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ORIGINAL PAPER

The use of poly(ethylene oxide) as hydrogen donor in type II photoinitiated free radical polymerization

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Abstract The aim of this study was to demonstrate hydrogen donating capability of poly(ethylene oxide) (PEO) in type II photoinitiated free radical polymerization for dental applications. Photopolymerization kinetics of the dental resin mixtures were monitored by Photo-DSC. H-NMR spectroscopic and GPC studies were also performed in order to gain insight to the hydrogen abstraction mechanism. The effect of molecular weight of PEO on the photoinitiation efficiency was investigated. Photolysis of solutions containing benzophenone and PEO in the presence of a radical scavenger namely, 2,2,6,6-tetramethylpiperidine-*N*-oxyl free radical (TEMPO) revealed that photoexcited benzophenone readily abstracts hydrogen from methylene groups present in PEO backbone. It was demonstrated that such photoinitiating system can be converted to a versatile grafting process. PEO possessing photochemically attached TEMPO units initiates the nitroxide mediated radical polymerization of styrene upon heating at 110 °C leading to the formation of poly(ethylene oxide-*g*-styrene) graft copolymer. Potential use of the photoinitiating system in dental formulations was also demonstrated. The polymeric nature, water solubility and nontoxicity make PEO a promising candidate as hydrogen donor in dental formulations.

Keywords Photopolymerization · Dental resin · Type II photoinitiating system · Hydrogen donor

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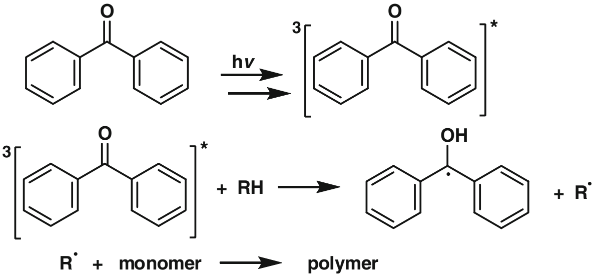
Introduction

Photoinitiated polymerization forms the basis of numerous applications in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics [1, 2]. Although photoinitiated cationic polymerization has gained importance in recent years, the most of the curing application are still based on the corresponding radical vinyl polymerization. Photoinitiated radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators [3]. Because the initiation is based on a bimolecular reaction, type II photoinitiators are generally slower than type I photoinitiators, which are based on unimolecular formation of radicals. However, due to the better optical absorption properties in the near-UV spectral region, these type of photoinitiators are preferred in applications where the long wavelength absorption is required. Photolysis of aromatic ketones, such as benzophenone, thioxanthones, benzil and quionones in the presence of hydrogen donors, such as alcohols [4, 5], amines [6–8], ethers [9, 10] or thiols [11, 12], leads to the formation of a radical produced from the carbonyl compound (ketyl-type radical) and another radical derived from the hydrogen donor [4, 13–15]**.** The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron. The overall mechanism of the photoinitiation is represented on the example of benzophenone in Scheme 1.

For efficient polymerization, the bimolecular H-abstraction reaction must compete with other side reactions, such as non-reactive quenching (i.e., through energy transfer) of the photoexcited initiator by monomer or oxygen. These systems are therefore more sensitive to oxygen, and polymerization in air may lead to relatively low curing rates. The selection of a co-initiator (H-donor) is undoubtedly of great importance. Tertiary amines are more reactive co-initiators than are alcohols or ethers [5]. However, the practical application of amines suffers from their usage in large amounts which is particularly important for curing applications since formulations containing amine at high concentrations causes a decrease in the pendulum hardness of the cured films due to the plasticizing effect of amines [16, 17]. In addition, the amine tends to cause discolorations, and is known to be both toxic and mutagenic [7]. We have recently reported one-component type II photoinitiators which do not require additional hydrogen donors and readily initiate the polymerization of both acrylate and styrene monomers in the presence and absence of air [18–21].

