

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Bifunctional Initiators. III. Photochemical Synthesis of Block Copolymers of Styrene and Methyl Methacrylate with the Aid of Azo-benzoin Initiators

Yusuf Yagcır^a; Aysen Önen^a

^a Department of Chemistry, Istanbul Technical University, Istanbul, Turkey

To cite this Article Yagcır, Yusuf and Önen, Aysen(1991) 'Bifunctional Initiators. III. Photochemical Synthesis of Block Copolymers of Styrene and Methyl Methacrylate with the Aid of Azo-benzoin Initiators', *Journal of Macromolecular Science, Part A*, 28: 1, 129 – 141

To link to this Article: DOI: 10.1080/00222339108052089

URL: <http://dx.doi.org/10.1080/00222339108052089>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

BIFUNCTIONAL INITIATORS. III. PHOTOCHEMICAL SYNTHESIS OF BLOCK COPOLYMERS OF STYRENE AND METHYL METHACRYLATE WITH THE AID OF AZO-BENZOIN INITIATORS*

YUSUF YAĞCI and AYSEN ÖNEN

Department of Chemistry
Istanbul Technical University
Maslak, Istanbul 80626, Turkey

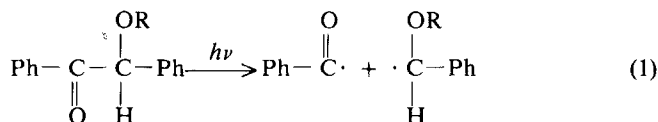
ABSTRACT

Block copolymers of styrene and methyl methacrylate were prepared by means of azo-benzoin initiators. In the first stage, prepolymers were synthesized by using these initiators. Photoactive prepolymers containing benzoin end groups were employed in the second stage for block copolymerization. The block copolymer structure was elucidated by means of extraction by appropriate solvents, GPC analysis, and IR and NMR spectral measurements. Mechanisms for initiation and possible termination for systems involving benzoin-type initiators are discussed in the light of results from studies of composition of the block copolymerization mixture. Structure and efficiency of the formation of the block copolymers depend greatly on both the relative reactivities of the photochemically derived radicals and the termination mode of polymerization.

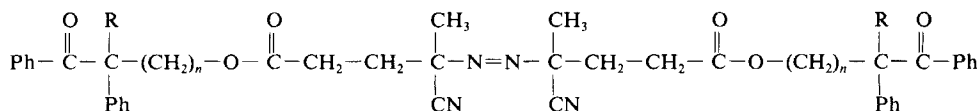
INTRODUCTION

Benzoin and its derivatives are well known, and they are extensively used as photoinitiators of free radical polymerization [1]. Upon photoexcitation, these compounds undergo α -scission with high quantum efficiencies according to the following reaction [2].

*For Parts I and II, see Refs. 3 and 5, respectively.



In a preceding paper [3], the synthesis and initiator properties of azo-benzoin initiators of the following structures were reported.



ACPB: R = H, $n = 0$

ABME: R = $-\text{OCH}_3$, $n = 1$

These bifunctional low molar mass initiators contain two chromophoric groups, the azo and benzoin groups, that differ significantly in thermal and photoactivity. The most effective use of these initiators can be made by thermolysis of the azo groups in the presence of monomer A and subsequent photolysis of the benzoin groups in the presence of monomer B. Since the benzoin moieties are contained as terminal groups in the polymer formed in the first step, a block copolymer can be formed in the second step. The structure of the block copolymer certainly depends on the mode of termination of the particular monomers involved in both polymerization steps.

This paper concerns the utilization of azo-benzoin initiators for the formation of block copolymers of styrene (St) and methyl methacrylate (MMA). By investigating the composition of the reaction products, i.e., block copolymer and homopolymers, we felt additional insight might be provided into the relative efficiencies of benzoyl and alkoxy benzyl radicals in polymerization.

