Articles

Synthesis and Characterization of Macrophotoinitiators of Poly(ϵ-caprolactone) and Their Use in Block Copolymerization

Mustafa Degirmenci, Gurkan Hizal, and Yusuf Yagci*

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

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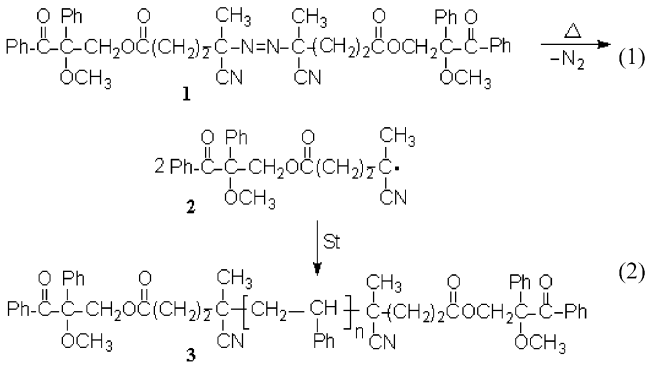
ABSTRACT: Novel end-chain and midchain functional macrophotoinitiators of poly(ϵ-caprolactone) have been synthesized. For this purpose, mono- and dihydroxy functional photoinitiators namely, benzoin (B) and 2-hydroxy-2-methyl-1-phenyl propan-1-one (HMPP), Darocure 1173, and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl propan-1-one (HE-HMPP), Irgacure 2959, respectively, were used as initiators for the stannous-2-ethylhexanoate ($Sn(Oct)_2$) catalyzed living ring-opening polymerization of ϵ-caprolactone. The gpc and IR, H NMR, UV, and fluorescence spectroscopic studies revealed that low-polydispersity poly(ϵ-caprolactone) with desired photoinitiator functionality at the end or in the middle of the chain were obtained. These prepolymers were used to induce radical polymerization of methyl methacrylate (MMA) upon irradiation via α-cleavage of the incorporated phenyl ketone groups. While end-chain functional macrophotoiniators led to the formation of both homo and block copolymers, only block copolymers of ϵ-CL and MMA were formed with midchain functional macrophotoinitiator. Successful blocking has been confirmed by a strong change in the molecular weight of the prepolymer and the block copolymer as well as by NMR spectral measurements.

Introduction

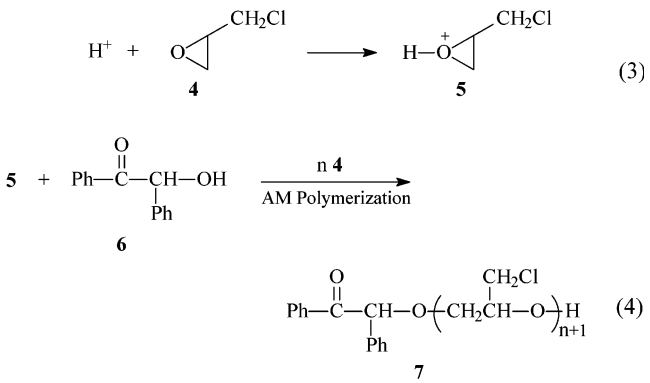
Polymers possessing side- or main-chain photo reactive groups capable of initiating polymerization reaction receive continuous interest due to their application in various fields of UV curing and in polymer synthesis.[1,2] In UV curing applications, the advantages expected from the polymeric photoinitiators include good compatibility, low migration, and low volatility, which reduces odor problems associated with the low molar mass photoinitiators.[3,4] Polymeric photoinitiators are also precursors for block or graft copolymers depending on the position of the photoinitiator moiety incorporated into the polymer chain. Many side- and main-chain photoinitiators have been synthesized, and their photochemistry and utilization in both applications have been reviewed extensively.[1−5] Previously, we synthesized polymers containing terminal photoactive benzoin groups by using azobenzoin initiators.[6−8] The thermal treatment of these initiators in the presence of styrene (St) leads to polystyrene chains with benzoin groups at both ends, as polystyryl radicals tend to terminate via recombination (Scheme 1).