Scheme 1 Type II photoinitiated free radical polymerization



PEO and its derivatives are finding a rapidly expanding range of chemical, biomedical applications resulting from their low cost and useful properties, such as solubility in aqueous and organic solvent [22]. Recently it has been shown that PEO films can be effectively cross-linked in the solid state or aqueous solution by UV irradiation in the presence of photoinitiators such as benzophenone [23, 24]. Cross-linked polymer based on PEO form an essential class of new materials with number of applications, such as drug delivery system, membranes, wound dressing.

As part of our continuing interest in developing alternative photoinitiating systems, we now report the possibility of using PEO as latent hydrogen donor for photoexcited aromatic carbonyl compounds further expanding the hydrogen donation concept to polymeric structures.

Experimental

Materials

PEOs (Hoechst AG, Frankfurt Germany), with different molecular weight, 2,2,6,6-tetramethylpiperidine-*N*-oxyl free radical (TEMPO, Aldrich) and camphorquionone (CQ, Aldrich) were used as received. Benzophenone (BP, Fluka), 2-isopropyl thioxanthone (ITX, Ward Blenksop), and thioxanthone (TX, Aldrich) were used after being recrystallized from ethanol. Methyl methacrylate (MMA, Aldrich) and styrene (St. Aldrich) were washed with 5% aq. NaOH solution, dried over $CaCl_2$, and vacuum distilled from CaH_2. Dichloromethane (CH_2Cl_2, Baker) was extracted first with sulfuric acid, then with 5% NaOH solutions. After washing with water, the dichloromethane was dried over anhydrous $CaCl_2$ and CaH_2. The adhesive monomer 2-(2-phosphono-ethoxymethyl)-acrylic acid ethyl ester (EAEPA) and the cross-linker *N,N*-diethyl-1,3-bis(acrylamido)propane (DEBAAP) were provided by IVOCLAR VIVADENT AG (FL-9494 Schaan). *N,N*-dimethyl aniline (NDMA, Aldrich) was distilled over calcium hydride before use.

Photopolymerization

Appropriate solutions of methyl methacrylate in dichloromethane, sensitizer (BP, TXs or CQ) and PEO 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 and a cooling system. At the end of given time, polymers were poured into cold methanol, filtered, dried, and weighted. Conversions were determined gravimetrically.

Model study

Photosensitizer (BP, 0.028 g, 75×10^{-3} mol L^{-1}) in CH_2Cl_2 (2 mL) solution, hydrogen donor (PEO, 0.27 g, 75×10^{-3} mol L^{-1}) and TEMPO (0.024 g,

75×10^{-3} mol L^{-1}) were put into a Pyrex tube, degassed with nitrogen and irradiated in the absence of monomer for 1.5 h at room temperature. The residue was purified by pouring the polymeric TEMPO intermediate in CH_2Cl_2 into *n*-hexane three times. This way, the low molecular weight by-products and the remaining TEMPO and BP were removed. After drying in a vacuum oven at room temperature for 24 h, polymeric TEMPO intermediate was obtained in 75% yield. In the subsequent step, polymeric TEMPO intermediate (0.084 g, 0.022 mol L^{-1}) in DMSO (1 mL), monomer (St, 1 mL, 4.3 mol L^{-1}) were added into tube and polymerization was carried out at 125 °C for 18 h via nitroxide mediated radical polymerization. At the end of reaction, the mixture was diluted with THF and precipitated in excess *n*-hexane. The solid was collected after filtration and dried at room temperature in a vacuum overnight. Polymer was obtained in 36% yield ($M_n = 12{,}500$, PDI = 1.64).

Photo DSC

Photo-DSC was conducted on a modified Perkin Elmer Diamond DSC equipped with a home-made aluminum cylinder. UV light (320–500 nm) was applied by a light guide (OmniCure Series 2000) with a light intensity of 18.40 mW cm^{-2} at the level of the surface of the cured samples. The mass of the samples was 8 mg, and the measurements were carried out in an isothermal mode at 30 °C under a nitrogen flow of 20 mL min^{-1}.

A dental primer formulation consisting of 40% EAEPA [molecular weight of EAEPA = 238 g mol^{-1}, theoretical enthalpy of EAEPA (ΔH_{0E}) = 62,900 J mol^{-1}], 20% DEBAAP [molecular weight of DEBAAP = 238 mol g^{-1}, theoretical enthalpy of DEBAAP (ΔH_{0D}) = 120,600 J mol^{-1}], and 40% water was used as a standard resin.