EXPERIMENTAL

Materials

St, MMA, and solvents were purified by conventional drying and distillation procedures. 4,4'-Azo-bis-(4-cyanopentanoyl)-bis benzoin (ACPB) and 4,4'-azo-bis-(4-cyanopentanoyl)-bis-(α -methylolbenzoin methyl ether) (ABME) were prepared as described previously [3].

Preparation of Photoactive Polystyrene

Bulk St containing a known amount of ACPB or ABME in Pyrex tubes was degassed in a vacuum system. For polymerization, the tubes were immersed in a constant temperature bath at 60°C. At the end of a given time the reaction mixtures were poured into a tenfold excess of methanol and the precipitated polymers were filtered off. The polymers were then purified by dissolving them in methylene chloride and precipitating them in methanol before they were used in photopolymerization experiments.

Photopolymerization

Appropriate solutions of above-obtained prepolymers and MMA were placed in Pyrex tubes. The mixtures were degassed in the usual manner prior to irradiation with an annular-type photoreactor (Applied Photophysics) equipped with lamps emitting at 350 nm at 25°C. At the end of a given reaction time, polymers were obtained from the reaction mixture by precipitation into methanol. The mixture of block copolymers and homopolymers was separated by successive extraction in boiling cyclohexane and acetonitrile.

Analysis

IR spectra were recorded on a Shimadzu IR-400 model spectrophotometer on films and on KBr disks. ¹H-NMR spectra were taken on a Bruker-200 spectrophotometer in CDCl₃ solution with tetramethylsilane as the internal standard. GPC chromatograms were obtained by using a Knauer M64 instrument equipped with a differential refractometer and a UV (254 nm) detector by using THF as the eluent at a flow rate of 1 mL/min. Molecular weights were calculated by using polystyrene standards.

RESULTS AND DISCUSSION

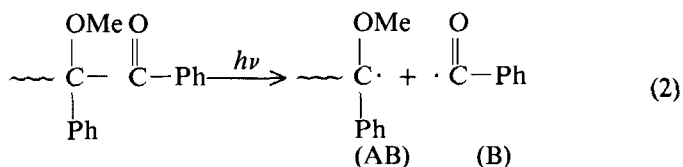
Azo-benzoin initiators have a sequential bifunctional character due to the presence of both a thermosensitive azo group and a thermally stable but photosensitive benzoin group in the structure. To test the sequential character of the azo-benzoin initiator, a series of two-stage polymeriza-

TABLE 1. Two-Stage Polymerization of Styrene with ACPB

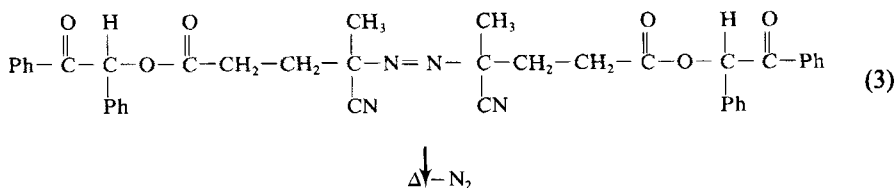
Run	Stage I heating time at 60°C, h	Stage II photolysis time ^a at 25°C, h	Conversion, %	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
I	2	—	6.81	26.69	1.51
II ^b	2	—	8.66	33.12	1.43
III	2	24	39.73	4.54	4.47

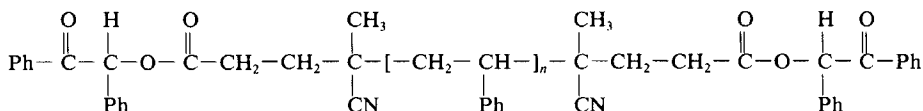
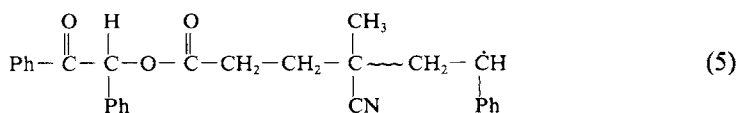
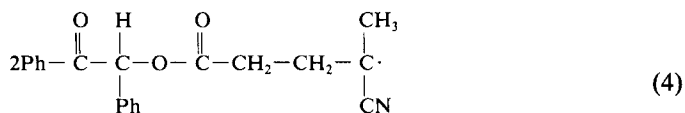
^a $\lambda = 350$ nm.^bKept at 25°C for 24 h.

tions of St were carried out. As can be seen from Table 1, conversion increased significantly when the polymerization mixture was irradiated in the second stage. Lower molecular weights and a broader molecular weight distribution as compared to the one-stage procedure were obtained. This may due to the fact that the benzoyl radical (B) is a better initiator than the alkoxy benzyl radical (AB) for St polymerization [4].

