst = 1600/10/1).

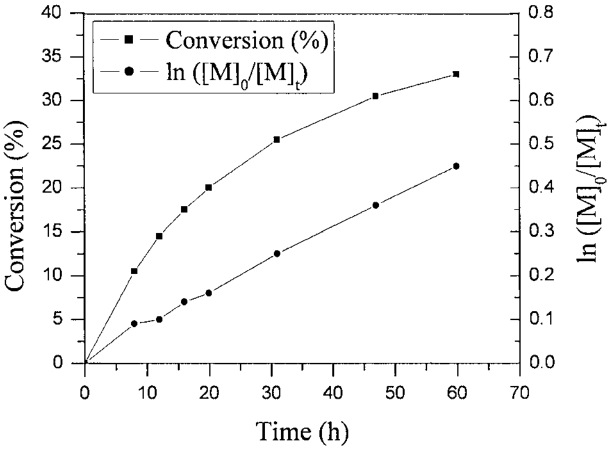


Figure 2 Time-conversion and Time-ln ($[M]_0/[M]_t$) relationship for photo-polymerization of styrene (monomer/initiator/catalyst = 1600/10/1).

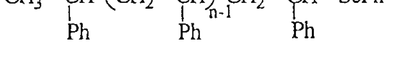
to the solution of styrene/1-PESePh/$PhSeSiR_3$ (λ_{max} = 410 nm) in a Pyrex glass photoreactor at room temperature. First, in order to obtain the information for the initiation ability of 1-PESePh/$PhSeSiR_3$ system, the polymerization was examined under various initiation concentrations but DMA/H_2A mole ratios were kept constant. The data are compiled in Table I.

The polymerization proceeded smoothly at all the concentrations. A higher molecular weight and polydispersity are observed ($M_n = 5350$ and $M_w/M_n = 1.6$ in Run-4) while a moderate molecular weight and narrower polydispersity are observed in Run-2 & 3. It shows that a higher monomer/initiator (styrene/1-PESePh) produces higher number-average molecular weight (M_n) and polydispersity while lower monomer/initiator ratio gives moderate number-average molecular weight and lower polydispersed polystyrene. Further, the polymer yield increased when ratio of styrene to initiating system increased. A similar finding has been reported for tetraethylthiuram disulfide having large transfer constant [19]. These results suggest that the catalyst not only works as a photoinitiator but also as a chain transfer agent [20].

The ^{1}H NMR signal ($CDCl_3$) at: $\delta = 7.2$–6.40 (—Ph), 4.40 [—CH(Ph)—SePh], 2.20–1.20 (—CH_2—CH—) and 1.02 (—CH_3) ppm exhibits the characteristic shifts. These results indicate that the polystyrene (macro-initiator) chain has -methyl group at one chain-end and —CH(Ph)—SePh, at the other chain-end.

Results for the system with the initial ratio of styrene: 1-PESePh: $PhSeSiR_3$ = 1600:10:1 (Run-4) are shown in Fig. 1. Here we took samples at different intervals of times and poured into excess of methanol. The polymer obtained was dried under vacuum at ~45°C for 12 h and then GPC was performed. It shows that M_n (number-average molecular weight) increases linearly with conversion from 1700 to 5350 and the polydispersity is 1.20 to 1.60. The $M_{n(GPC)}$ is close to the $M_{n(th)}$, a theoretical number-average molecular weight, computed from $M_{n(th)} = ([St]_0/[1\text{-PESePh}]_0)$ X $M_{w(St)}$ X conversion. The efficiencies of initiator (f) as calculated from $f = M_{n(th)}/M_{n(GPC)}$ are around 1.0. In a plot of In ($[M]_0/[M]_t$) versus time as shown in Fig. 2, a straight line is observed, indicating that the kinetics are of first order in monomer conversion. From this figure, the polymer yields and M_n values of the resulting polymers were also found to increase with the reaction time. This means that the concentration of the propagating radical is constant during the polymerization. From these results, it is clear that the styrene polymerization with 1-PESePh/$PhSeSiR_3$ initiating system at room temperature proceeds in a controlled/"living" manner as expected. However, the polydispersities (M_w/M_n) are 1.20–1.60 which are similar to the values obtained from the living radical polymerization with sulfur compounds by Otsu *et al.* [8]. So, the polymers produced using the initiation system are well defined, not only with narrow polydispersity index but also with precise end group i.e., α-methyl and ω-phenylseleno group. The presence of an ω-phenylseleno end group (further studies are in progress) in the obtained polystyrene suggests that polymerization proceeds via a controlled/"living" radical polymerization process.

