Use of *N,N*-Dimethylaniline End-Functional Polymers in Photoinduced Block Copolymerization

A. Ekrem Muftuoglu, Ioan Cianga,* Seda Yurteri, Yusuf Yagci

Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

Received 4 September 2003; accepted 22 January 2004
DOI 10.1002/app.20468
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: *N,N*-Dimethylaniline functional polystyrenes with well-defined structures and low polydispersities were synthesized by atom transfer radical polymerization of styrene in bulk at 110°C using 4-(dimethylamino)benzyl 4-(bromomethyl) benzoate as initiator in conjunction with a cuprous complex [Cu(I)Br/bipyridine]. These polymers were further used in block copolymerization with methyl methacrylate and cyclohexene oxide (CHO) by photoinduced radical and radical-promoted cationic polymerization routes, respectively. In the former case, macroradical generation was achieved with benzophenone sensitizer by photoexcitation followed by hydrogen abstraction from amino end groups. A visible light initiating system was used in the radical-promoted cationic polymerization of CHO. The system involves a xanthene dye (erythrosin B) as the sensitizer, an aromatic *N,N*-dimethyl amino group and diphenyl iodonium hexafluorophosphate as the radical source and radical oxidizer, respectively. Whereas pure block copolymers were obtained in the free-radical route, the free-radical–promoted cationic polymerization yielded both block and homopolymers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 387–394, 2004

Key words: atom transfer radical polymerization (ATRP); radical polymerization; photopolymerization; cationic polymerization; block copolymers

INTRODUCTION

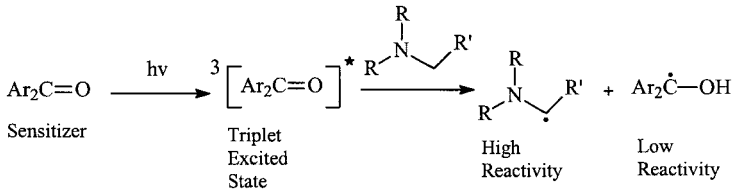
Block copolymers have gained great importance because of their exceptional physical properties. They are readily applied in various industrial areas, such as in the manufacture of adhesives, surfactants, fibers, thermoplastics, and thermoplastic elastomers.[1,2] A number of synthetic methods for the preparation of block copolymers have been developed. Among them living ionic polymerization techniques yielded the best results. However, its use is limited to a certain number of monomers that can be polymerized through ionic means. Transformation polymerization is another technique that eliminates the disadvantage of the former. In this method, different polymerization mechanisms are combined, making it possible to use a greater number of monomers with different chemical structures.[3–5]

Free-radical polymerization is usually used as one of the routes of transformation polymerization because of its advantages over other methods. It is less sensitive toward impurities present in the reaction mixture and is applicable to a wide range of monomers.[6,7] Recent developments in the field of mediated radical polymerization methods, particularly atom transfer radical polymerization (ATRP) and stable radical mediated radical polymerization (SFRP), opened new ways of combining different polymerization routes.[8–12] Evidently, block copolymers possessing at least one segment with well-defined structure and narrow polydispersity were obtained when mediated radical polymerization was used as one of the polymerization modes in the transformation process.

Photoinitiated polymerization is an important method used for the production of coatings, inks, adhesives, and photolithography. Using this method commercially important olefinic monomers, epoxides, and vinyl ethers can be polymerized by free-radical and cationic modes, respectively. Although photoinitiated cationic polymerization has gained importance in recent years, the corresponding free-radical polymerization is still the most widely used route in such applications. Photoinitiated radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators.[7,13] Because the initiation is based on a bimolecular reaction, polymerizations promoted by type II photoinitiators are generally slower than those using type I photoinitiators, which are based on unimolecular formation of radicals. On the other hand, type II photoinitiators possess better optical absorption properties in the near-UV spectral region. Photolysis of aromatic ketones, such as benzophenone, thioxanthones, benzyl, and quinones, 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.[14–16] The photopolymerization of vi-

* On leave from P. Poni Institute, Romania.
Correspondence to: Y. Yagci (yusuf@itu.edu.tr).

© 2004 Wiley Periodicals, Inc.



Scheme 1

nyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers because of the steric hindrance and the delocalization of the unpaired electron. The overall mechanism of the photoinitiation is represented in Scheme 1.

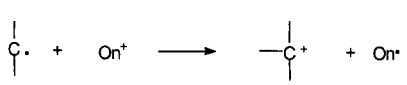
After the pioneering work on the use of onium salts such as sulfonium and iodonium salts with nonnucleophilic counter anions as cationic photoinitiators, cationic polymerization also became the focus of increased interest.[17–19] Various modes of photoinitiation involving both direct and indirect photolysis of onium salts have been described. Among the several indirect systems developed to extend the applicability of onium salt photoinitiators toward longer wavelengths, the so-called radical-promoted cationic polymerization appeared to be the most elegant and fairly flexible method.