The mass of the samples was 7.5 ± 0.5 mg, and a PI concentration of 0.022 mmol g^{-1} CQ was used for standard conditions. In all cases, an equimolar amount of a co-initiator was used. By integrating the area under the exothermic peak, the conversion of the acrylate groups (C) or the extent of the reaction was determined according to Eq. 1:

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \tag{1}$$

where ΔH_t is the reaction heat evolved at time t, and $\Delta H_0^{\text{theory}}$ is the theoretical heat for complete conversion.

Analysis

^{1}H-NMR spectra were recorded on a Bruker 250 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. Molecular weights were determined by gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL min^{-1} and a Waters 410 differential refractometer detector.

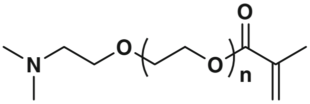


Fig. 1 Structure of PEO-macroinimer

Results and discussion

In our previous study [25] PEO-macroinimer (*macro*molecule-*ini*tiator-mono*mer*) of the following structure (Fig. 1), possessing both polymerizable and radical generation sites was used for the formation of hydrogels of various swelling capacities and moduli of elasticity.

Hydrogen abstraction from one of the methyl groups adjacent to the amino group by a photoexcited benzophenone molecule [26, 27] leads to the formation of macroinimer and ketyl radicals, where the latter radical is known to undergo radical coupling and is thus, ineffective in initiating the polymerization reactions. It became evident that the hydrogen abstraction also occurs from PEO itself without the requirement of additional hydrogen donors. Thus, a portions of the initially difunctional macroinimer becomes trifunctional as a result of the hydrogen abstraction reaction from either terminal amino groups or PEO backbone, which seems to be responsible for the formation of an infinite network in the reaction system.

These observations prompted us to perform independent detailed investigations to confirm hydrogen abstraction reactions between photoexcited various aromatic carbonyl compounds acting as type II photoinitiators and PEO. Thus, PEO with various molecular weights was used as a hydrogen donor for the polymerization of MMA in the presence BP. The results are compiled in Table 1. For comparison, photopolymerizations by using either TX or ITX are also included. As can be seen, BP is not an efficient photoinitiator in the absence of the co-initiator, PEO. The presence of PEO is important for effective photoreduction and photopolymerization. As can be seen from the data presented in Table 2, the chain length of the PEO affects the overall conversion of MMA. When the molecular weight of PEO is increased, the conversion decreases significantly which may be attributed to the limited mobility. The interaction of photoexcited sensitizer with hydrogen donating PEO is suppressed at more viscous media. The overall reaction pathway is depicted in Scheme 2.

Notably, one of the consequences of the hydrogen abstraction from PEO is the formation of graft copolymers, since initiating radicals are generated on the backbone of PEO. This was confirmed by the molecular weight increases observed in all cases as well as the spectral evidences. For example the IR spectra of the resulting polymers possess both characteristic ester carbonyl and main chain ether bands at 1,730 and 1,100 cm^{-1}, respectively.

To confirm further, the hydrogen donating capability of PEO spectroscopically, we performed a model study by using a typical radical scavenger, namely TEMPO in the same photoinduced process in the absence of monomer. The photochemically generated radicals are readily scavenged by TEMPO (Scheme 3). ^{1}H-NMR spectra of the initial PEO and the reaction products are presented in Fig. 2. As can be seen, the characteristic protons of PEO appear at 3.6 ppm ($–O–CH_2–$) (Fig. 2a). After

Table 1 Comparison of initiator efficiency in photoinitiated free radical polymerization of MMA[a]

Run	PS	[PS] mol L^{-1}	[PEO][b] mol L^{-1}	Conversion (%)[c]	M_n^d	PDI[d]
P-1	BP	5×10^{-3}	5×10^{-3}	47	58,800	1.90
P-2	BP	5×10^{-3}	10×10^{-3}	30	48,000	1.80
P-3	BP	10×10^{-3}	5×10^{-3}	50	46,000	1.80
P-4	TX	5×10^{-3}	5×10^{-3}	31	53,700	2.45
P-5	ITX	5×10^{-3}	5×10^{-3}	46	55,600	1.95
P-6	BP	5×10^{-3}	–	No polymer	–	–