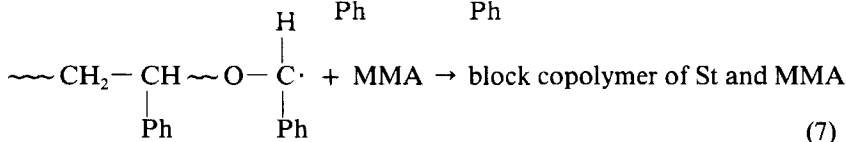
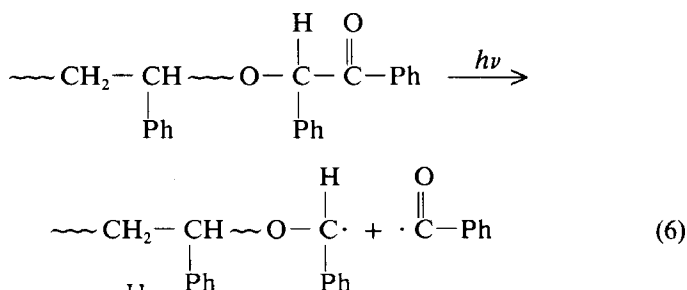


In order to employ block copolymerization experiments, polystyrenes (PSt) with various molecular weights, possessing benzoin and benzoin methyl ether end groups, were prepared according to the following sequence of reactions.





Details of the kinetics and mechanisms of the polymerization of St initiated by the thermolysis of these type of initiators were reported previously [3, 5]. UV irradiation of the resulting prepolymers caused α -scission and yielded benzoyl radicals and polymer-bound radicals according to Reaction (6).



Either or both of these radicals may then initiate the polymerization

TABLE 2. Block Copolymerization of the PSt Initiator, Obtained by the Thermolysis of ACPB, with MMA in Benzene Depending on the Molecular Weight of the PSt Initiator

$\overline{M}_n \times 10^{-4}$ (prepoly- styrene)	Conversion, ^b %	Composition of the reaction mixture			Block copolymer ^c composition, PMMA, %
		PSt, %	MMA, %	PSt- <i>b</i> - PMMA, %	
22.44	30.71	2	70	28	80
27.10	31.48	4	71	25	38
32.09	14.9	9	62	29	26
43.01	20.00	18	59	23	20

^a $\lambda = 350$ nm, $[M] = 7.5$ mol/L, $[I] = 1.4 \times 10^{-4}$ mol/L, photolysis time = 3 h, temperature = 25°C.

^bOverall MMA conversion.

^cDetermined by NMR analysis.

of the second monomer according to the polymerization conditions. In this connection we refer to the work of Pappas [6] who demonstrated that both radicals are equally effective as initiators in the polymerization of methyl acrylate (MA) and MMA. In our case it would appear necessary for the polymer-bound alkoxy benzyl radical to initiate polymerization for successful block copolymerization (Reaction 7). Typical results concerning the block copolymerization of St and MMA using photoactive polystyrenes obtained from ACPB and ABME are presented in Tables 2–5.