Many photochemically formed radicals can be oxidized by onium salts according to the reaction shown in Scheme 2.

The cations thus generated are used as initiating species for cationic polymerization.[20]

The use of xanthene dyes in the generation of oxidizable radicals was previously reported.[21] The effect of various xanthene dyes, such as rose bengal, eosin B, erythrosin B, rhodamine B, and methylene blue, on the efficiency of cationic polymerization of cyclohexene oxide was examined. It was found that erythrosyn B, with the lowest oxidation potential but bearing two negative charges, was the most efficient among these. Different from aliphatic amines, which terminate the growth of cationic chains, aromatic amines were found to be efficient in initiation with negligible contribution in termination because of their lower basicity.

As will be shown below, both photoinduced free-radical and free-radical–promoted cationic polymerization methods have been used in block copolymerization. First, polystyrenes possessing aromatic amine end groups were prepared by ATRP using suitably functionalized initiators. Subsequently, macroinitiators thus obtained were photolyzed in the presence of benzophenone or a dye at appropriate wavelengths, to generate polymeric radicals by hydrogen abstraction. These radicals either initiated free-radical polymerization or were oxidized to the carbocations capable of initiating cationic polymerization.



Scheme 2

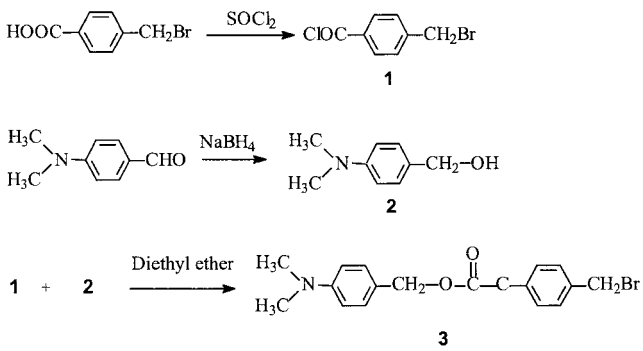
EXPERIMENTAL

Materials

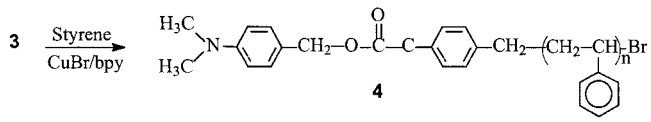
2-Bromopropionyl bromide (Aldrich, Milwaukee, WI), α-bromo-*p*-toluic acid (Acros Organics, Morris Plains, NJ), 4-(dimethylamino)-benzaldehyde (Aldrich), $NaBH_4$ (Merck, Darmstadt, Germany), CuBr (Aldrich), 2,2′-bipyridine (bpy) (Merck), benzophenone, and erythrosin B (Aldrich) were used as received. Thionyl chloride (Fluka, Buchs, Switzerland), triethylamine (TEA; Mallinckrodt Baker, Phillipsburg, NJ), and *N,N*-dimethylaniline (Aldrich) were distilled over calcium hydride before use. Diethyl ether and dichloromethane were purified by usual drying and distillation methods. Styrene (St, Aldrich), cyclohexene oxide (CHO, Aldrich), and methyl methacrylate (MMA, Aldrich) were purified by the conventional methods and distilled at reduced pressure from calcium hydride (CaH_2) before use.

Synthesis of 4-(bromomethyl)-1-benzene carbonyl chloride[22] (1)

α-Bromo-*p*-toluic acid (16.128 g, 0.075 mol) and 80 mL of thionyl chloride were refluxed for 12 h. Thionyl chloride was removed by distillation under reduced



Scheme 3



Scheme 4

pressure and the remaining reddish liquid was extracted several times with dry hexane. The solution was concentrated and, upon cooling, 4-(bromomethyl)-1-benzene carbonyl chloride (**1**) was deposited as pale yellow crystals. A second crystallization from hexane furnished the pure product as white crystals. Yield: 63%. m.p. (DSC): 33–34°C.

^{1}H-NMR ($CDCl_3$) (δ, ppm): 8.12–8.11 (d, 2H, Ar *ortho* to CO), 8.09–8.06 (d, 2H, Ar *ortho* to CH_2), 4.63 (s, 2H, CH_2Br). ^{13}C-NMR ($CDCl_3$) (δ, ppm): 167.32 (Cdbond]O), 147,93 (C_{Ar}—CH_2), 133.87 (C_{Ar}—CO), 132.89 (C_{Ar} *ortho* to CO), 132.16 (C_{Ar} *ortho* to CH_2), 33.65 (CH_2). IR (cm^{-1}): 1772 and 1740 (C═O).

The band at 1685 in the spectrum of the initial acid disappeared in the spectrum of 4-(bromomethyl)-1-benzene carbonyl chloride.

ANAL. calcd for C_8H_6BrClO: C, 41.15%; H, 2.59%. Found: C, 41.73%; H, 1.94%.

