SYNTHESIS OF BLOCK AND STAR COPOLYMERS BY PHOTOINDUCED RADICAL COUPLING PROCESS

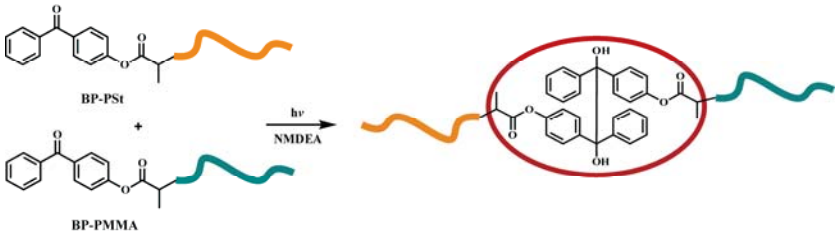
Gokhan Temel[1], Binnur Aydogan[2], Nergis Arsu[1], Yusuf Yagci[2]

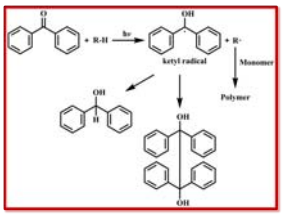
[1]*Department of Chemistry, Yildiz Technical University, Davutpasa, Istanbul 34210, Turkey*

[2]*Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey*

ABSTRACT

The general design for the synthesis of AB diblock, and A_2B and AB_2 star copolymers based on the statistical coupling of poly(styrene) (PSt) and poly(methyl methacrylate) (PMMA) macromolecules containing photoreactive benzophenone is presented. The proposed mechanism assumes hydrogen abstraction of photoexcited benzophenone moiety by NMDEA. Ketyl radicals resulting from abstraction reaction undergo radical-radical coupling to form benzpinacol structure at the core. Formation of A_2B and AB_2 type star copolymer upon irradiation of solutions containing appropriate combinations of end- and mid-chain functional polymers was also demonstrated.



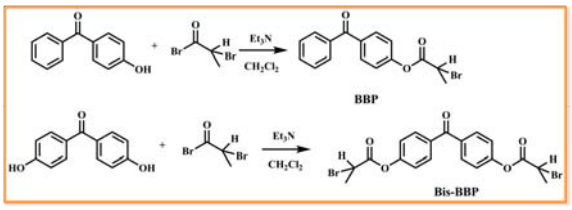


PHOTOINITIATING MECHANISM OF BENZOPHENONE

Photolysis of aromatic ketones in the presence of hydrogen donors, such as alcohols, amines, or thiols leads to the formation of a radical produced from the carbonyl compound (ketyl type radical) and another radical derived from the hydrogen donor. Photopolymerization is initiated by the radical produced from the hydrogen donor. Ketyl radicals, also formed in the process, are usually unreactive toward vinyl monomers and participate in coupling and further hydrogen abstraction reactions.

SYNTHESIS & RESULTS

Synthesis of Mono- and Bifunctional ATRP Initiators



Synthesis of End-Functionalized Polymers

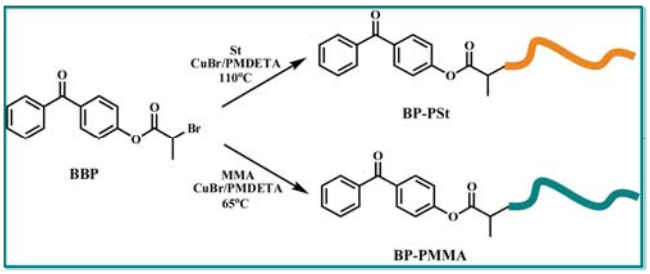


Table 1. Synthesis of Benzophenone End- and Middle-Functionalized PSt and PMMA via ATRP[a]

Monomer	$[M]_0$ (mol L^{-1})	Conv. (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,NMR}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n	Polymer
St[b]	8.5	31	3420	3320	3480	1.05	BP-PSt
MMA[c]	4.6	34	3660	8750	9540	1.24	BP-PMMA
St[d]	8.5	21	4700	5910	6120	1.11	BP-$(PSt)_2$
MMA[e]	4.6	25	5330	13400	15770	1.30	BP-$(PMMA)_2$

[a] Polymerization Time = 20 min.
[b] $[M]_0$:$[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 100:1:1:1, the polymerization was carried out at 110°C in bulk.
[c] $[M]_0$:$[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 100:1:1:1 (MMA/Toluene = 1(v/v)), the polymerization was carried out at 65°C.
[d] $[M]_0$:$[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 200:1:2:2, the polymerization was carried out at 110°C in bulk.
[e] $[M]_0$:$[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 200:1:2:2 (MMA/Toluene = 1(v/v)), the polymerization was carried out at 65°C.

