Synthesis and Characterization of One-Component Polymeric Photoinitiator by Simultaneous Double Click Reactions and Its Use in Photoinduced Free Radical Polymerization

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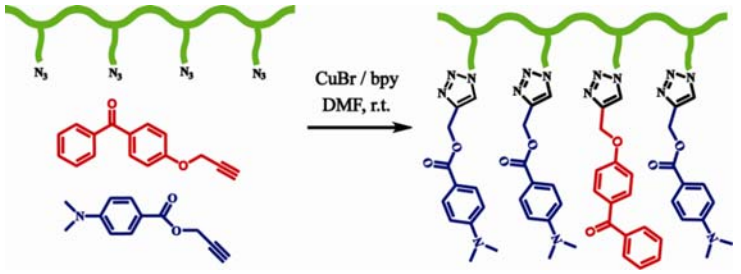
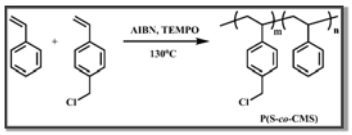
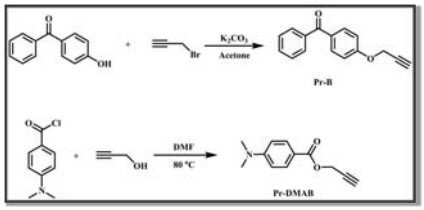
ABSTRACT: A polystyrene copolymer (PS-B-DMAB) possessing both benzophenone and dimethylamino moieties in the side chain was synthesized by a combination of nitroxide-mediated radical polymerization (NMRP) and simultaneous double "click" reactions. First, a random copolymer of styrene (S) and chloromethylstyrene (CMS) with 32 mol % CMS content was prepared by NMRP process. Then, chloromethyl groups were converted to azide groups by reacting with NaN3 in DMF. The other two click components, namely, propargyl benzophenone (Pr-B) and propargyl 4-(dimethylamino)benzoate (Pr-DMAB), were prepared independently by the etherification and esterification reactions, respectively. Then, in the final stage, the obtained alkyne functional chromophoric (Pr-B) and hydrogen-donating (Pr-DMAB) molecules were anchored to azide-modified polystyrene (PS-N3) in one-step by "click chemistry". The final polymer (PS-B-DMAB) and the intermediates were characterized in detail by spectral analysis and laser flash photolysis studies.



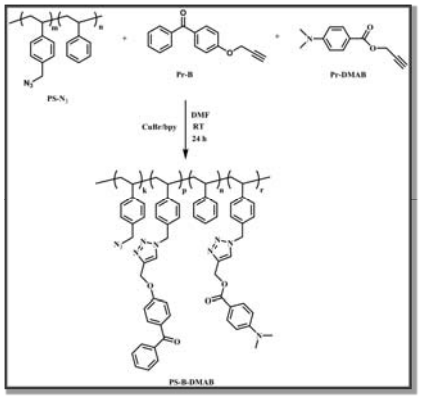
Nitroxide-Mediated Radical Copolymerization of Styrene and Chloromethylstyrene



Propargylation of Benzophenone and Dimethylaminophenyl Derivatives



Synthesis of One-Component Polymeric Photoinitiator by Simultaneous Double Click Reaction



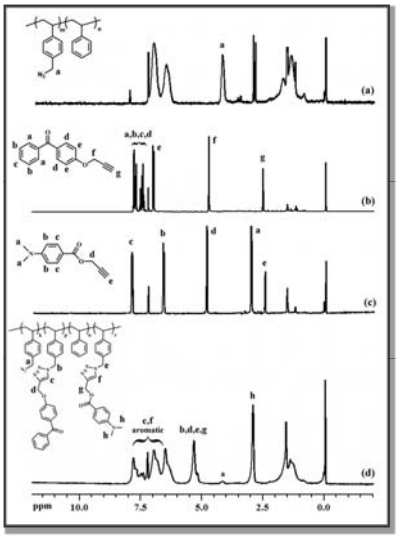


Figure 1. ^{1}H NMR spectra of a) PS-N_3, b) Pr-B, c) Pr-DMAB, and d) PS-B-DMAB in $CDCl_3$.

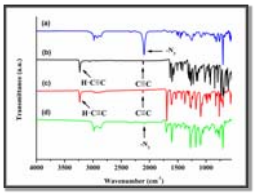


Figure 2. FT-IR spectra of a) PS-N3, b) Pr-B, c) Pr-DMAB, and d) PS-B-DMAB.

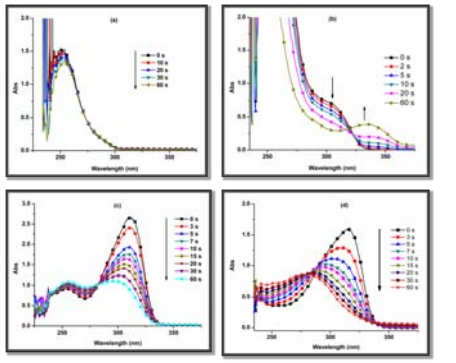


Figure 3. Absorption spectra of a) B ($2.5x10^{-5}$ mol L^{-1}), b) B ($2.5x10^{-5}$ mol L^{-1})/ DMA ($7.5x10^{-5}$ mol L^{-1}) c) B ($2.5x10^{-5}$ mol L^{-1})/ EDAB ($7.5x10^{-5}$ mol L^{-1}) and d) PS-B-DMAB ($1.3x10^{-5}$ mol L^{-1}, in terms of benzophenone moieties) in $CHCl_3$.

