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ARTICLE

Novel Polymer Synthesis Methodologies Using Combinations of Thermally- and Photochemically-induced Nitroxide Mediated Polymerization

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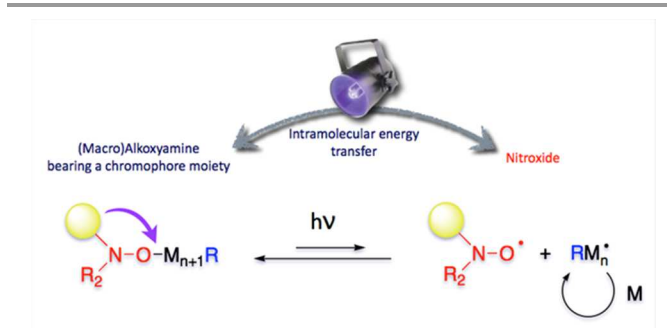
The combination of thermally- and photochemically-induced polymerization using light sensitive alkoxyamines was investigated. The thermally driven polymerizations were performed *via* the cleavage of the alkoxyamine functionality, whereas the photochemically-induced polymerizations were carried out either by nitroxide mediated photo-polymerization (NMP2) or by a classical type II mechanism, depending on the structure of the light-sensitive alkoxyamine employed. Once the potential of the various structures as initiators of thermally- and photo-induced polymerizations was established, their use in combination for block copolymer syntheses was investigated. With each alkoxyamine investigated, block copolymers were successfully obtained and the system was applied to the post-modification of polymer coatings for application in patterning and photografting.

Introduction

The synthesis of block, or more generally segmented copolymers has been achieved through numerous methodologies including the coupling of telechelic building blocks and the sequential addition of monomers using living polymerization systems.^{1, 2} Another common approach for the synthesis of block copolymers entails the use of dual initiators, which possess two distinct initiation sites capable of selectively initiating concurrent polymerization mechanisms or conditions.¹ Several examples of dual initiators involve the combination of the most commonly encountered free radical polymerization processes, namely thermal and photochemical mechanisms.^{1, 3} For example, the combination of azo-peroxides^{4, 5} or azo-benzoin^{6, 7} functionalities allows the preparation of block copolymers through sequential thermal and photochemical polymerization processes. Atom transfer Radical Polymerization (ATRP) and photopolymerization have also been combined using an alkyl halide coupled with Norrish Type I^{8, 9} and Type II¹⁰ photoinitiators. Significantly, the combination of photopolymerization and controlled radical polymerization allows the preparation of coatings that can be post-functionalized on demand. Although enabling post-functionalized materials, such systems require complex dual initiators, that commonly involve demanding multi-step

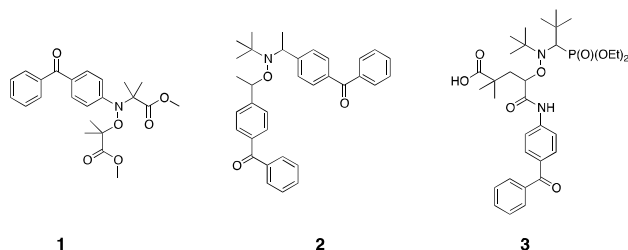
syntheses. Therefore, in order to efficiently combine thermal and photochemical driven polymerization processes, there is a clear need for the development of alternative strategies to match these requirements.

To this end, we recently introduced the so-called nitroxide-mediated photopolymerization¹¹⁻¹³ (NMP2 Scheme 1) technique using light sensitive alkoxyamines. In this process the irradiation of alkoxyamines bearing a chromophore directly attached to the (hidden) nitroxide moiety leads to a reversible equilibrium between the alkoxyamine and the generated nitroxide and alkyl radicals, allowing for a controlled radical photo-polymerization.



Scheme 1. Mechanism of the NMP2 process.

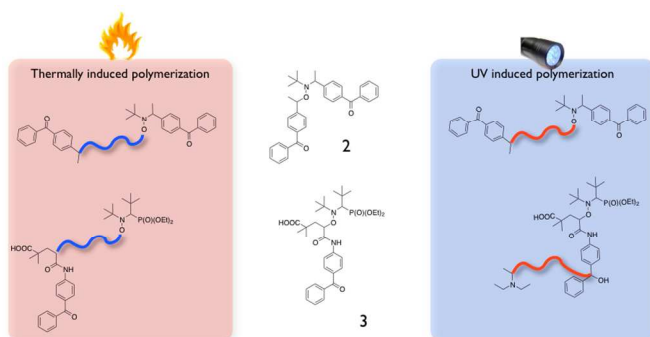
This novel approach was demonstrated through the polymerization of *n*-butyl acrylate initiated with **1** (Scheme 2), which reached 80 % conversion in 500 s, and which displayed a partial living character.¹¹ The cleavage of various light sensitive alkoxyamines under UV irradiation was later studied and led to the conclusion that the distance between the chromophore and the aminoxyl group is a key parameter^{14, 15} for efficient radical generation, even if the dissociation mechanism still remains unclear.