Such photoactive polymers can be used in the preparation of block copolymers of monomers with different chemical nature such as those with liquid crystalline properties.[9] Similarly, activated monomer (AM) polymerization was used to produce polymers with terminal benzoin groups.[10,11] The process was easily adapted so that benzoin type photoinitiators containing hydroxyl group were used as initiators in the activated monomer polymerization (Scheme 2).

Scheme 1



Scheme 2



In a preceding paper,[12] we applied a recently developed novel precision polymerization, atom transfer radical polymerization (ATRP), to incorporate photoini-

* Corresponding author. E-mail: yusuf@itu.edu.tr.

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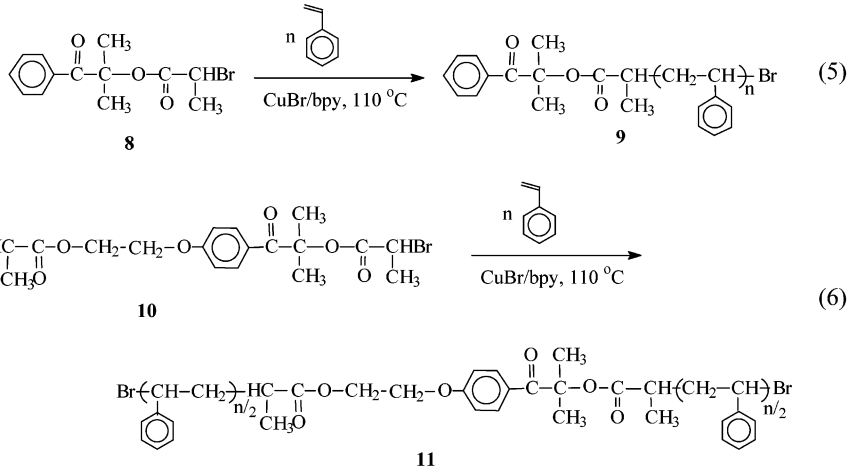
Scheme 3



(5)

(6)

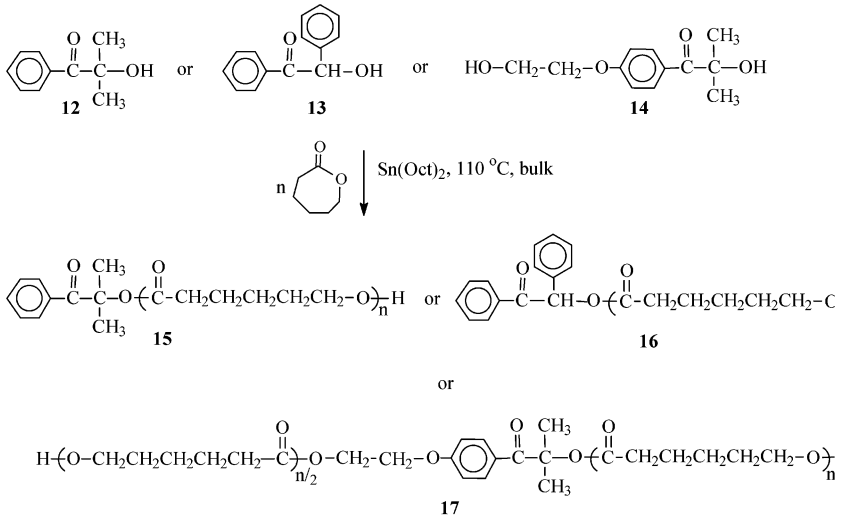
8 **9** **10** **11**

Table 1. Synthesis of Photoactive Poly(ϵ-Caprolactone)[a]

run	initiator	[I] × 10^2 (mol·L^{-1})	time (h)	polymer	convn (%)	$M_{n\ theor}$	$M_{n\ GPC}$	M_w/M_n	$M_{n\ H-NMR}$	$M_{n\ UV}$
A	**12**	41	48	**15**	90	2420	2600	1.08	3650	2560
B	**13**	45	72	**16a**	84	2150	2500	1.13	4200	3050
C	**13**	45	96	**16b**	100	2500	3300	1.57	4170	4000
D	**14**	22	90	**17**	100	4800	4400	1.56	5100	5300