Synthesis of [4-(dimethylamino)phenyl]methanol[22] (2)

4-(Dimethylamino)benzaldehyde (7.4595 g, 0.05 mol) and 25 mL of methanol were charged to a 100-mL, round-bottom flask, equipped with magnetic stirrer, condenser, and dropping funnel. $NaBH_4$ (1.89 g, 0.05 mol), dissolved in 10 mL methanol, was added slowly. The mixture was heated at solvent reflux for 2 h, and then stirred at room temperature overnight. The contents of the flask were poured into water and the solution was extracted several times with CH_2Cl_2. After drying the resulting solution over $MgSO_4$ and removing the solvent, the product was obtained as a pale yellow liquid. Chromatography using a silica-gel column and diethyl ether as eluent afforded [4-(dimethylamino)phenyl]methanol (**2**) as a colorless liquid. Yield: 96%.

^{1}H-NMR (acetone-d_6) (δ, ppm): 7.25–7.21 (d, 2H, *Ar ortho* to CH_2), 6.76–6.71 (d, 2H, *Ar ortho* to N), 4.54 (s, 2H, CH_2), 4.3 (s, 1H, O*H*), 2.89 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$) (δ, ppm): 150.41 (C_{Ar}—N), 129.76 (C_{Ar}—CH_2), 128.73 (C_{Ar} *ortho* to CH_2), 113.11 (C_{Ar} *ortho* to N), 65.13 (CH_2), 41.18 (CH_3). IR (cm^{-1}): 3380, 1008 (OH).

The peak at 1660 cm^{-1}, attributed to the aldehyde group in the spectrum of starting material, was not present in the spectrum of **2**.

ANAL. calcd for $C_9H_{13}NO$: C, 71.49%; H, 8.67%; N, 9.26%. Found: C, 70.85%; H, 9.13%; N, 9.58%.

Synthesis of 4-(dimethylamino)benzyl 4-(bromomethyl) benzoate[22] (3)

[4-(Dimethylamino)phenyl]methanol (**2**) (3.02 g, 0.02 mol), 25 mL of dry diethyl ether, and TEA (3.066 g, 0.03 mol) were charged to a 100-mL, three-neck, round-bottom flask, fitted with a condenser, a magnetic stirrer, nitrogen inlet–outlet, and an addition funnel containing 4-(bromomethyl)-1-benzenecarbonyl chloride (**1**) (3.5025 g, 0.015 mol) in 30 mL of diethyl ether. The flask was placed in an ice-water bath. The mixture was stirred under nitrogen as the solution of **1** was added dropwise over a period of 1 h. Then the mixture was stirred at 0°C for 4 h and 1 h more at room temperature. The white precipitate that formed was removed by filtration. The solution was washed three times with water. After drying over $MgSO_4$, the solution was passed through a silica gel column. The solvent was removed and the crude product was recrystallized twice from hexane. White crystals were obtained. Yield: 57%. m.p. (DSC) 90–91°C.

^{1}H-NMR ($CDCl_3$) (δ, ppm): 8.05–8.02 (d, 2H, Ar *ortho* to CO), 7.56–7.53 (d, 2H, Ar *ortho* to CH_2Br), 7.43–7.40 (d, 2H, Ar *ortho* to CH_2O), 6.75–6.69 (d, 2H, Ar *ortho* to N), 5.26 (s, 2H, Ar—CH_2—O), 4.58 (s, 2H, CH_2Br), 2.96 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$) (δ, ppm): 166.28 (C═O), 150.80 (C_{Ar}—N), 142.26 (C_{Ar}—CH_2Br), 131.15 (C_{Ar}—CH_2O), 130.68 (C_{Ar} *ortho* to CH_2O), 129.19 (C_{Ar} *ortho* to C═O), 128.67 (C_{Ar}—C═O), 128.55 (C_{Ar} *ortho* to CH_2Br), 112.57 (C_{Ar} *ortho* to N), 67.56 (CH_2—O), 40.88 (CH_3), 31.30 (CH_2—Br). IR (cm^{-1}): 1700 (C═O ester).

ANAL. calcd for $C_{17}H_{18}BrNO_2$: C, 58.63%; H, 5.21%; N, 4.02%. Found: C, 59.15%; H, 4.87%; N, 4.34%.