Scheme 2. Alkoxyamines investigated as initiators for NMP2

Among the alkoxyamines examined, alkoxyamine **2**, prepared via the Grubbs procedure,^{16, 17} showed a selective NO-C cleavage of the aminoxyl function upon UV irradiation.¹² Furthermore, as is the case for a large range of alkoxyamines, systems analogous to **2** were also successfully used as efficient initiator-control agents for conducting thermal NMP reactions.^{16, 17}

Among the alkoxyamines bearing a chromophore group previously investigated, compound **3** is particularly interesting. Indeed, it appears that despite the presence of the benzophenone moiety, UV irradiation (Xe-Hg lamp) of **3** does not induce the formation of nitroxides.¹⁴ However, despite its lack of reactivity in NMP2 processes, it was envisioned that the incorporated benzophenone moiety could potentially act as a Type II photoinitiator in combination with a co-initiator (e.g. amine). Since photosensitive alkoxyamines **2** and **3** could, in principle, be activated by either a thermal or photochemical process, the aim of the work described herein is to establish whether such compounds could be applied to the synthesis of block copolymers through sequential (and in any order) thermal- and photo-polymerizations.



Scheme 3. The two different polymerization modes that could be used with **2** and **3**. An amine is used as co-initiator for UV-induced polymerization with **3**.

In the case of alkoxyamine **2**, the combination of these processes would lead to the synthesis of AB block copolymers end-capped by the nitroxide moiety. However, in the case of **3**, this compound would be expected to act in a similar manner to dual initiators where different functionalities are involved in each process (Scheme 3). It has to be noted that this approach could be performed using ATRP since Yagci and coworkers¹⁸ already described the combination of ATRP and visible light radical polymerization using $\text{Mn}_2(\text{CO})_{10}$ as photopolymerization activator. The recent advances in photo ATRP¹⁹⁻²¹ and RAFT^{22, 23} could also lead to an efficient switch between thermal and photo activation.

Experimental Part

Materials.

Isobornyl acrylate (iBA), 2,2,3,3,3-pentafluoropropyl acrylate, styrene (S), methyldiethanolamine (MDEA), triethylamine, and ethyldimethylaminobenzoate (EDB) were purchased from Aldrich and were used as received. Ebecryl 605 (a bisphenol A epoxy diacrylate oligomer diluted with 25% of tripropyleneglycol diacrylate monomer) and trimethylolpropane triacrylate (TMPTA) were obtained from Allnex. Solvents (benzene, diethyl ether, pentane) were purchased from SDS and used as received. Alkoxyamines **2** and **3** were prepared as described in ref [12] and [14] respectively.

Instrumentation.

¹H (300.13 MHz) and ¹³C (75.44 MHz) NMR spectra in CDCl₃ were recorded on a Bruker AC-300 spectrometer using 5 mm o.d. tubes. Chemical shifts are reported as δ -values in parts per million (ppm) relative to residual CHCl₃ as the internal reference (¹H: δ 7.26, ¹³C: δ 77.23), and coupling constants (J) are reported in Hertz (Hz).

The SEC analyses were performed using an EcoSEC system from TOSOH equipped with a differential refractometer detector. THF was used as an eluent with 0.25 vol.% toluene as flow marker at a flow rate of 0.3 mL min⁻¹ after filtration on Alltech PTFE membranes with a porosity of 0.2 μm . The column oven was kept at 40 °C and the injection volume was 20 μL . One ResiPore Pre-column (50 mm, 4.6 mm) and two ResiPore columns (250 mm, 4.9 mm) from Polymer Laboratories were used in series. The system was calibrated using polystyrene (PS) standards in the range 100–400,000 g.mol⁻¹ which were purchased from Agilent. Universal calibration was used for PiBA using Mark-Houwink parameters²⁴ (PS $K = 0.0141 \text{ mL.g}^{-1}$, $\alpha = 0.7$; PiBA $K = 5.0 \times 10^{-3} \text{ mL.g}^{-1}$, $\alpha = 0.75$).