[a] Temperature = 110 °C, $[\epsilon\text{-CL}]_0$ = 9.02 mol L^{-1}(in bulk), [I]/[ϵ-CL] = 1/20 and $[Sn(Oct)_2]/[I]$ = 1/400 for the initiators **12** and **13**, and [I]/[ϵ-CL] = 1/40 and $[Sn(Oct)_2]/[I]$ = 1/200 for the initiator **14**.

Scheme 4



(7)

12 **13** **14** **15** **16** **17**

tiator moieties into the end-chain and midchain of the polymers. Thus, polystyrenes with precise functionalities and narrow molecular weight distributions were prepared by using respective halide functional initiators in the ATRP system according to the reactions shown in Scheme 3.

Because of various applications, particularly in the biomedical field, homo- and copolymers of polylactones such as poly(ϵ-caprolactone) receive interest. Tin octoate, $Sn(O(O)CCH(C_2H_5)C_4H_9)_2$, in short $Sn(Oct)_2$, is the initiator most widely used[13] to synthesize designed polymers based on poly(ϵ-caprolactone). In particular, when used in conjunction with hydroxyl functional compounds or prepolymers, telecehelics, linear and star-shaped block copolymers, or networks can be obtained[14−22] via corresponding alkyl octoate formation. The aim of this study was to prepare new kinds of macrophotoinitiators of poly(ϵ-caprolactone) that have a potential to initiate light-induced free radical polymerization.

Experimental Section

Materials. Benzoin (B) (Aldrich) was recrystallized from ethanol. 2-hydroxy-2-methyl-1-phenyl propan-1-one (HMPP), Darocure 1173, and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl propan-1-one (HE-HMPP), Irgacure 2959, photoinitiators were received from Ciba Specialty Chemicals and used without further purification. Stannous 2-ethyl-hexanoate (stannous octoate) (Sigma) was used as received. ϵ-Caprolactone (Aldrich) was vacuum distilled over calcium hydride.

Ring-Opening Polymerization. Certain amounts of monomer (ϵ-caprolactone), stannous octoate and photoinitiators (benzoin, HE-HMPP, or HMPP) were added under nitrogen into previously flamed and nitrogen-purged Schlenk tubes equipped with a magnetic stirrer. The detailed polymerization conditions are given in Table 1. The ϵ-CL polymerizations were carried out in bulk at 110 °C. After a given time the mixtures were diluted with CH_2Cl_2 and poured into 10-fold excess of cold methanol. The polymers were collected after filtration and drying at room temperature in a vacuum for 3 days.

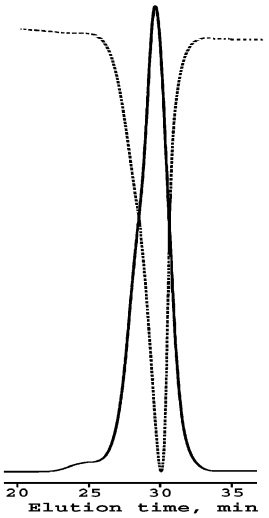


Figure 1. GPC trace of **16**: refractive index signal (−) and UV signal at $\lambda = 330$ nm (- - -).

Photopolymerization. Photopolymerizations were carried out in bulk. Appropriate solutions of monomer (MMA) containing given amounts of macrophotoinitiators (15 or 16 or 17) were placed in Pyrex tubes and degassed with nitrogen prior to irradiation by a merry go round type photoreactor equipped with 15 Philips 8 W/06 lamps emitting light nominally at $\lambda >$ 300 nm and a cooling system. At the end of a given time, polymers were poured into methanol, filtered off, dried, and weighted. Conversions were determined gravimetrically.

