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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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

### Photoinduced Block Copolymerization Using 4, 4'-Azobis (4-Cyanopentanoic Acid) and Lead Tetraacetate

Yusuf Yağci<sup>a</sup>; Aysen Önen<sup>a</sup>

<sup>a</sup> Department of Chemistry, Istanbul Technical University, Istanbul, TURKEY

**To cite this Article** Yağci, Yusuf and Önen, Aysen(1991) 'Photoinduced Block Copolymerization Using 4, 4'-Azobis (4-Cyanopentanoic Acid) and Lead Tetraacetate', Journal of Macromolecular Science, Part A, 28: 1, 25 — 29

**To link to this Article:** DOI: 10.1080/00222339108054379

**URL:** <http://dx.doi.org/10.1080/00222339108054379>

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PHOTOINDUCED BLOCK COPOLYMERIZATION USING  
4,4'-AZOBIS(4-CYANOPENTANOIC ACID) AND LEAD TETRAACETATE

Yusuf Yağci and Aysen Önen  
Istanbul Technical University, Department of Chemistry,  
Maslak-Istanbul 80626, TURKEY

ABSTRACT

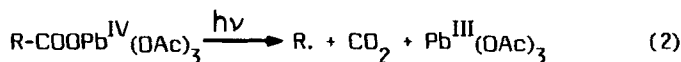
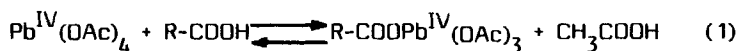
Styrene (St)/Methyl methacrylate (MMA) block copolymers were obtained by using a two-step procedure. In the first step, St was polymerized using 4,4'-azobis(4-cyanopentanoic acid) (ACPA) as initiator yielding polymers with carboxyl end groups. Subsequently, photoinduced polymerization of MMA initiated by carboxyl terminated polymers in conjunction with lead tetraacetate ( $\text{Pb}(\text{OAc})_4$ ) provided formation of block copolymers.

INTRODUCTION

Photochemical synthesis of block copolymers have a number of technical and theoretical advantages over other methods. Because of the applicability at low temperatures, side reactions leading to the formation of homopolymers are minimized. Further, the reactive sites can be produced at definite positions of the macromolecule due to the selective absorptivity of chromophores. Various methods for the photochemical synthesis of block copolymers have been treated recently by two review articles<sup>1,2</sup>.

Recently we have been investigating the possibility of preparing block copolymers utilizing azo-initiators<sup>3-10</sup>. Moreover, attachment of functional<sup>11,12</sup> and photosensitive<sup>13,14</sup> groups to polymers may easily be achieved using appropriate azo initiators.

Upon irradiating carboxylic acids in the presence of lead tetraacetate ( $\text{Pb}(\text{OAc})_4$ ) with UV light, free radicals are produced according to the following reactions<sup>15</sup>.



Sato et.al.<sup>16</sup> used the same reaction principle to graft benzyl methacrylate onto poly(N-acryloyl)-L-valine microspheres possessing side carboxyl groups. This paper describes block copolymerization of methyl methacrylate (MMA) with polystyrene (PSt) using the photoreaction of terminal carboxyl groups with lead tetraacetate.

## EXPERIMENTAL

### Materials:

4,4'-azobis(4-cyanopentanoic acid) (Aldrich) and lead tetraacetate (Fluka) were both used as purchased. Styrene (St), methyl methacrylate (MMA) and solvents were purified by conventional drying and distillation procedures.

### Polymerization of Styrene:

Appropriate solutions of St containing a given amount of ACPA was degassed in the usual manner. Polystyrene (PSt) was obtained by precipitating into methanol after heating at 70 C for 1 h.

### Synthesis of Block Copolymers Consisting of Styrene and Methyl methacrylate Blocks:

Appropriate solutions of above obtained prepolymers and MMA contained in pyrex tubes. The mixture was degassed in the usual manner prior to irradiation with an Annular type photoreactor (Applied photophysics). At the end of given 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.

Gel permeation chromatograms of polymers were obtained with the aid of a Knauer M64 type instrument, using THF as the eluent at a flow rate of 1 ml/min. Molecular weights were calculated according to the polystyrene standards.

TABLE 1.  
Polymerization of styrene initiated by ACPA at 70 C in DMF.  
Polymerization time: 60 min., [St]= 6.9 mol/l.

Run	[ACPA] (mol/l)	Conversion (%)	$M_n \times 10^{-3}^b$ (g/mol)
1	$5 \times 10^{-3}$	3.52	45.80
2	$5 \times 10^{-2}$	11.64	13.30
3	$2 \times 10^{-1}$	50.51	5.43

<sup>b</sup> Calculated by GPC

## RESULTS AND DISCUSSION

ACPA was used as an initiator in order to obtain polystyrenes with terminal carboxyl groups. The results presented in Table 1 show the molecular weight of polymer can be controlled simply by varying the initiator concentration.

