Investigation of Aliphatic Polyesters as Hydrogen Donor in Photoinitiated Free Radical Polymerization

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In the present study, it has been demonstrated that polyesters were used as hydrogen donors in photoinitiated free radical polymerization of methyl methacrylate, N-methyl-2-pyrolidone and methacrylic acid by using one of the following photosensitizers; benzophenone, thioxanthone and 2-hydroxythioxanthone. The effect of molecular weight of poly(ethylene adipate) on the photoinitiation efficiency was investigated. The 2,2,6,6-tetramethylpiperidine-N-oxyl free radical attached polyesters were used as a model study. The synthesized polymer was characterized by ^{1}H NMR, FTIR and gel permeation chromatography.

Key Words: Photochemistry, Photopolymerization, Polyesters, Hydrogen donor, Photosensitizer.

INTRODUCTION

During the last 25 years, photopolymerization science and technology has drawn significant attention for various industrial applications, such as coatings, adhesives, printing inks, photo-resists, optical waveguides and microelectronics[1-3]. 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 (benzoin ether, acylphosphine oxides) and hydrogen abstraction-type (benzophenone, thioxanthone, benzil, anthraquinone and camphorquinone) initiators[4,5]. 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. Among type II photoinitiators, benzophenone (BP) as a H-abstraction photoinitiators widely used in UV-curing systems due to its low cost, high photoefficiency and solubility. Thioxanthone derivatives have recently received interest because of their characteristic absorption of near UV range[6-11]. Photolysis of aromatic ketones, such as benzophenone, thioxanthones, benzil and quinones in the presece of hydrogen donors, such as alchols, amines, ethers 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. The selection of co-initiator (H-donor) is undoubtedly of great importance[4]. For example, tertiary amines are more reactive co-initiators than are alcohols or ethers. However the practical application of amines suffer 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[12]. In addition, the amine tends to cause discolorations and is known to be both toxic and mutagenic. Because of these disadvantages, developing alternative photoinitiating systems take great interest. Polyesters is widely used polymers in many applications. So, to investigate the irradiation behaviour and hydrogen donating properties of polyesters may have great interest. In this aim, we investigated aliphatic polyesters as hydrogen donor in photoinitiated free radical polymerization.

EXPERIMENTAL

Methyl methacrylate (MMA, 99 %, Aldrich), styrene (S, 99 %, Aldrich) were washed with 5 % aq. NaOH solution, dried over CaH_2 and vacuum distilled from CaH_2. N-Vinyl-2-pyrrolidone (NVP, 99 %, Aldrich), methacrylic acid (MAA, % 99, Merck) 2,2,6,6-tetramethylpiperidine-N-oxyl free radical (TEMPO, Aldrich), benzophenone (BP, 99 %, Merck), thioxanthone (TX, Aldrich), tetrahydrofuran (THF, 99.8 %, J.T. Baker) was dried and distilled over benzophenone-Na. Other solvents were purified by conventional procedures. Dimethylformamide (DMF, +99 %, Aldrich), dimethyl sulphoxide (DMSO, 99 %, Aldrich), cyclohexanone (99 %, Sigma-Aldrich), methylethyl ketone (99 %, Sigma-Aldrich), methanol (99 %, Acros Organics), diethylether (98 %, sigma-

Aldrich). Dichloromethane (99.9 %, HPLC grade, Aldrich) was distilled from CaH_2.

^1H NMR spectra were recorded on Varian AS-400 spectrometers in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum one-B spectrometer. Molecular weights and polydispersities of the linear polymers were determined by gel-permeation chromatography (GPC) using a Viscotek GPCmax auto sampler system consisting of a pump, three ViscoGEL GPC columns (G2000HHR, G3000HHR and G4000HHR), a Viscotek UV detector and a Viscotek differential refractive index (RI) detector with THF as eluent at a flow rate of 1.0 mL/min at 3000 ºC. Both detectors were calibrated with polystyrene standards having narrow molecular weight distribution and so the quoted molecular weights of the polymers are expressed in terms of polystyrene equivalents. Data were analyzed using Viscotek OmniSEC Omni-01 software.

Synthesis of 2-hydroxythioxanthone: The synthesis of 2-hydroxythioxanthone (TX-OH) was conducted according to the literature[13]. The crude products were recrystallized from 1,4-dioxane/water (v/v 80:20).