Characterizations. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded on a Jasco FT/IR-3 spectrometer. UV−vis spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Gel permeation chromatography (gpc) analyses were performed with a setup consisting of an Agilent 1100 RI apparatus equipped with three Waters Ultrastyragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min and a refractive index detector. Molecular weights were calculated with the aid of polystyrene standards by using the following conversion formula:[23] $M_{PCL} = 0.259 M_{PSt}^{1.073}$.

Results and Discussion

The synthesis of macrophotoinitiators of poly(ϵ-caprolactone) depicted in Scheme 4 involved the reaction of photoinitiators, namely benzoin (B), 2-hydroxy-2-methyl-1-phenyl propan-1-one (HMPP), and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl propan-1-one (HE-HMPP), with ϵ-caprolactone (ϵ-CL) in the presence of stannous octoate catalyst. In view of the reported role of hydroxyl groups as initiators in ring-opening polymerization, this reaction was expected to produce polymers containing a photoiniator group on one end or on the middle of the chain, derived from a single or two terminal units of the photoinitiators, respectively (Scheme 4).

As can be seen from Table 1, the measured and calculated $\bar{M}_n$values are in good agreement indicating that each photoinitiator added to the solution generates one or two growing ends depending on the initiator functionality. Some discrepancy observed with the values calculated by spectral methods may be due to the inaccuracy of the molecular weight determination by end group analysis.

The gpc traces are unimodal and narrow, indicating that no side reactions occurred. Moreover, dual detection by refractive index and UV measurements provides clear evidence for the complete functionalization. As can be seen from Figure 1, gpc traces of poly(ϵ-caprolactone) prepared from benzoin measured by UV ($\lambda = 330$ nm) and refractive index appear at the same elution volume.

In the ^{1}H NMR spectra of the polymer samples can be found not only the specific signals of poly(ϵ-caprolactone) (PCL) but also absorptions belonging to the rests of initiators. For instance, in Figure 2 is shown the ^{1}H NMR spectrum of a polymeric photoinitiator, **16**, in $CDCl_3$ which is typical of this series of compounds.

A summary of the ^{1}H NMR chemical shifts for these photoinitiators is given in Table 2. The incorporation of alkoxyphenyl ketone groups into polymers was also evidenced by UV absorption measurements. Figure 3 shows the absorption spectra of precursor **13**, together with the PCL, **16**, obtained. It can be seen that polymeric photoinitiators have spectra which are typical for benzoyl chromophores absorbing strongly in far UV and