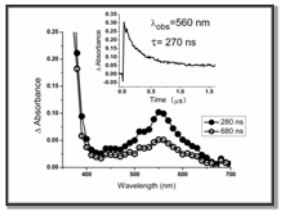


Figure 4. Transient optical absorption spectrum recorded at 280 and 680 ns following laser excitation (355 nm, 5 ns) in nitrogen saturated $CHCl_3$ solution of PS-B-DMAB (concentration= $2x10^{-3}$ mol L^{-1} in terms of benzophenone moieties).

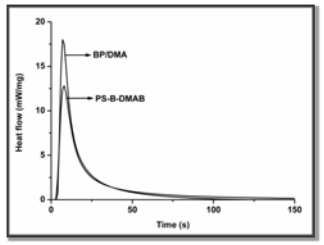


Figure 7. Heat flow vs. time for the polymerization of TMPTA initiated by PS-B-DMAB and BP/DMA systems, cured at 30°C by UV light with an intensity of 53 mW cm^{-2}. (The photoinitiator concentration is 0.0015 M in terms of BP moieties.)

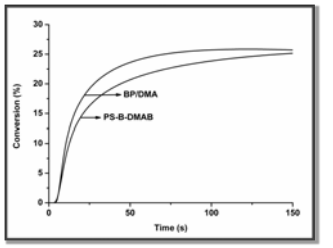


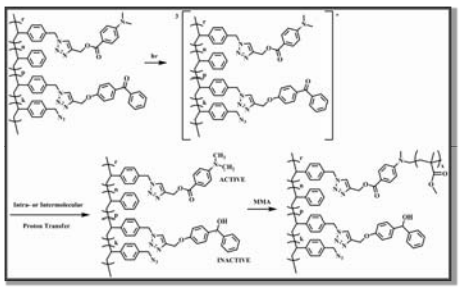
Figure 8. Conversion vs. time for the polymerization of TMPTA initiated by PS-B-DMAB and BP/DMA systems, cured at 30°C by UV light with an intensity of 53 mW cm^{-2}. (The photoinitiator concentration is 0.0015 M in terms of BP moieties.)

Table 1. Potoinitiated free radical polymerization of MMA at λ_{max}=350 nm. [a]

Run	Photoinitiator[b] (mol L^{-1})	Solvent	R_p x 10^5 (mol L^{-1} s^{-1})	Mn[c] (g mol^{-1})
1	B ($1x10^{-2}$)	$CHCl_3$	-	-
2[d]	B ($1x10^{-2}$)	$CHCl_3$	13.63	17350
3	PS-B-DMAB ($1x10^{-2}$)	$CHCl_3$	4.99	50900
4	PS-B-DMAB ($1x10^{-2}$)	$CHCl_3$[e]	7.14	111300
5	PS-B-DMAB ($2x10^{-3}$)	THF	5.52	45790
6	PS-B-DMAB ($2x10^{-3}$)	DMF	7.14	90500

[a] [MMA] = 4.68 mol L^{-1}, Time = 2 h.
[b] The photoinitiator concentration is given in terms of benzophenone moieties.
[c] Determined by GPC according to linear polystyrene standards.
[d] Benzophenone/ N,N-dimethylaniline: 1/ 3 is used as photoinitiating system.
[e] Carried out under nitrogen atmosphere.

Photoinitiated Free Radical Polymerization of Methyl Methacrylate (MMA) by Using Polymeric Photoinitiator (PS-B-DMAB)



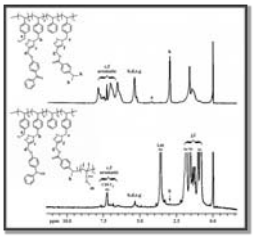


Figure 5. ^{1}H NMR spectra of PS-B-DMAB and poly(styrene-graft-methyl methacrylate) (P(S-g-MMA)), obtained after photolysis in the presence of MMA).

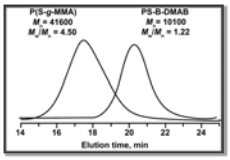


Figure 6. GPC traces of PS-B-DMAB and poly(styrene-graft-methyl methacrylate) (P(S-g-MMA), obtained after photolysis in the presence of MMA).

References

(1) Temel G, Aydogan B, Arsu N, Yagci Y. *Macromolecules* **2009**, *42 (16)*, 6098–6106.
(2) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 1-176.
(3) Jiang, X. S.; Yin, J. *Macromolecules* **2004**, *37*, 7850–7853.
(4) Ajayaghosh, A. *Polymer* **1995**, *36*, 2049–2053.