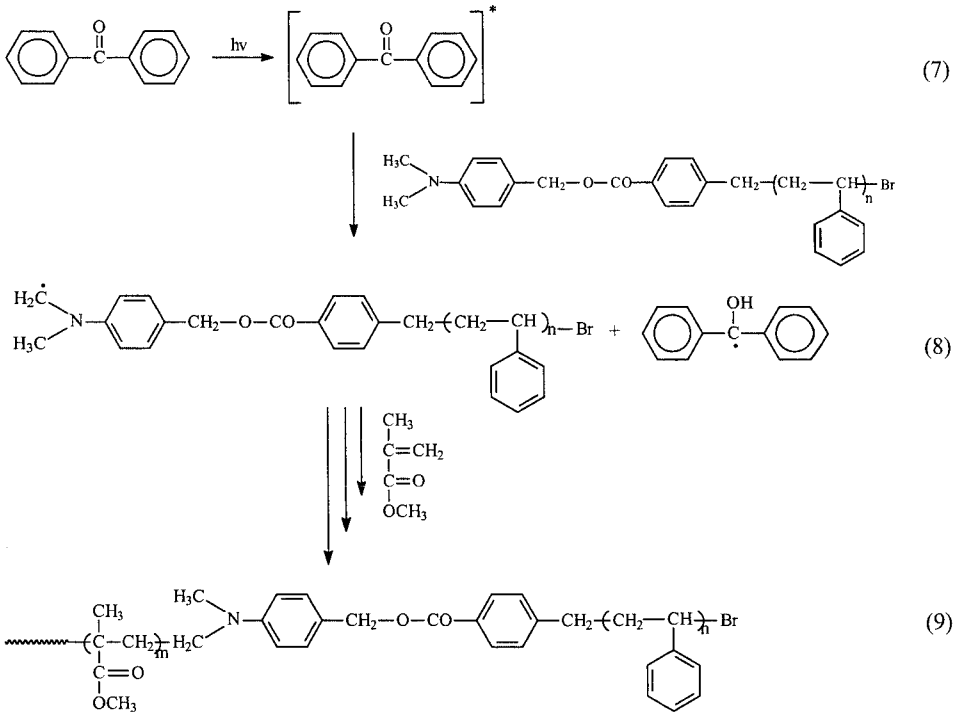
General procedure for ATRP reactions

A round-bottom flask, equipped with a magnetic stirrer and a lateral neck with tap, was used. The system

TABLE I
ATRP of St in Bulk Using Bromine Terminal Initiator[a]

Run	Initial concentration (mol L^{-1})	Polym. time (min)	Polymer	Conversion (%)	M_n Theoretical	M_n ^{1}H-NMR[b]	M_n GPC	M_w/M_n
1	0.15	47	**4a**	26.4	1950	2000	1850	1.24
2	0.08	120	**4b**	18	2400	2500	2600	1.34
3	0.08	380	**4c**	45	5500	4800	4950	1.37
4	0.02	1620	**4d**	43	20,000	20,200	19,500	1.5

[a] Bulk, Initiator = **3**, $[I]_0$/[CuBr]/[bpy] = 1/1/3 molar, temperature 110°C.
[b] M_n value determined by ^{1}H-NMR was calculated from the ratio of integrals corresponding to aromatic protons and dimethylamino ones.



Scheme 5

was vacuumed and backfilled with dry nitrogen several times. Catalyst (CuBr), ligand bipyridine (bpy), initiator, and St were introduced under an inert atmosphere. The flask was placed in an oil bath warmed at 110°C and the mixture was stirred at that temperature. After a given time, the mixture was diluted with THF and poured into a 10-fold excess of methanol. The precipitated solid was collected by filtration and dried at 40°C and reduced pressure overnight. To remove complex salts the polymers were dissolved in THF and the resulting solution was passed through a silica-gel column. The solution was then treated with excess methanol to precipitate the polymer that was collected and dried as described above.

General procedure for photopolymerization reactions

Solutions of monomers (CHO or MMA), either in bulk or in dichloromethane, sensitizer (benzophenone, dye, etc.), coinitiator (*N,N*-dimethylaniline), and onium salt (diphenyl iodonium hexafluorophospate) were added to Pyrex tubes and degassed with nitrogen before irradiation. The tubes were irradiated at room temperature in a merry-go-round type photoreactor equipped with 15 Philips lamps and emitting light nominally at 350 nm. Alternatively, a monochromatic light source was used in cases for which a wider range of wavelengths interfered with the reacting species.

TABLE II
Photoinduced Radical Polymerization of MMA in Bulk and Solution Using Various Macroinitiators with Differing Chain Lengths[a]

Run[b]	[M] (mol L^{-1})	Macro-initiator	Irradiation time (min)	Conversion (%)	Blocking yield (%)	M_n	M_w/M_n	St/MMA, r.u. GPC	St/MMA, r.u. ^{1}H-NMR
5[b]	9.43	3	60	22.4	—	25,500	1.48	—	—
6[b]	9.43	4a	60	7.3	48	20,370	1.93	1/9.6	1/10.2
7[s]	4.72	4b	15	2.8	100	4140	1.66	1/0.7	1/0.3
8[s]	4.72	4b	30	10.2	100	4630	1.86	1/0.9	1/0.6
9[s]	4.72	4b	60	21.2	100	6000	1.86	1/1.5	1/1.1
10[s]	4.72	4b	120	41.2	100	8580	2.02	1/2.5	1/2.3

[a] $[I] = 5 \times 10^{-2}$ mol L^{-1}.
[b] Superior b indicates bulk; superior s indicates solution

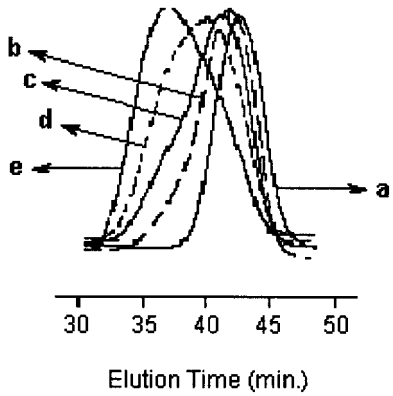


Figure 1 GPC traces of (a) PSt (Table I, Run 2) and block copolymers (PSt-*b*-PMMA) at different conversions: (b) 2.8; (c) 10.2; (d) 21.2; and (e) 41.2.