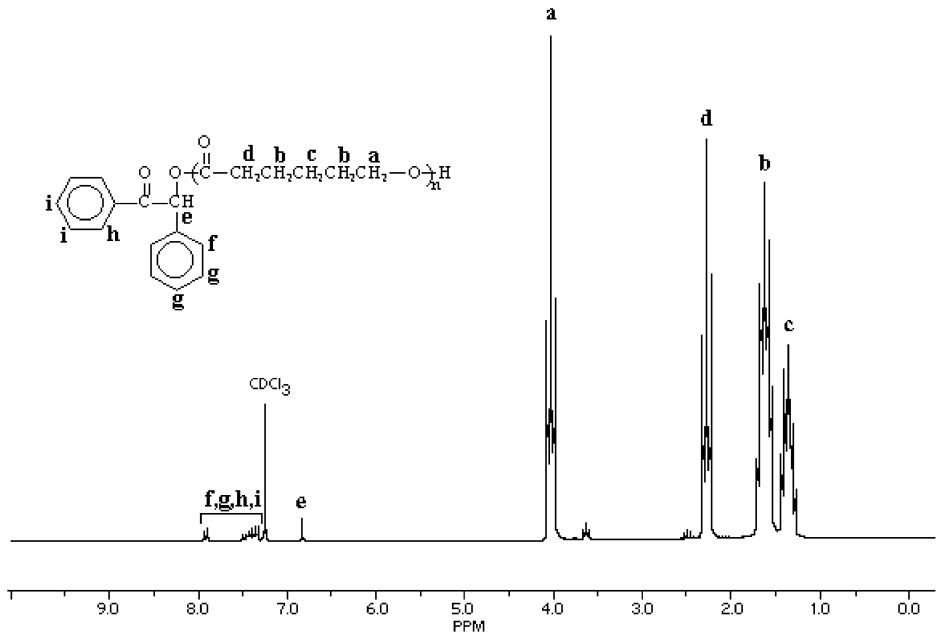


Figure 2. ^{1}H NMR spectrum of **16** in $CDCl_3$.

Table 2. Spectral Characterization of Macrophotoinitiators

	^{1}H NMR		UV	
macrophotoinitiator	group	δ (in ppm)	λ_{max} (nm)	ϵ (L mol^{-1}cm^{-1})
15	CH_2−O	4.00−4.06 (t, 2H)	320	96 (104)[a]
	CH_2−CH_2−CH_2−CH_2−CH_2−O and CO−C(CH_3)$_2$−O	1.56−1.68 (m, 10H)		
	CH_2−CH_2−CH_2−CH_2−CH_2−O	1.29−1.41 (m, 2H)		
	CO−CH_2	2.25−2.31 (t, 2H)		
	Ar-*H*	6.80−7.48 (m, 5H)		
16	CH_2−O	4.01−4.06 (t, 2H)	320	201 (217)[a]
	CH_2−CH_2−CH_2−CH_2−CH_2−O	1.56−1.73 (m, 4H)		
	CH_2−CH_2−CH_2−CH_2−CH_2−O	1.29−1.41 (m, 2H)		
	CO−CH_2	2.25−2.31 (t, 2H)		
	Ar−*CH*	6.83 (s, 1H)		
	Ar-*H*	7.32−7.92 (m, 10H)		
17	CH_2−O	4.00−4.05 (t, 2H)	320	117 (286)[a]
	CH_2−CH_2−CH_2−CH_2−CH_2−O and CO−C(CH_3)$_2$−O	1.56−1.73 (m, 10H)		
	CH_2−CH_2−CH_2−CH_2−CH_2−O	1.28−1.41 (m, 2H)		
	CO−CH_2	2.25−2.37 (t, 2H)		
	Ar-*H*	6.86−8.06 (m, 4H)		
	O−CH_2−CH_2−O	4.12−4.54 (m, 4H)		

[a] Values in parentheses indicate the molar extinction coefficients of the precursor low molar mass photoinitiators.

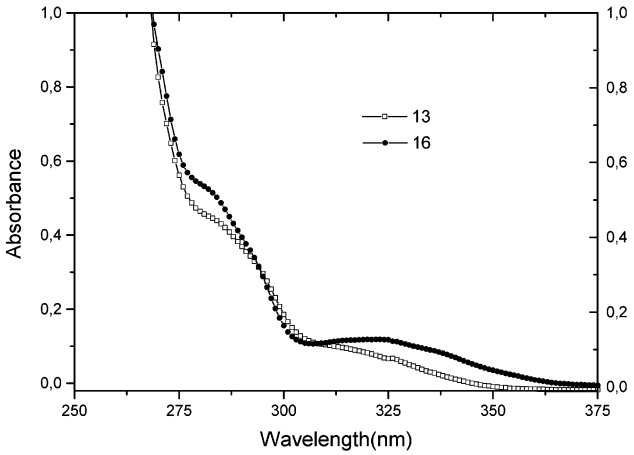


Figure 3. Absorption spectra of **13** (3.77×10^{-4} mol L^{-1}) and **16** (2.08 g L^{-1}) in CH_2Cl_2.