In all cases, homopolystyrene formation may be due to the primary radical combination of polymeric alkoxy benzyl radicals. PSt molecules, which for any reason fail to acquire benzoin end groups during the synthetic procedure in the first step, are also automatically included in the nonblock PSt component. The molecular weight and concentration of the PSt initiator influence the yield and the block copolymer ratio in the mixture. Furthermore, the PMMA ratio in the macromolecular chain decreases with increasing molecular weight of PSt initiator in the polymerization system. The highest amount of block copolymer formation was obtained by using benzoin-attached PSt with the lowest molecular weight and at the highest concentration (see Table 3). GPC analysis clearly indicates the formation of block copolymer; Fig. 1 shows the

TABLE 3. Block Copolymerization^a of the PSt Initiator, Obtained by the Thermolysis of ACPB, with MMA at Different PSt/MMA Ratios

[PSt] × 10 ⁻⁴ , mol/L	PSt/MMA ratio × 10 ⁻⁴ , mol/mol	Conversion, ^b %	Composition of the reaction mixture			Block copolymer ^c composition, PMMA, %
			PSt, %	PMMA, %	PSt- <i>b</i> - PMMA, %	
1.2	15.9	18.08	1	81	18	38
2.4	31.9	13.94	4	66	30	37
3.6	47.8	14.73	8	57	35	38
4.8	63.8	9.61	9	30	61	40

^aλ = 350 nm, [M] = 7.5 mol/L, photolysis time = 3 h, temperature = 25°C, \bar{M}_n of PSt = 1.61×10^{-5} .

^bOverall MMA conversion.

^cDetermined by NMR analysis.

TABLE 4. Block Copolymerization^a of the PSt Initiator, Obtained by the Thermolysis of ABME, with MMA in Benzene Depending on the Molecular Weight of the PSt Initiator

$M_n \times 10^{-4}$ (prepoly- styrene)	Conversion, ^b %	Composition of the reaction mixture			Block copolymer ^c composition, PMMA, %
		PSt, %	PMMA, %	PSt- <i>b</i> - PMMA, %	
10.46	23.34	1	81	18	38
19.52	34.99	3	73	24	34
26.23	13.00	7	63	30	31

^a $\lambda = 350$ nm, $[M] = 7.5$ mol/L, $[I] = 1.8 \times 10^{-4}$ mol/L photolysis time = 3 h, temperature = 25°C.

^bOverall MMA conversion.

^cDetermined by NMR analysis.

GPC chromatogram recorded with the prepolymer, mixture, and extraction products. The new peak at a higher molecular weight is ascribed to the block copolymer. Furthermore, dual detection by RI and UV (Fig. 1) allowed a clear assignment of this peak to the block copolymer since homopoly(methyl methacrylate) (PMMA) is transparent at the wavelength (254 nm) of the UV detector. The block copolymer structure was also assigned by means of IR and NMR spectral measurements. The IR spectra of the purified block copolymers show the characteristic band of PMMA at 1720 cm^{-1} in addition to the usual PSt bands. The NMR spectrum of a typical block copolymer displays signals at 0.8–1.1 ppm (CH_3), 1.4–2.0 ppm (CH_2), 3.6 ppm ($\text{O}-\text{CH}_3$), and 6.55–7.05 ppm (C_6H_5) (Fig. 2).

A different sequence of the same procedure may also be used to prepare block copolymers. For this purpose, MMA (9.4 mol/L) was polymerized by utilizing ABME as an initiator at a concentration of 10^{-5} mol/L at 60°C for 3 h. The resulting polymer was presumed to contain only one benzoin methyl ether moiety per macromolecular chain since propagating MMA radicals terminate mainly by disproportionation [7]. Terminally photoactive PMMA ($M_n = 13.4 \times 10^4$) was used to attempt photoinitiated block copolymerization of St (5.76 mol/L) in benzene. St

TABLE 5. Block Copolymerization of the PSt Initiator, Obtained by the Thermolysis of ABME, with MMA at Different PSt/MMA Ratios

[PSt] $\times 10^4$, mol/L	PSt/MMA ratio $\times 10^4$, mol/mol	Conversion, ^b %	Composition of the reaction mixture			Block copolymer ^c composition, PMMA, %
			PSt, %	PMMA, %	PSt- <i>b</i> - PMMA, %	
1.6	21.2	17.58	1	87	12	19
3.4	45.2	14.10	15	59	26	26
5.2	69.1	14.33	18	54	28	24
7.0	93.0	14.57	19	50	31	20

^a $\lambda = 350$ nm, $[M] = 7.5$ mol/L, photolysis time = 3 h, temperature = 25°C, \bar{M}_n of PSt initiator = 1.13×10^5 g/mol.