BP benzophenone, *TX* thioxanthone, *ITX* isopropyl thioxanthone

[a] Polymerization time = 90 min

[b] $M_{nPEO} = 1{,}800$, PDI = 1.06

[c] Overall MMA conversion

[d] Estimated by GPC based on polystyrene standards

Table 2 Comparison of molecular weight of PEO in photoinitiated free radical polymerization of MMA

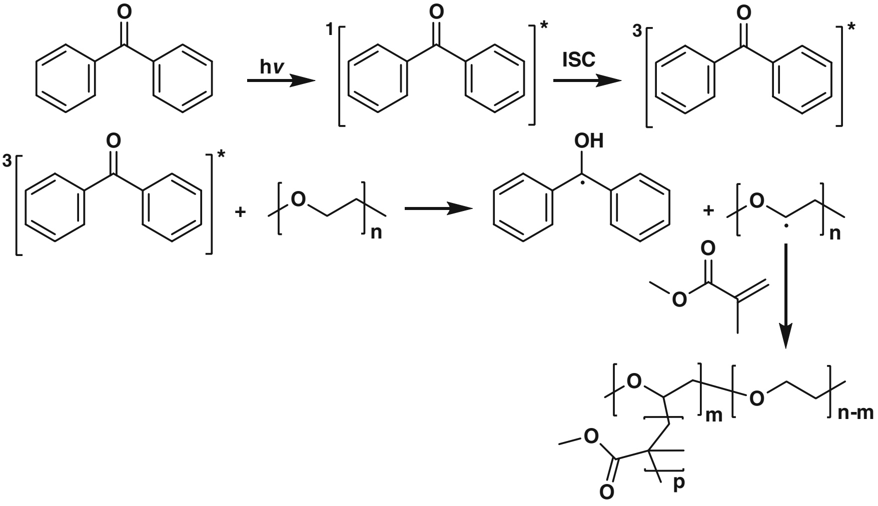
Run	M_{nPEO}	PDI_{PEO}	Conversion (%)[c]	M_n^d	PDI[d]
P-7	1,300	1.01	99	120,000	2.10
P-8	1,500	1.02	72	87,000	1.95
P-9	1,800	1.06	47	59,000	1.90

[a] [PS = (BP)] = 5×10^{-3} mol L^{-1}, polymerization time = 90 min

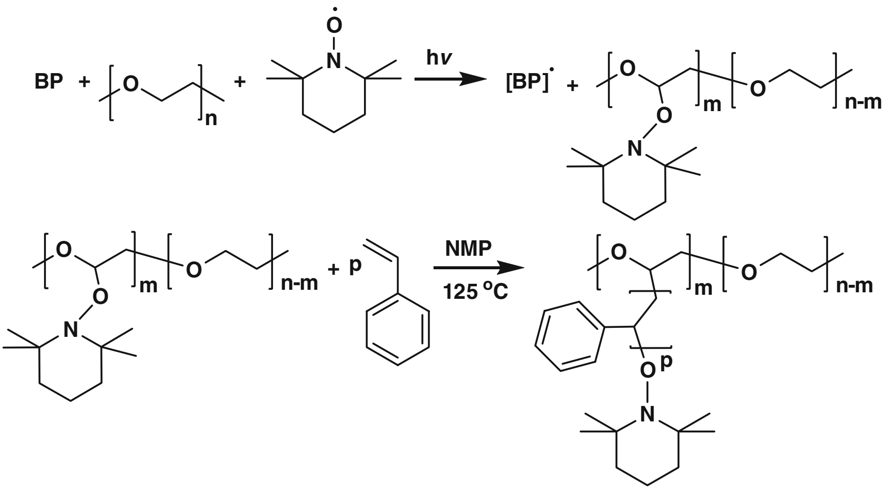
[b] [PEO] = 5×10^{-3} mol L^{-1}

[c] Overall methyl methacrylate conversion

[d] Estimated by GPC based on polystyrene standards



Scheme 2 Photoinitiated free radical polymerization by PEO as hydrogen donor



Scheme 3 Model study of capping photochemically generated PEO radicals with TEMPO radical and subsequent NMP