The viscous solution, either alone or dissolved in dichloromethane, was poured into methanol for precipitation. Finally, the solid polymers were collected by filtration at reduced pressure and dried overnight at reduced pressure.

Characterization

GPC chromatograms were obtained by using a Waters instrument (Waters Chromatography Division/Millipore, Milford, MA) equipped with an R410 differential refractometer and 600E pump and THF as the eluent at a flow rate of 1.0 mL/min. Monodisperse polystyrene standards were used for calibration. ^{1}H-NMR measurements were carried out in $CDCl_3$ solution using a Bruker (Darmstadt, Germany) 250 MHz instrument. The IR spectra were recorded using a Shimadzu IR-470 infrared spectrophotometer (Shimadzu, Kyoto, Japan).

RESULTS AND DISCUSSION

A dimethylamino-terminated ATRP initiator **3** was prepared, to explore the possibility of using photoinduced radical and cationic polymerization strategy to synthesize block copolymers from well-defined prepolymers. Compound **3** was synthesized by the esterification of **1** and **2** in diethyl ether, as described previously, according to the following reactions (Scheme 3).

The ATRP of St in bulk was performed by using **3** as the initiator, CuBr as a catalyst, and dNbipy as a complexing ligand (Scheme 4).

The reaction conditions and results are presented in Table I. In all cases the conversions were determined gravimetrically. As expected, polymers with increasing chain lengths were obtained upon decreasing the initial concentration of the initiator and increasing the polymerization time. The molecular weights deter-