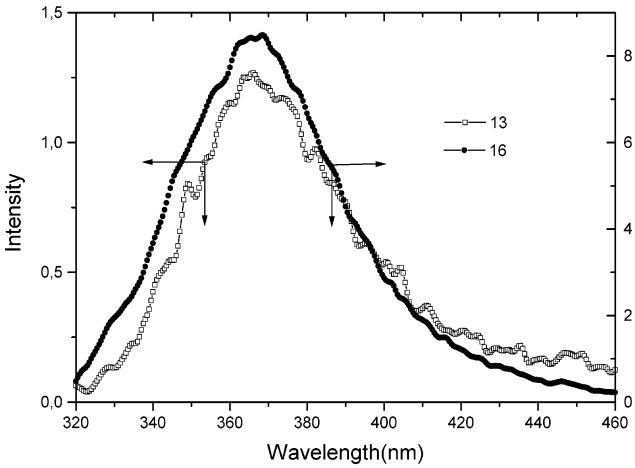


Figure 4. Fluorescence spectra of **13** (1.41×10^{-3} mol L^{-1}) and **16** (10.67 g L^{-1}) in $CHCl_3$. λ_{exc} = 310 nm.

possessing an absorption maximum of the n → π^* transitions around 320 nm ($\lambda_{max} \approx 320$ nm, $\epsilon \approx 100-200$ L mol^{-1} cm^{-1}).[24] Thus, they are suitable for use in formulations that do not absorb strongly in this region. Notably, the extinction coefficient of the polymeric photoiniators, in particular the midchain initiator, **17**, are lower than those of the precursors. This behavior may be due to the restricted mobility of the chromophoric groups tethered to polycaprolactone.

Table 3. Photoinduced Polymerization of Bulk MMA (9.42 mol L^{-1}) by Using Poly(ϵ-Caprolactone) (100 g L^{-1}) Photoinitiators with λ_{inc} > 300 nm

				homoPMMA		PCL-*b*-PMMA	
run	PCL	irradiation time (min)	convn[a] (%)	%	$M_n \times 10^{-3}$ [b]	%	$M_n \times 10^{-3}$ [b]
E	**15**	150	9	54	6	46	130
F	**16a**	105	14	36	6.8	64	93
G	**16b**	105	14	28	0	72	93
H	**17**	75	21	0		100	79
I[c]	**14**	35	17	100	56		

[a] MMA conversion. [b] Determined by GPC according PMMA standards. [c] [**14**] = 2.3×10^{-2} mol L^{-1}.

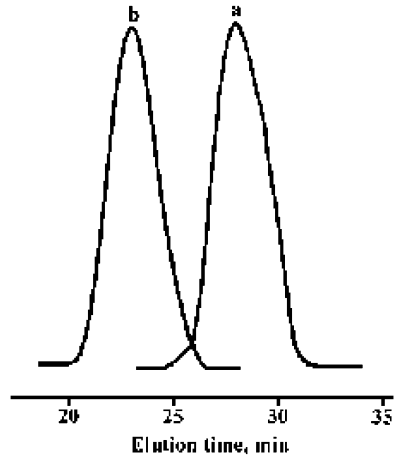


Figure 5. GPC traces of PCL, **17** (a), and PCL−PMMA block copolymer (Table 3, run H) (b).

Figure 4 shows the fluorescence emission of the related compounds **13** and **16** in chloroform at room temperature. Both spectra show the vibrational structures of the benzoin chromophore. Notably, the fluorescence intensity is higher in the case of polymer indicating limited self-quenching[25,26] due to the low mobility. Similar behavior was noted in the fluorescence emission studies of the other photoiniators, **12** and **14**, and the corresponding polymers, **15** and **17**. These spectroscopic investigations suggest that the photochromophoric phenyl ketone groups were conserved under the polymerization conditions.