Synthesis of aliphatic polyesters: The synthesis of poly(ethylene adipate) (PEA) were conducted according to the literatures[14,15]. Polymers were precipitated in cold methanol.

Photopolymerization: Appropriate solutions of methyl methacrylate in dimethylformamide, sensitizer (BP, TX and TXOH) and PEA 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. ght intensity was 1.04 mW/cm^2 as measured by DeltaOhm model HD-9021 radiometer. 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} mmol) in DMF (3 mL) solution, hydrogen donor (PEA, 0.195 g, 75×10^{-3} mmol) and TEMPO (0.096 g, 300×10^{-3} mmol) 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 DMF 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 55 % yield (Fig. 2).

Polymerization of styrene using TEMPO functionalized polyester in bulk media: Polyester TEMPO intermediate (0.06 g, 0.022 mol L^{-1}) in DMF (1 mL), monomer (St, 1 mL, 4.3 mol L^{-1}) were added into schlenk tube and polymerization was carried out at 125 ºC for 24 h *via* nitroxide mediated radical polymerization. At the end of reaction, the mixture was diluted with THF and precipitated in excess methanol. The solid was collected after filtration and dried at room temperature in a vacuum overnight. Polymer was obtained in 40 % yield. (Mn = 11, 200, PDI = 1.72).

RESULTS AND DISCUSSION

Poly(ethylene adipate) (PEA) with different molecular weights was used as a hydrogen donor for the polymerization of MMA in the presence BP. The results are given in Table-1. For comparison, photopolymerizations by using either TX or TXOH are also added. As can be seen, BP is not an efficient photoinitiator in the absence of the co-initiator, PEA. The presence of PEA is important for effective photoreduction and photopolymerization. As can be seen from the data presented in Table-2, the chain length of the polyesters affects the overall conversion of MMA. When the molecular weight of polyesters is increased, the conversion increases but after defined value of molecular weight of polyesters, the conversion decreases. This may be attributed to the limited mobility. The interaction of photoexcited sensitizer with hydrogen donating PEA is suppressed at more viscous media. The overall reaction pathway is depicted in Fig. 1.

One of the results of the hydrogen abstraction from PEA is the formation of graft copolymers, since initiating radicals are generated on the backbone of PEA. This was confirmed by the spectral evidences. The hydrogen donating capability of PEA 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 (Fig. 2). ^1H NMR spectra of the initial PEA and the polyester TEMPO product are presented in Fig. 3. As can be seen, the characteristic protons of PEA appear at 4.27 ppm ($-O-CH_2-$), 2.35 ppm ($-CO-CH_2-(CH_2)_2-CH_2-$) and 1.67 ppm ($-CO-CH_2-(CH_2)_2-CH_2-$). Polyester TEMPO shows three characteristic peaks at 4.5, 1.6 and 1.0 ppm. we observed $-CH_3-$ protons belonging to tempo at 1.2 ppm but because of the overlapping, we couldn't observe $-CH_2-$ peaks expected at around 1.6 ppm. We also observed peaks around at 4.5 ppm which belongs to $-CH-$ protons attached to polyester.

TABLE-1
COMPARISON OF INITIATOR EFFICIENCY IN PHOTOINITIATED FREE RADICAL POLYMERIZATION OF METHYL METHACRYLATE

Run	PS	PS (mol L^{-1})	PEA[b](mol L^{-1})	Conversion (%)[c]	M_n[d]	PDI
1	BP	5.5×10^{-3}	5.5×10^{-3}	25.01	37200	1.73
2	BP	5.5×10^{-3}	11×10^{-3}	25.01	54800	1.44
3	BP	11×10^{-3}	5.5×10^{-3}	25.72	34800	1.67
4	TX	5.5×10^{-3}	5.5×10^{-3}	15.47	49300	3.60
5	T XOH	5.5×10^{-3}	5.5×10^{-3}	9.19	76350	3.02
6	BP	5.5×10^{-3}	–	No polymer	–	–