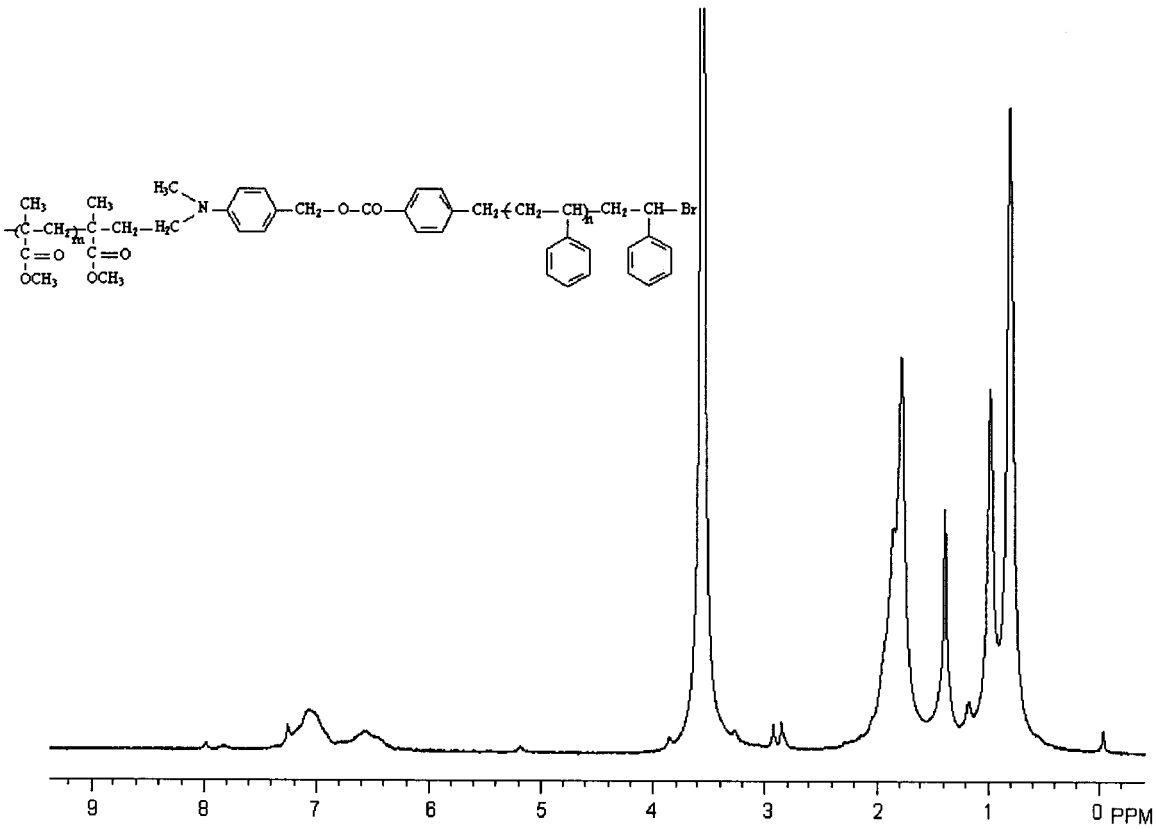
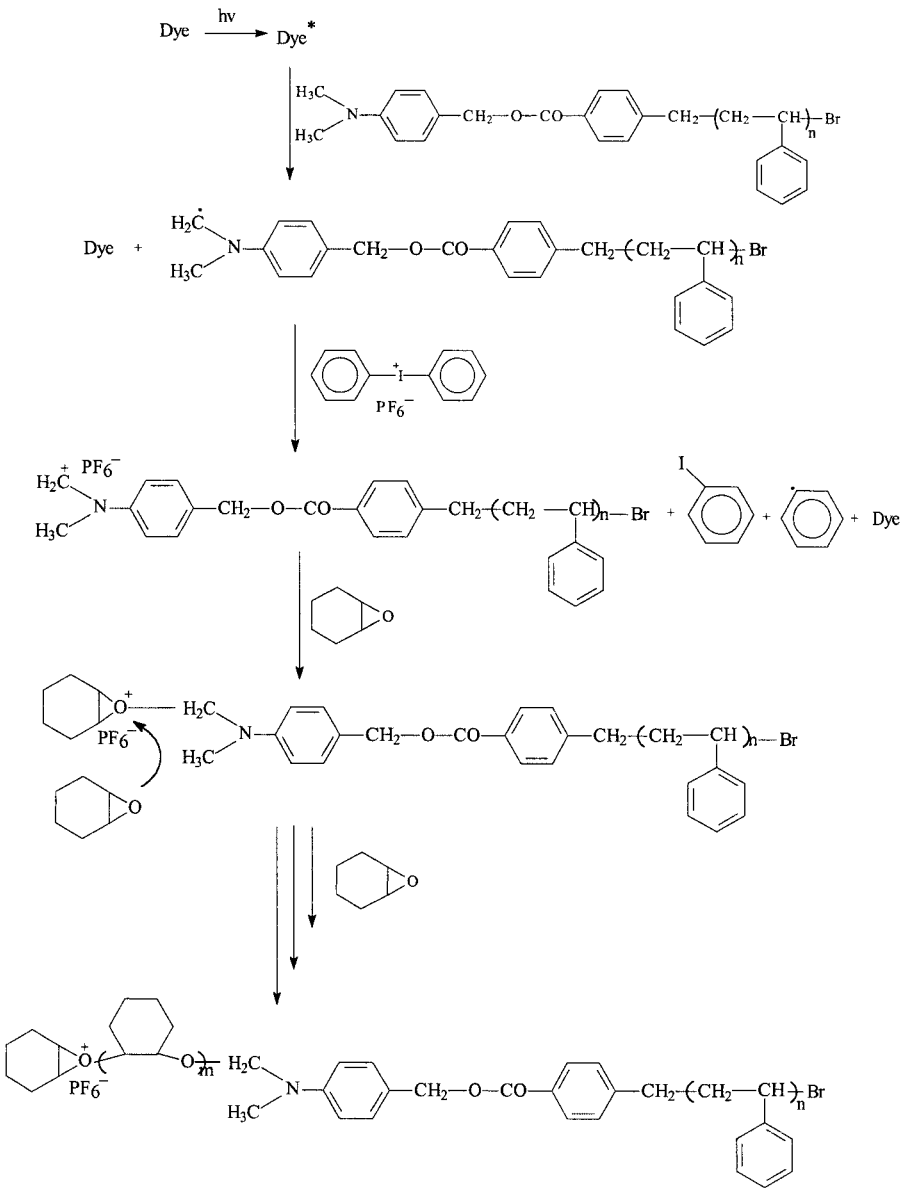


Figure 2 ^{1}H-NMR spectrum of poly(St-*b*-MMA) (Table II, Run 8).



Scheme 6

mined by ^{1}H-NMR were calculated from the ratio of integrals corresponding to aromatic protons and dimethylamino ones at about 6.58–7.05 and 2.87 ppm, respectively. The molecular weights determined by GPC and ^{1}H-NMR agreed well with the theoretical values calculated according to the following equation:

TABLE III
Photoinduced Radical Promoted Cationic Polymerization of CHO in Bulk Using Various Macroinitiators with Differing Chain Lengths[a]

Run	Macro-initiator	$[I] \times 10^2$ (mol L^{-1})	Conversion (%)	Blocking yield (%)	M_n	M_w/M_n
11	3	2	39	—	5100	1.69
12	4a	2	25	70	4430	1.73
13	4c	2	5.6	24	6000	1.22

[a] Bulk, $[M]$ = 9.90 mol L^{-1}; λ_{inc} = 525 nm; irradiation time = 120 min.