We have also tested the photoinitiation capability of these polymers. Typical results concerning photochemically induced polymerization of bulk methyl methacry-

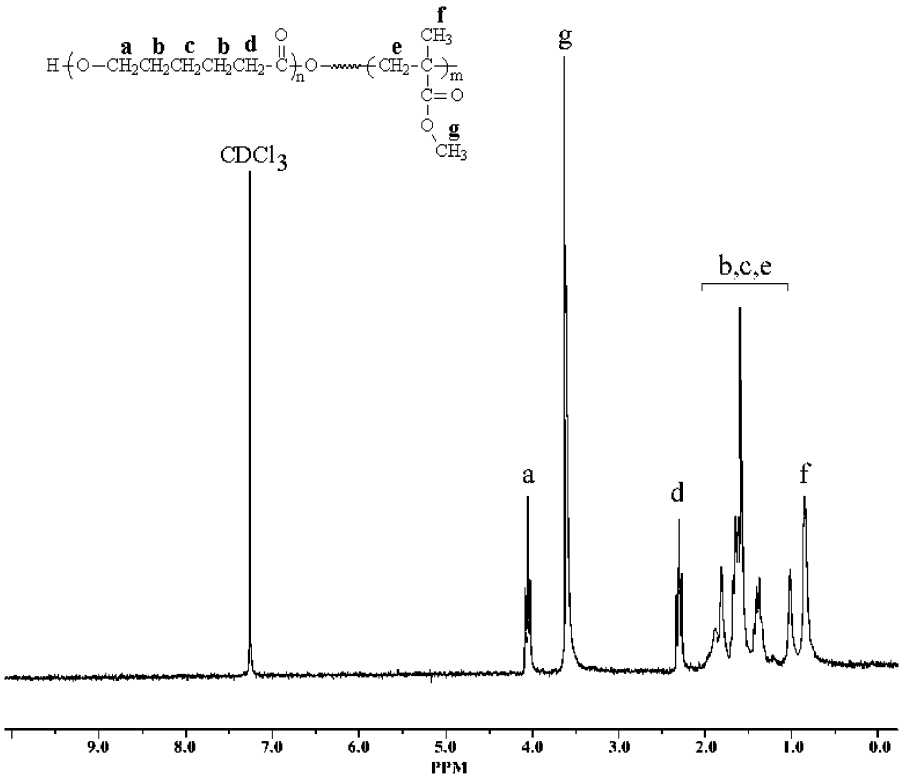
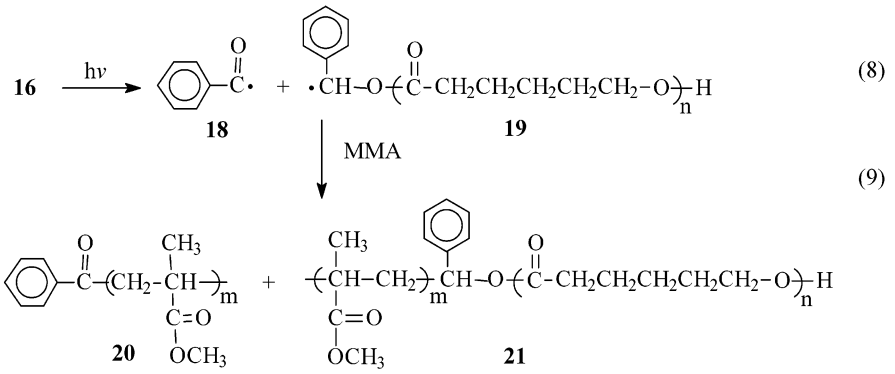


Figure 6. ^{1}H NMR spectrum of PCL−PMMA block copolymer (Table 3, run H) in $CDCl_3$.