BP: Benzophenone, TX: thioxanthone, TXOH. [a]polymerization time = 2 h. [b]M_{nPEA} = 2600, PDI=2.28. [c]Overall methyl methacrylate conversion. [d]Estimated by GPC based on polystyrene standards.
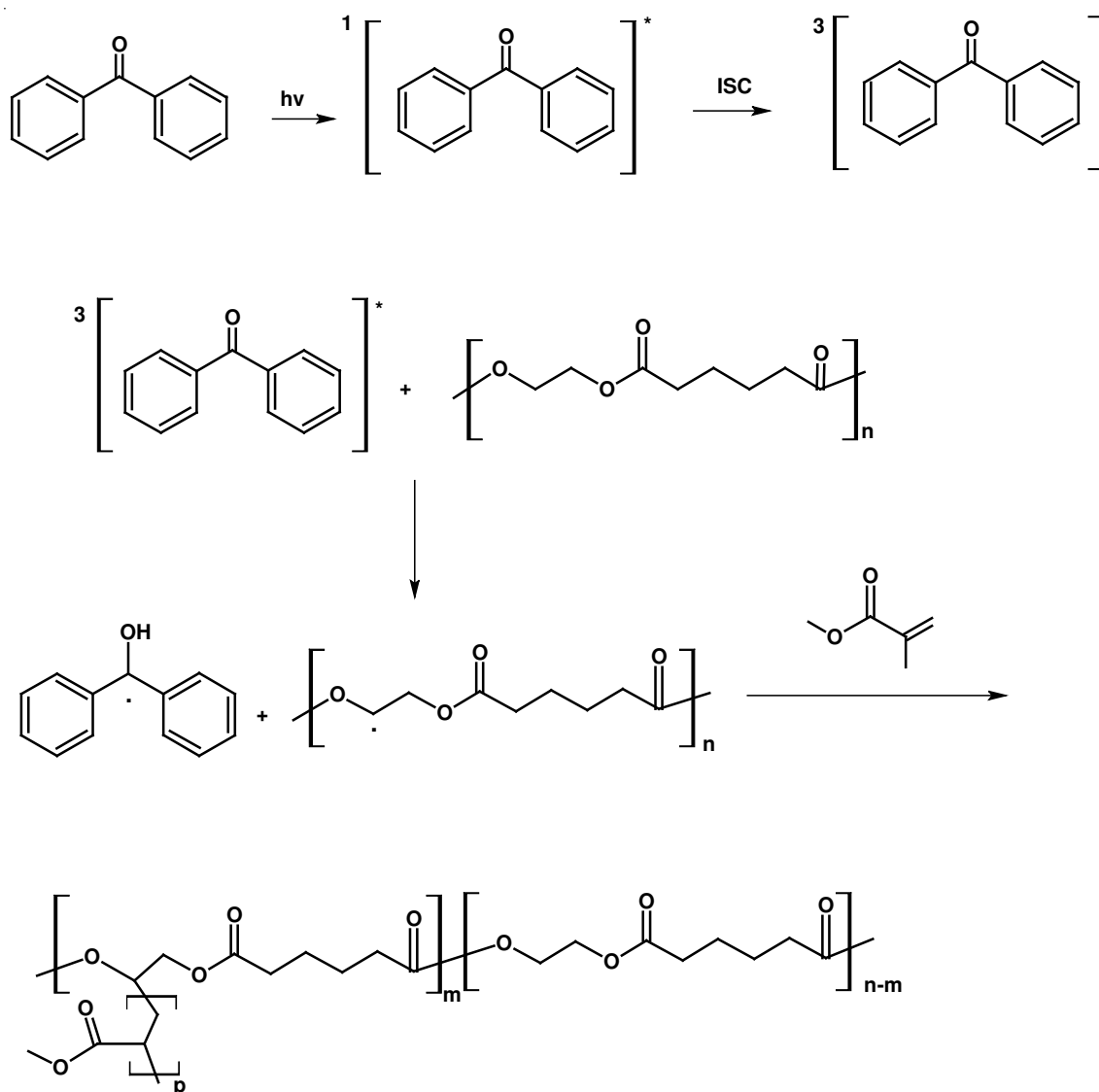
Fig. 1. Photoinitiated free radical polymerization by poly(ethyl adipate) as hydrogen donor
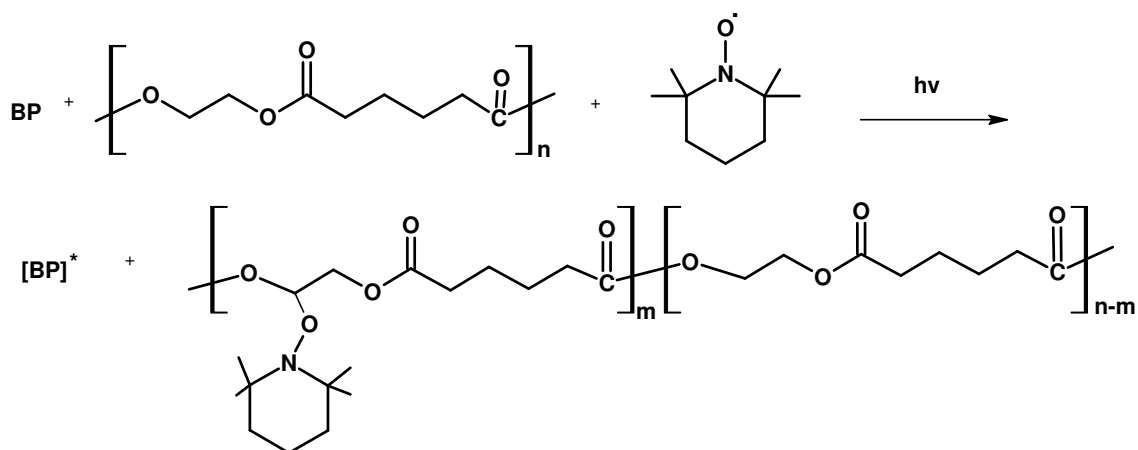