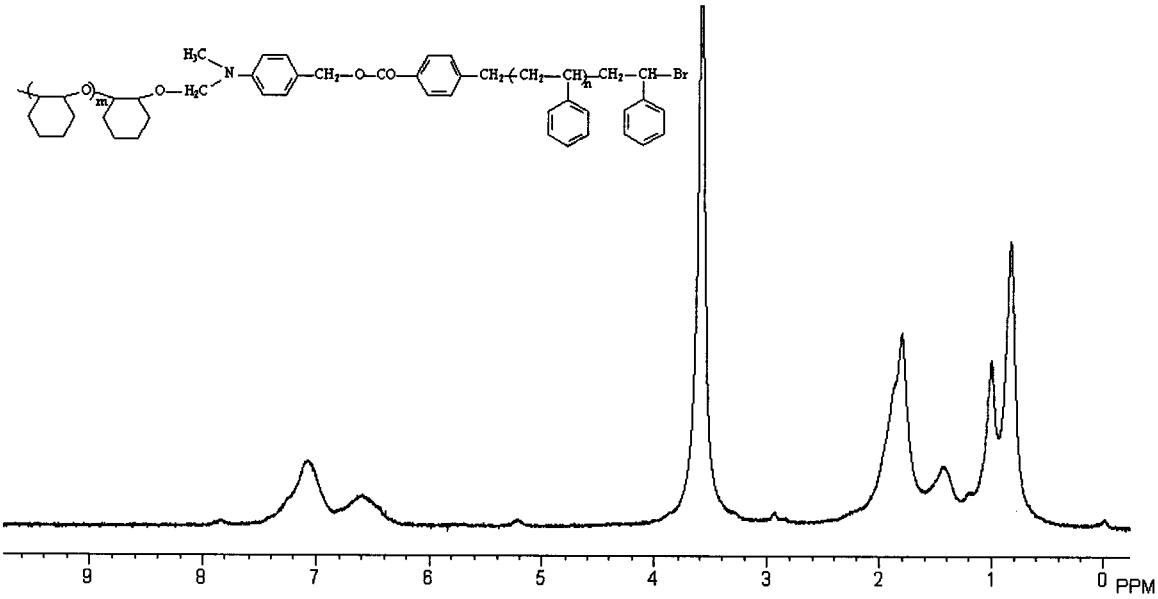


Figure 3 ^{1}H-NMR spectrum of poly(St-*b*-CHO) (Table III, Run 12).

$$\bar{M}_{n\text{th}} = \frac{[M_0]}{[I_0]} \times 104 \times (\text{conversion}) + \bar{M}_{n,\text{initiator}}$$

where M_0 and I_0 are the initial molar concentrations of the monomer and initiator, respectively.

The molecular weight distributions were narrow, which is characteristic of a mediated polymerization. However, a slight increase in the polydispersities was observed for longer polymerization times, indicating the presence of some side reactions taking place.

Subsequent to the preparation of the macroinitiators by ATRP, several experiments were carried out to explore the photopolymerization of MMA and CHO by radical and radical-promoted cationic polymerization routes, respectively. The former involves hydrogen abstraction by the photoexcited benzophenone from the dimethylamino-bearing chain end. This leads to the formation of a carbon-centered radical, which initiates the free-radical polymerization of MMA, as depicted in Scheme 5. Polymerizations were performed in a merry-go-round type photoreactor in which light was emitted nominally at 350 nm. The results are summarized in Table II.

Polymerization in neat MMA gave a polymer that gave rise to a bimodal GPC trace, which is typical for these conditions given that MMA is known to autopolymerize, and part of the initial PSt was not involved in the formation of block polymer (Table II, Run 6). However, after extraction with various solvents, pure block copolymers with about 50% blocking yield were obtained. As a control experiment this procedure was repeated with low molar mass initiator **3**. Much higher conversion was observed (Table II, Run 5). Thus, terminal amino groups participate effectively in the radical-generation process. Furthermore, repetition of the polymerization in solution generated materials with almost ideal blocking. The effect of the reaction time on the polymerization was also examined. Notably, the conversion increased from 2.8 to 41.2 by increasing irradiation time. The molecular weights were also increased, as reflected by the shift of the initial GPC peak to higher elution volumes (Fig. 1). The composition of copolymers was estimated from ^{1}H-NMR data by comparing the ratio of the peak intensities at 3.6 ppm (–OCH_3 of the PMMA segment) to that appearing at 6.5–7 ppm (aromatic protons of the PSt segment) (Fig. 2).

A relatively good correlation between the composition of copolymers estimated from GPC and ^{1}H-NMR data was observed. The results are presented in Table II. Some observed differences may be attributable to the differences in the hydrodynamic volumes of the corresponding segments of PSt and PMMA.