^bOverall MMA conversion.

^cDetermined by NMR analysis.

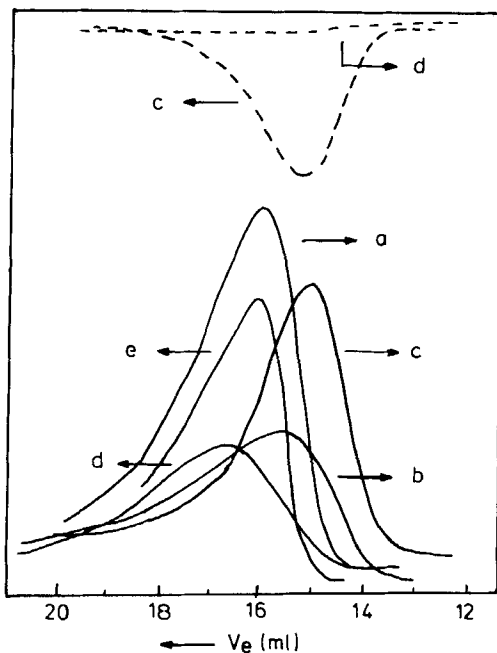


FIG. 1. Gel permeation chromatograms recorded with the products formed on block copolymerization. (a) Prepolystyrene. (b) Crude block copolymer. (c) Pure block copolymer after extraction with boiling cyclohexane and acetonitrile. (d) Homopoly(methyl methacrylate) (acetonitrile soluble part). (e) Homopoly(styrene) (cyclohexane soluble part). (—) RI detection; (- - -) UV detection.

containing PMMA at a concentration of 3×10^{-4} mol/L was irradiated for 3 h at 25°C.

It is interesting to note that the resulting polymer mixture gave a 90% yield of block copolymer after extraction of homopolymers with 3% overall St conversion. High yield of block copolymer is entirely consistent with the usual assumption that the termination reaction in styrene polymerization occurs by combination. In this way, less reactive PMMA-bound alkoxy-benzyl radicals also contribute to the formation of block copolymer by coupling with the propagating styryl radical derived from either a benzoyl or a alkoxy-benzyl radical. In this connection, it should be pointed out that several other bifunctional initiators have been reported in the literature. Among them, azo-peroxide initia-

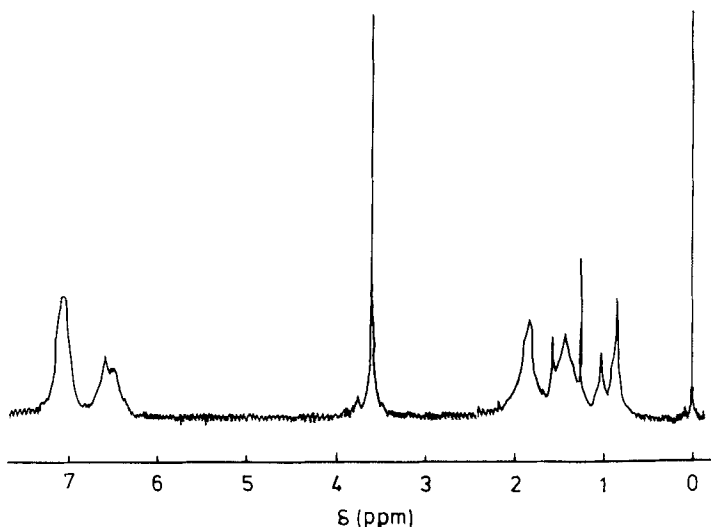


FIG. 2. ^1H -NMR spectrum of the block copolymer.

tors proved to be adequate in the synthesis of methyl methacrylate-styrene-based [8-11] and methyl methacrylate-acrylonitrile-based [12] block copolymers.