Fig. 2. Model study of capping photochemically generated poly(ethyl adipate) radicals with TEMPO radical

Many literatures[16-20] reported that TEMPO incorporated polymers were used successfully as a polymeric initiator for nitroxide mediated radical polymerization (NMP) of styrene to afford graft copolymers. Experimentally subsequent bulk polymerization of styrene using above TEMPO functionalized polyester was carried out at 125 ºC. ^{1}H NMR spectra of poly(ethylene adipate)-g-polystyrene are also showed in Fig. 4. As can be seen, characteristic protons of polystyrene appear between 7.24 and 6.28 ppm (aromatic protons) and 1.98-1.0 ppm -CH$_2$-CH- (aliphatic protons). We also observed small peak around at 4.27 ppm (-O-CH$_2$-) and 2.38 ppm (-O-CH$_2$-(CH$_2$)$_2$-CH$_2$-) which belongs to polyester.

TABLE-2
COMPARISON OF MOLECULAR WEIGHT
OF PEA IN PHOTOINITIATED FREE RADICAL
POLYMERIZATION OF METHYL METHACRYLATE

$M_{n\,PEA}$	Conversion (%)[c]	$M_n{}^d$	PDI[d]
2600	25.01	37200	1.73
3000	28.59	29600	1.65
7800	36.62	28900	1.77

[a][PS = (BP)] = 5.5×10^{-3} mol L^{-1}, polymerization time = 2 h. [b][PEA] = 5.5×10^{-3} mol L^{-1}. [c]Overall methyl methacrylate conversion. [d]Estimated by GPC based on polystyrene standards.
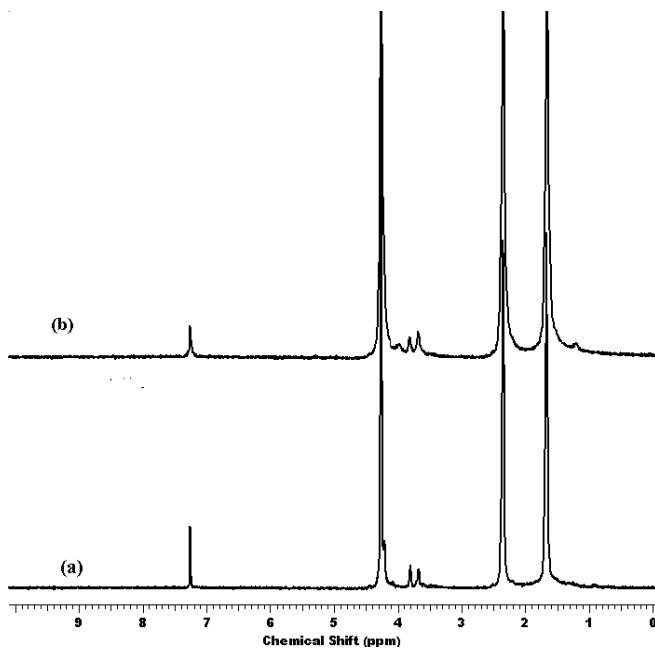