Similar to the free-radical process, the amino-terminated polymers were used successfully as polymeric initiators for free-radical–promoted cationic polymerization of CHO to afford block copolymers. In this case, polymeric radicals, generated upon monochromatic irradiation of CHO, in bulk containing a dye sensitizer and the macroinitiator, were oxidized by a diphenyl iodonium salt. The polymeric carbocations thus formed initiated cationic polymerization to yield block copolymers. The overall process of the block copolymerization is shown in Scheme 6. It should be pointed out that at the irradiation wavelength, 525 nm, the iodonium salt is transparent and all the emitted light is absorbed by erythrosin B. Therefore, direct decomposition of the iodonium salt can be disregarded. Notably, the three components of the initiating system are indispensable for the polymerization to occur. Either no polymer or a negligi-

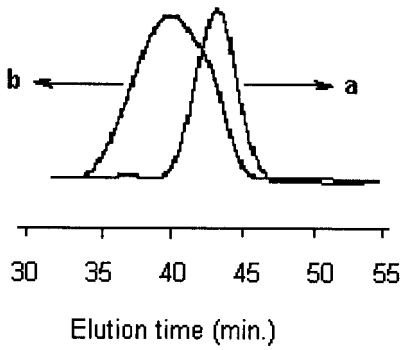


Figure 4 GPC traces of (a) PSt (Table I, Run 1) (b) poly(St-*co*-CHO) (Table III, Run 12).

ble amount of polymer is formed in the absence of one or more compounds.

As can be seen from the data presented in Table III, the chain length of the macroinitiator, irradiation time, and the concentration of CHO affect both the conversion and the blocking yield. Block copolymer formation was evidenced by both ^{1}H-NMR and GPC analysis (Figs. 3 and 4). Besides block copolymers, homopolymers of CHO are also formed and consequently block yields are relatively low. Homopolymer formation is attributed to the participation of phenyl radicals formed from the decomposition of the iodonium salt according to the reaction.[12] This represents a further cation-generation process.

CONCLUSIONS

It has been demonstrated that well-defined amino-terminated polymers can successfully be used in photoinduced polymerizations to prepare block copolymers of structurally different monomers. In this approach the ATRP is combined with photoinduced radical or cationic polymerization.

References

1. Noshay, A.; McGrath, J. A. Block copolymers: Overview and Critical Survey; Academic Press: New York, 1977.
2. Goodman, I. Developments in Block Copolymers; Applied Science: London, 1982.
3. Yagci, Y.; Mishra, M. K., In: Macromolecular Design: Concept and Practice; Mishra, M. K., Ed.; Polymer Frontiers Int.: New York, 1994; Chapter 10.
4. Yagci, Y.; Mishra, M. K. Polymeric Materials Encyclopedia; CRC Press: Boca Raton, FL, 1996; p. 789.
5. Yagci, Y. In: Advanced Functional Molecules and Polymer; Nalwa, H. S., Ed.; Gordon & Breach Science: Amsterdam, 2001; Vol. 1, Chapter 4.
6. Davidson, S. Exploring the Science, Technology and Applications of U.V. and E.B. Curing; SITA Technology: London, 1999.
7. Dietliker, K. Chemistry and Technology of U.V. and E.B. Formulation for Coating, Inks and Paints, Vol. III; SITA Technology: London, 1991.
8. Li, I. Q.; Howell, B. A.; Dineen, M. T.; Kastl, P. E.; Lyons, J. W.; Meunier, D. M. Macromolecules 1997, 30, 5195.
9. Moineau, C.; Minet, M.; Teyssie, P.; Jerome, R. Macromolecules 1999, 32, 8277.
10. Zhang, Z.; Ying, S.; Shi, Z. Polymer 1999, 40, 1341.
11. Sedjo, R. A.; Mirous, B. K.; Brittain, W. J. Macromolecules 2000, 33, 1492.
12. Erel, I.; Cianga, I.; Serhatli, E.; Yagci, Y. Eur Polym J 2002, 38, 1409.
13. Pappas, S. P. UV Curing: Science and Technology; Technology Marketing Corp.: Norwalk, CT, 1978.
14. Ledwith, A.; Purbrich, M. D. Polymer 1973, 14, 521.
15. Davidson, R. S. In: Advances in Physical Chemistry; Bethel, D.; Gold, V., Eds.; Academic Press: London, 1983.
16. Ledwith, A.; Bosley, J. A.; Purbric, M. D. J Oil Colour Chem Assoc 1978, 61, 95.
17. Crivello, J. V.; Lam, J. H. W. J Polym Sci Polym Chem Ed 1980, 18, 2677.
18. Crivello, J. V.; Lam, J. H. W. J Polym Sci Polym Chem Ed 1980, 18, 2967.
19. Crivello, J. V.; Lam, J. H. W. Macromolecules 1979, 10, 1307.
20. Yagci, Y.; Reetz, I. Prog Polym Sci 1998, 23, 1485.
21. Bi, Y.; Neckers, D. C. Macromolecules 1994, 27, 3683.
22. Yurteri, S.; Cianga, I.; Yagci, Y. Macromol Chem Phys 2003, 204, 1771.