Scheme 5



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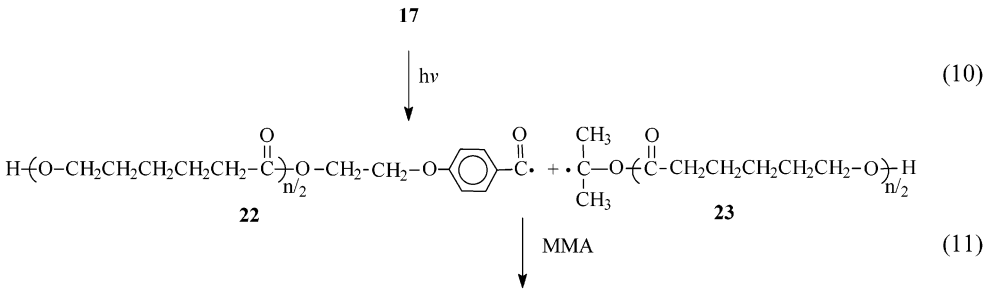
(9)

Scheme 6



(10)

(11)

Block copolymer of CL and MMA

late (MMA) at 25 °C by using PCL photoinitiators are shown in Table 3. It should be pointed out that a control experiment without a polymeric initiator gave only negligible amount of polymer after the same irradiation time. UV irradiation of the polymeric photoiniators caused α-scission and yielded benzoyl, **18**, and polymer bound radicals **19**, according to the following reaction as shown for the case of benzoin linked polymer, **16** (Scheme 5).

Either or both of these radicals may then initiate the polymerization of MMA. In this connection we refer to the work of Pappas[23,27] who demonstrated that both radicals are equally effective as initiators in the polymerization of MMA. In our case it would appear necessary for the polymer-bound radical to initiate polymerization for successful block copolymerization. However, homopoly(methyl methacrylate), **20**, formation is inevitable when end-chain functional macrophotoinitiators, **15** and

16, were employed. Macroinitiator **16** gave a lower percent of homopolymerization relative to **15**. This is probably due to the difference in the reactivity of the polymer bound radicals, namely substituted benzyl and alkoxy propyl radicals, toward olefinic compounds since benzoyl radicals are formed in each case. Although the bimolecular rate constant for the reaction of hydroxy propyl radicals with MMA was found[28] to be $k = 5.4 \times 10^5$ L mol^{-1} s^{-1}, the corresponding value for substituted benzyl radicals is not known. A different situation was encountered in the case of **17** (Scheme 6). Upon irradiation of this initiator in the presence of MMA, radical sites are formed only at macromolecules. No additional free radicals, which can initiate homopolymerization, are produced in this reaction.

This is the great advantage of **17** over the other initiators, **15** and **16**, where the decomposition of functional molecules leads, apart from macroradicals, also isolated small radicals capable of initiating homopolymerization. Figure 5 shows the GPC chromatograms of **17** and block copolymer formed there from. The new peak at lower elution volume is ascribed to the block copolymer. Notably, no peak pertaining to residual homopolymer was detected.

The block copolymer structure was also assigned by means of NMR spectral measurements. Typical signals for both MMA and CL units were detected (Figure 6). Aromatic protons corresponding to the photoinitiator moieties were not detected due to the relatively high molecular weight of the block copolymer. For comparison, photopolymerization initiated by low-molar mass photoinitiator, **14** was also included in Table 3. Notably, initiation efficiency is rather low in the case of polymeric photoiniator which is in agreement with the observations made on para substituted hydroxy acetophenone derivatives.[29] The overall efficiency of radical generation process was found to be lower for both oligomer and the dodecyl substituted derivatives.

Conclusions

Using mono- and dihydroxy functional free radical photoiniators, we successfully prepared polymeric photoiniators by ring-opening polymerization of ϵ-CL using $Sn(Oct)_2$ through corresponding alkyl octoate formation. Such prepared narrowly distributed macrophotoiniators can be used in photopolymerization of vinyl monomers such as MMA. The type of macrophotoiniator influences the polymerization products. While both homo and block copolymers are formed with the end-chain functional photoinitiators, the midchain functional photoiniator yields purely block copolymers. In addition, these photoinitiators represent a class of potentially useful materials in biomedical applications due to their potential benefits of biocompatibility and nontoxicity of PCL backbone and polymeric nature of the photoiniator. Further studies in this line are now in progress.

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