In order to confirm the living nature of the system, the chain extension experiment was investigated under controlled experiments in fixed conditions. A solution mixture of styrene (2.1 $\times 10^{-6}$ m^3) and macroinitiator (0.2 g) [$M_n = 5350$, $M_w/M_n = 1.60$, Run-4] in THF (10^{-5} m^3) were



$$CH_3-\underset{Ph}{CH}-(CH_2-\underset{Ph}{CH})_{n-1}-CH_2-\underset{Ph}{CH}-SePh$$

(Macro-initiator)

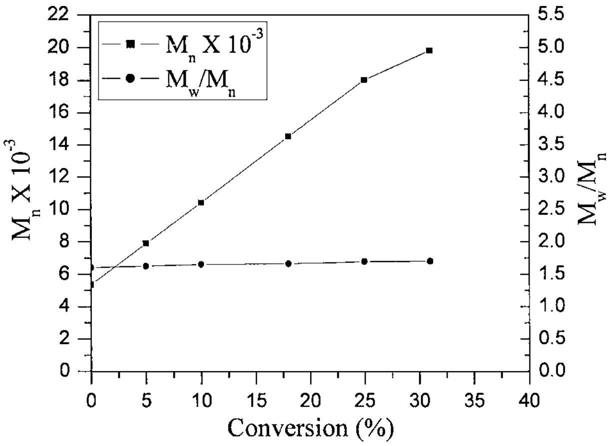


Figure 3 M_n-conversion and M_w/M_n-conversion relationship for photo-polymerization of styrene with macro-initiator (pre-polymer, obtained in Run-4 with $M_n = 5350$).

carried out at room temperature. Upon irradiation of this solution, a conversion of styrene monomer to 31% was achieved after 50 h irradiation. As can be seen from Fig. 3 (here at 0% conversion, $M_n = 5350$ which means we have started with macro-initiator), polymer yields and M_n increases with irradiation time. These results show that PS having a seleno group at ω-chain end effectively works as a polymeric photo-iniferter. The molecular weight (M_n) increases linearly from 5350 to 19800 and polydispersity index slightly increased from 1.60 to 1.70.

According to the results mentioned above, we proposed a mechanism for the controlled/"living" radical polymerization as depicted in the Scheme I. The potentiality of $PhSeSiR_3$ to initiate the radical chain sequences was envisaged by considering the expected dissociation of the radical anion ($[PhSeSiR_3]^{\bullet -}$ into silyl radical ($^{\bullet}SiR_3$) useful for chain initiation and PhSeSePh which formed after the oxidative dimerization of the corresponding $PhSe^-$ anion and it also participates in the termination step [21].

The efficient generation of silyl radical (SiR_3) and phenylselenide anion ($PhSe^-$) by the mesolysis [22–24] of $[PhSeSiR_3]^{\bullet -}$ by the visible light (410 nm) initiated photo induced electron transfer (PET) activation of $PhSeSiR_3$, provided a unique opportunity for radical chain initiation and group transfer reactions. The silyl radical ($^{\bullet}SiR_3$) abstracts ($^{\bullet}SePh$) radical from 1-PESePh forming a new free radical (I). Thus, 1-PESePh acts as an initiator. The styrene monomers insert into this new radical to afford polymer as in Scheme I. The propagation would take place by the addition to the resulting carbon radical to styrene. This polymerization would be terminated by coupling of the polymer radical with the stable seleno radical. There would be a dynamic equilibrium between active radical species (III) and dormant species (II).

Well-defined polystyrene with α-methyl($-CH_3$) and ω-seleno($-SePh$) end group, medium number–average molecular weight (M_n) and narrow polydispersity was synthesized using a new initiating system consisting of 1-PESePh/$PhSeSiR_3$ The 1-PESePh functions as a photoiniferter for the living polymerization of styrene. Since the polymer chain is end-functionalized by seleno group, therefore, it can be used as a macroinitiator to undergo chain extension via conventional controlled/"living" radical polymerization process.

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Further investigations of end-functionality and mechanism for polymerization are in progress and will be communicated soon. We are getting encouraging results; therefore, it prompted us to send the urgent article as a communication.

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