Fig. 3. (a) ^{1}H NMR spectra of PEA, (b) ^{1}H NMR spectra of TEMPO functionalized PEA in CDCl₃
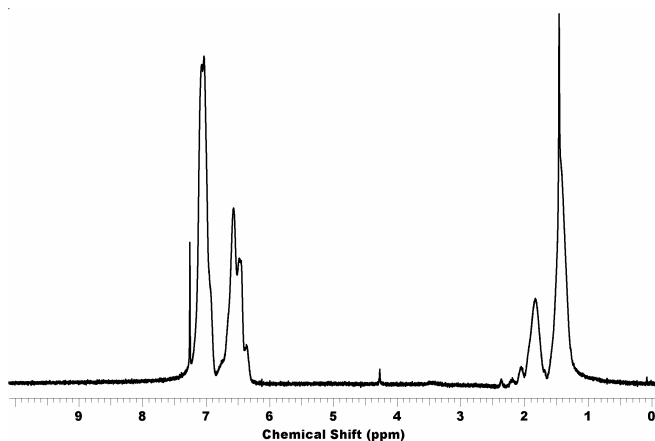

Fig. 4. ^{1}H NMR spectra of PEA-g-PS in CDCl₃

There are so many solvents tested in our trials and dimethylformamide (DMF) is the most appropriate among these solvents for the photopolymerization (Table-3). Obviously, the situation seems to be complex and two effects are combined. First, BP dissolves in DMF better than it dissolves in other solvents. Second, although radical polymerizations are not sensitive to the polarity of the solvent[21-23], triplet-state lifetime of photoinitiators which involve electron transfer such as thioxanthone species, may depend on some polarity effects. The electron transfer mechanism of thioxanthone has been

TABLE-3
COMPARISION OF SOLVENTIN PHOTOINITIATED FREE
RADICAL POLYMERIZATION OF METHYL METHACRYLATE

Run	Solvent	Conversion (%)[c]
7	DMF	25.01
8	DMSO	8.22
9	THF	19.34
10	MEK	10.64
11	CYCHEX	19.24

DMF N,N-dimethylformamide, DMSO dimethyl sulfoxide, THFtetrahydrofuran, MEK methyl ethyl ketone,[a][PS = (BP)] = 5.5×10^{-3} mol L^{-1}, polymerization time = 2 h. [b][PEA] = 5.5×10^{-3} mol L^{-1}. [c]Overall methyl methacrylate conversion. [d]Estimated by GPC based on polystyrene standards.

extensively investigated by spectroscopic and laser flash photolysis techniques in the literature[24,25].

We also used polyesters as hydrogen donor to test the polymerization ability of the other monomer such as styrene, N-vinyl-2-pyrrolidone, methacrylic acid (Table-4). When there is benzophenone and polyester as a hydrogen donor in the environment, polymerization of styrene cannot initiate. Although aromatic carbonyl/amine combinations represent an effective photoinitiator system for the polymerization of (meth)acrylates, they seem to be less reactive toward styrene monomers because of the high quenching rate of the monomer and the low reactivity of R-amino radicals with styrene[26].

TABLE-4
POLYMERIZATION OF DIFFERENT MONOMERS IN DMF

Run	Monomer	Monomer (mmol L^{-1})	Conversion (%)[c]	$M_n{}^d$	PDI[d]
12	MMA	10	25,01	37200	1.73
13	NVP	10	12,29	1700	1.54
14	MAA[e]	10	43,10	125650	2.12
15	S	10	No polymer	–	–

NVP N-vinyl-2-pyrrolidone, MAA methacrylic acid, [a][PS = (BP)] = 5.5×10^{-3} mol L^{-1}, polymerization time = 2 h. [b][PEA] = 5.5×10^{-3} mol L^{-1}. [c]Overall each monomer conversion. [d]Estimated by GPC based on polystyrene standards. [e]Water was used as a solvent.

Conclusion

It has been shown that poly(ethyl adipate) 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 non-toxicity. The initiating system can also be used in photografting for the preparation of amphiphilic copolymers.

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