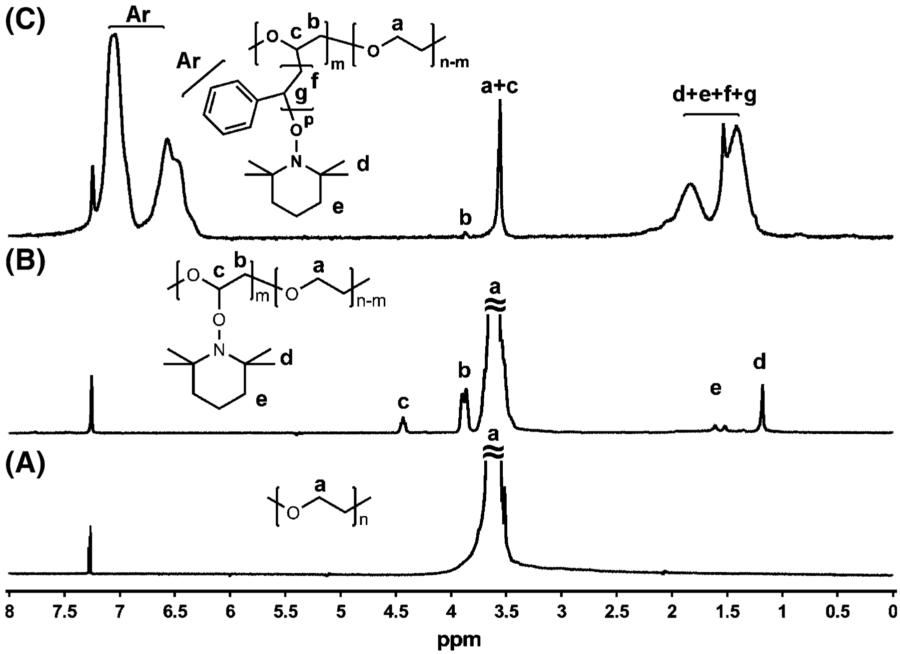


Fig. 2 ^{1}H-NMR spectra of **a** PEO, **b** TEMPO functionalized PEO and **c** P(EO-*g*-St) in $CDCl_3$

scavenging with TEMPO some portion of these peaks shifted to 3.9 and 4.4 ppm (–O–CH– and –CH_2–O protons, respectively) (Fig. 2b). The characteristic protons of the TEMPO moiety are also visible at 0.9, 1.2 and 1.3 ppm.

Similar to literature reports [28–32] TEMPO incorporated polymers were used successfully as a polymeric initiator for nitroxide mediated radical polymerization (NMP) of St to afford graft copolymers. Experimentally subsequent bulk polymerization of styrene using above functionalized dendrimer was carried out at 125 °C. The ^{1}H NMR spectrum of the resulting graft copolymer (Fig. 2c) exhibits in addition to the precursor PEO repeating polystyrene (PSt) (such as 6.2–7.2 ppm attributed to the aromatic protons and 1.2–1.8 ppm methylenes and methenes protons) and PEO.

Figure 3 shows the GPC traces of the initial PEO and of the polymer obtained by photoinitiation. The GPC traces of the graft copolymers are shifted to higher molecular weights and no significant amounts of unreacted starting PEO remained in the analyzed materials. In this connection, it should be pointed out that the unreacted PEO is soluble in methanol and removed during precipitation. Moreover, the traces corresponding to the graft copolymer is unimodal. This observation clearly indicates that all of the initiator was implied in the copolymerization reactions, and no significant homopolymerization processes occurred.