Synthesis of Mid-Functionalized Polymers

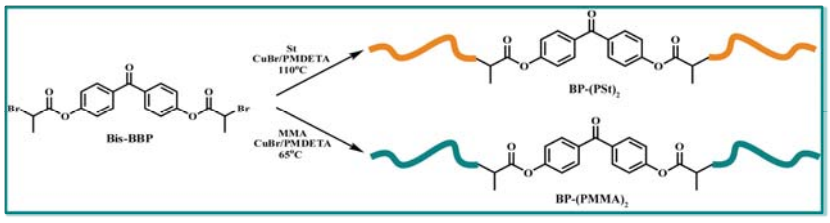
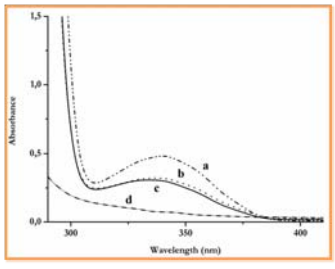
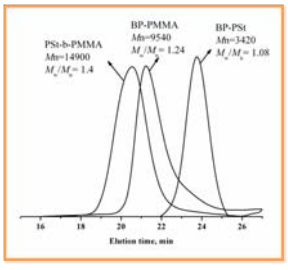


Table 2. Photoinduced Coupling of Benzophenone Functional Polymers in THF/DMF (1/1) at 350 nm

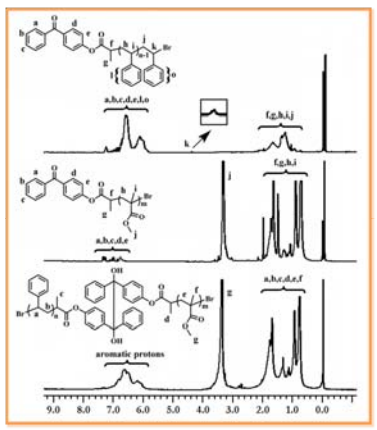
Polymer A [mol L^{-1}]	Polymer B [mol L^{-1}]	NMDEA [mol L^{-1}]	Coupled Polymer	Conversion[a] (%)	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n
BP-PSt [10.65×10^{-3}]	BP-PMMA [10.65×10^{-3}]	[10.65×10^{-2}]	AB	76	14900	1.43
PSt-BP-PSt [5.55×10^{-3}]	BP-PMMA [5.55×10^{-3}]	[5.55×10^{-2}]	A_2B	82	23850	1.38
BP-PSt [10.65×10^{-3}]	PMMA-BP-PMMA [10.65×10^{-3}]	[10.65×10^{-2}]	AB_2	80	25250	1.20



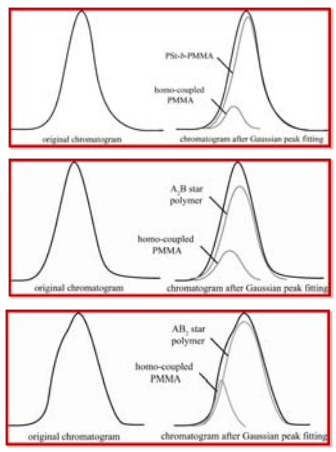
UV spectra of benzophenone (a), BPPMMA (b), BP-PSt (c), and PSt-b-PMMA (d) in CH_2Cl_2



GPC traces of BP-PSt, BP-PMMA, and PSt-b-PMMA



^{1}H NMR spectra of BP-PSt, BP-PMMA and PSt-b-PMMA in $CDCl_3$



GPC curve of polymers (left) and same chromatograms after Gaussian peak fitting (right). RI detection in THF

References

(1) Temel, G.; Aydogan, B.; Arsu, N.; Yagci, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 2938–2947.
(2) Goldbach, J. T.; Lavery, K. A.; Penelle, J.; Russell, T. P. *Macromolecules* **2004**, *37*, 9639–9645.
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