Assuming propagating polystyryl radicals terminate by radical-radical combination, the resulting polymers are expected to possess two  $-COOH$  end groups. More detailed accounts on this respect have been given elsewhere<sup>2</sup>. Polystyrene having terminal carboxyl groups was used in photoinduced polymerization of MMA in the presence of  $Pb(DAc)_4$  (reactions 1 and 2,  $R = PSt$ ). Table 2 and 3 summarize the results of the block copolymerization of MMA with polystyrene.

The rate of MMA conversion ( $R_p$ ) and weight increase of polymer ( $\Delta m$ ) were found to be almost constant with increasing quantities of

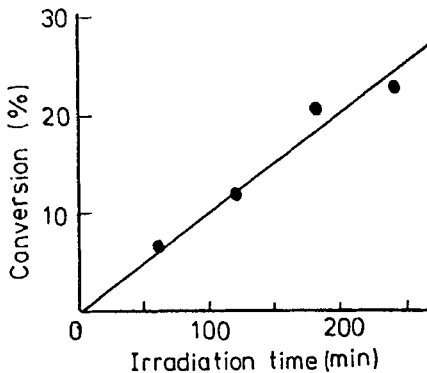


Figure 1: Time-Conversion (%) curve for photoinduced polymerization of methyl methacrylate at room temperature in benzene.  $[PSt]=27.17g/l$ ,  $M_n=5434 g/mol$ ,  $[MMA]=6.53 mol/l$ ,  $[Pb(DAc)_4]=1.5 \times 10^{-2} mol/l$ .

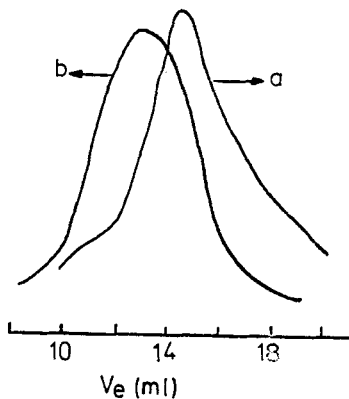


Figure 2: GPC chromatograms of a) Prepolystyrene obtained by using ACPA (Table 1, Run 3) b) Block copolymer of styrene and methyl methacrylate (Table 2, Run 5).

TABLE 2.

Photoinduced polymerization of methyl methacrylate by  $\text{PSt/Pb(OAc)}_4$  at room temperature in benzene.  $[\text{PSt}] = 27.17 \text{ g/l.}$ ,  $M_n = 5434 \text{ g/mol.}$ , Time of irradiation = 240 min.,  $[\text{M}] = 6.53 \text{ mol/l.}$

Run	$\text{Pb(OAc)}_4$ ( mol/l )	$R_p \times 10^5$ ( mol/l.sec.)	$\Delta m^a \times 10^{-2}$
4	$3.7 \times 10^{-3}$	5.04	2.67
5	$7.5 \times 10^{-3}$	6.53	3.46
6	$1.5 \times 10^{-2}$	9.30	4.93
7	$2.25 \times 10^{-2}$	9.81	5.19

<sup>a</sup> Relative increase in mass of polymer.  $\Delta m = \frac{(m_{\text{final}} - m_{\text{start}})}{m_{\text{start}}} \times 100$

TABLE 3.

Photoinduced polymerization of methyl methacrylate by  $\text{PSt/Pb(OAc)}_4$  at room temperature in benzene.  $[\text{Pb(OAc)}_4] = 1.5 \times 10^{-2} \text{ mol/l.}$ ,  $[\text{M}] = 6.53 \text{ mol/l.}$ ,  $M_n$  of  $\text{PSt} = 5434 \text{ g/mol.}$ , Time of irradiation = 300 min.

Run	$[\text{PSt}]$ (g/l)	$R_p \times 10^5$ (mol/l.sec.)	$\Delta m \times 10^{-2}$
8	5.66	8.35	27.17
9	11.33	7.74	12.30
10	22.66	8.13	6.46
11	34.00	7.42	3.93

$\text{PSt}$  and increase with increasing quantities of  $\text{Pb(OAc)}_4$ . Similar results were obtained by Sato et.al.<sup>16</sup> for poly(acryloyl-L-valine)/ $\text{Pb(OAc)}_4$  photoinitiating system. Total conversion of  $\text{MMA}$  is directly proportional to the irradiation time as can be seen from Figure 1.

Extraction with boiling cyclohexane removed only about 1 % from the resulting block copolymers indicating very low content of unreacted  $\text{PSt}$ . By GPC analysis the formation of block copolymer was clearly evidenced as can be seen from Figure 2. where GPC chromatograms recorded with the prepolymer and block copolymer are shown.

## ACKNOWLEDGEMENT

The authors thank to Alexander von Humboldt Foundation for donating GPC instrument.

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