For the evaluation of the hydrogen donation of PEO in the dental formulations, photo DSC experiments using the water-borne primer formulation consisting of a mixture of EAEPA, DEBAAP, and water (2:1:2) was used [33, 34]. To investigate the influence of the molecular weight PEO, CQ (0.022 mmol L^{-1}) and PEO (0.022 mmol L^{-1}) concentration were used. For comparison, a second set of formulation was prepared with a CQ/NDMA in a concentration as usually applied under practical conditions. Photo-DSC plots of these experiments are shown in Fig. 4. Figure 5 displays a plot of the conversion versus irradiation time derived from Fig. 4.

By changing the molecular weight of PEO, usually applied for dental formulations the same tendency but with slightly decreased photoreactivity was

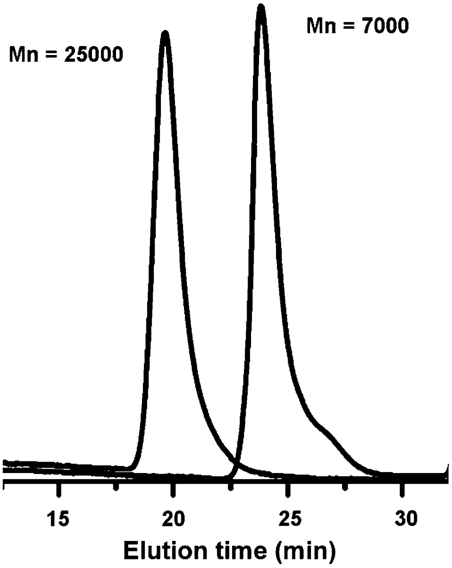


Fig. 3 GPC traces of **a** PEO and **b** P(EO-*g*-MMA)

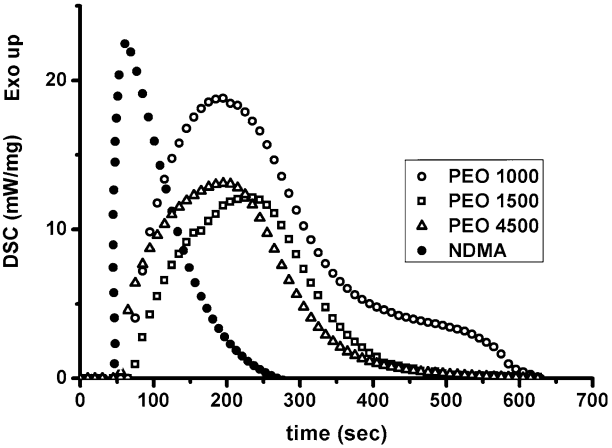


Fig. 4 Photo-DSC of dental formulations with NDMA and different molecular weight PEOs as hydrogen donor, cured at 30 °C by UV light with an intensity of 18.4 mW cm^{-2}

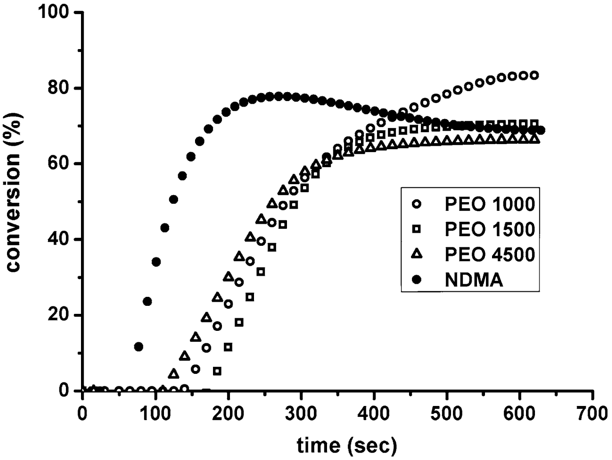


Fig. 5 Time versus conversion for polymerization of different dental formulations calculated from Fig. 4 data according to Eq. 1

found comparing to CQ/NDMA system. However, the calculated data clearly show no significant decrease in the final conversion with PEO instead of NDMA as the co-initiator.

Conclusion

It has been shown that PEO can act as a hydrogen donor for type II photoinitiation. The obvious advantage of this initiation is the elimination of amine based hydrogen donors and to provide alternative hydrogen donors with easily availability and nontoxicity. Moreover, the water solubility of PEO provides the use of initiating system in water-borne formulations. The initiating system can also be used in photografting for the preparation of amphiphilic copolymers.

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