However, there are various drawbacks which quite often retard practical application of these initiators for the synthesis of block copolymers. These drawbacks essentially apply to the thermal sensitivity of both the azo and peroxide groups although at different rates. Upon heating under mild conditions, peroxide groups, in addition to the azo group, also decompose to a significant extent, in which case they contribute to the formation of unfunctionalized prepolymer and consequently homopolymer. High temperature conditions at the second stage are an additional reason for the presence of homopolymer. For example, very low block copolymer yields were obtained [13] when 4,4'-azo-bis-(4-cyano pentanoyl)-benzoyldiperoxide was used as a bifunctional initiator in the synthesis of poly(methyl methacrylate-*b*-styrene) and poly(methyl methacrylate-*b*-acrylonitrile) block copolymers. Compared with other types of bifunctional initiators, azo-benzoin initiators have several attractive aspects. The thermal stability of the benzoin groups allows the synthesis of polymers with photosensitive end groups. Low temperature reactions in the photochemical step prevent side reactions and decrease the impor-

block copolymers are obtained in high yield (up to 90%) with very low residual homopolymer content.

CONCLUSION

Block copolymerization via azo-benzoin initiators provides a versatile two-stage method applicable to vinyl monomers. The radicals, benzoyl and alkoxy-benzyl, are produced at different rates, but both are effective in initiating polymerization. It is clear that the efficiency of the block copolymerization greatly depends on the kinetic behavior of the free radical polymerizable monomer involved in the photochemical step.

ACKNOWLEDGMENT

The authors would like to thank the Alexander von Humboldt-Stiftung for donating the gel permeation chromatography instrument.

REFERENCES

- [1] S. P. Pappas, *U.V. Curing: Science and Technology*, Technology Marketing Corp., Norwalk, Connecticut, 1978.
- [2] A. Ledwith, J. P. Russel, and L. H. Sutcliffe, *J. Chem. Soc., Perkin Trans. II*, 1925 (1972).
- [3] A. Onen and Y. Yağci, *J. Macromol. Sci. - Chem.*, *A27*, 743 (1990).
- [4] H. J. Hageman, F. P. B. van der Maeden, and P. C. G. Janssen, *Makromol. Chem.*, *180*, 2531 (1979).
- [5] A. Onen and Y. Yağci, *Angew. Makromol. Chem.*, *181*, 191 (1990).
- [6] L. H. Carlblom and S. P. Pappas, *J. Polym. Sci., Polym. Chem. Ed.*, *15*, 1381 (1977); S. P. Pappas and A. K. Chattopadhyay, *J. Polym. Sci., Polym. Lett. Ed.*, *13*, 483 (1975).
- [7] R. P. Taylor, J. C. Bevington, and H. W. Melville, *J. Polym. Sci.*, *12*, 449 (1954).
- [8] M. Schulz, G. West, and S. Qurk, *Z. Chem.*, *14*, 150 (1974).
- [9] C. Simionescu, K. G. Sik, E. Comanita, and S. Dumitru, *Angew. Makromol. Chem.*, *126*, 73 (1984).
- [10] J. Pijirma and H. Lee-Pet Chou, *J. Appl. Polym. Sci.*, *24*, 2051 (1979).

- [9] C. Simionescu, K. G. Sik, E. Comanita, and S. Dumitru, *Angew. Makromol. Chem.*, **126**, 73 (1984).
- [10] J. Pijirma and H. Lee-Pet Chou, *J. Appl. Polym. Sci.*, **24**, 2051 (1979).
- [11] C. Simionescu, K. G. Sik, E. Comanita, and S. Dumitru, *Eur. Polym. J.*, **20**, 467 (1984).
- [12] A. S. Shaikh, S. Dumitru, E. Comanita, and C. Simionescu, *Polym. Bull.*, **3**, 363 (1980).
- [13] C. Simionescu, K. G. Sik, S. Dumitru, E. Comanita, and M. Pastravanu, *Ibid.*, **15**, 503 (1986).

Received February 5, 1990

Revision received June 15, 1990