A Krüss drop shape analysis system DSA 100 was used for the measurement of the water/polymer contact angle. The support used was a glass slide with the studied polymer coated on the top surface, a drop of water (20 μL) was then brought into contact with the polymer.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a VG SCIENTA SES-2002 spectrometer equipped with a

concentric hemispherical analyzer. The incident radiation used was generated by a monochromatic Al $K\alpha$ x-ray source (1486.6 eV) operating at 420 W (14 kV; 30 mA). Photo-emitted electrons were collected at a take-off angle of 90° from the surface substrate, with electron detection in the constant analyser energy mode (FAT). Widescan spectra were recorded with a pass energy of 500 eV and for high resolution spectra (C1s and F1s) the pass energy was set to 100 eV. The analysed surface area was approximately 3 mm² and the base pressure in the analysis chamber during experimentation was about 10⁻⁹ mbar. Charging effects on these insulated samples were compensated by the use of a Flood Gun. The spectrometer energy scale was calibrated using the Ag 3d5/2, Au 4f7/2 and Cu 2p3/2 core level peaks, set respectively at binding energies of 368.2, 84.0 and 932.6 eV. Spectra were subjected to a Shirley baseline and peak fitting was made with mixed Gaussian-Lorentzian components with equal full-width-at-half-maximum (FWHM) using CASAXPS version 2.3.17 software. The surface composition expressed in atom% was determined using integrated peak areas of each component and the transmission factor of the spectrometer, the mean free path and the Scofield sensitivity factors of each atom. All the binding energies (BE) are referenced to the aliphatic carbon C1s - (CHx)- at 285.0 eV and given with a precision of 0.1 eV.

Polymerization experiments.

Thermally induced polymerizations were performed as follows: a solution of monomer (S or iBA) and the alkoxyamine ($[M]_0:[\text{alkoxyamine}]_0 = 200:1$) was introduced to a 100 mL three neck round bottom flask fitted with septum, condenser and temperature probe, and the solution was deoxygenated by argon bubbling (30 min). The mixture was then heated to 120 °C with vigorous magnetic stirring. The polymerization was monitored at various time intervals to determine the monomer conversion by ¹H NMR and M_n / \bar{D} by SEC. The obtained mixture was then added drop-wise to cold methanol (0 - 5 °C) with stirring. The precipitated polymer was then filtered off and dried in vacuo (5×10^{-2} mbar).

The UV-induced polymerizations were performed as follows: a stock solution of the monomer (5 mL, S or iBA) and the alkoxyamine ($[M]_0:[\text{alkoxyamine}]_0 = 200:1$) was prepared and equal samples of the mixture (1 mL) were placed in several vials. The vials were then deoxygenated by argon bubbling (30 min) and placed in a Rayonet reactor, equidistant from the lamps for 5 min (16 lamps @ 365 nm).

Film Photopolymerization Experiments

The conditions for photopolymerization experiments are given in the figure captions. The photocurable formulations were deposited on a BaF₂ pellet in laminate (the formulation is sandwiched between two polypropylene films) (25 μm thick) for irradiation with the UV light (Hamamatsu LC8). The evolution of the double bond content of trimethylolpropane triacrylate (TMPTA) were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 1630 cm⁻¹.²⁵

Laser Flash Photolysis

Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd/YAG laser ($\lambda_{\text{exc}} = 355$ nm, 9 ns pulses; energy reduced down to 10 mJ) from Continuum (Minilite) and an analyzing system consisted of a ceramic xenon lamp, a monochromator, a fast photomultiplier and a transient digitizer (Luzchem LFP 212).²⁶

Profilometry

For re-initiation experiments, a first polymer layer is synthesized through a thermal process. The polymerization is then spatially re-initiated in the light irradiated area. The final polymerized structure was washed with acetone. Shape and thickness of the pattern were determined using STIL workstation equipped with a 350 μm optical sensor using a working speed set at 300 Hz.

Results and Discussion

Thermally Induced Nitroxide Mediated Polymerization.

As alkoxyamines **2** and **3** had not previously been investigated under thermal NMP conditions, it was first necessary to examine their respective thermally based polymerization behaviours. The polymerization of styrene and isobornyl acrylate were first investigated since they should give good insight into the propagation control qualities of such alkoxyamines. The polymerizations of styrene were first carried out at 120 °C with a targeted M_n of 20,000 g.mol⁻¹ (Figure 1a). For both alkoxyamines, a high degree of control was observed with narrow molecular weight distributions obtained in each case ($\bar{D} = 1.15$ and 1.1 at 75 and 85 % conversion respectively). This result is in good agreement with the previously published results on the SG1 nitroxide²⁷ and the 2,2-dimethyl-4-phenyl-3-azapentane-3-oxyl nitroxide (also called Grubb's nitroxide).¹⁶

The results are rather different when isobornyl acrylate was tested. Isobornyl acrylate was chosen since the corresponding polymer could be isolated by precipitation and thus tested as a macro-initiator without any residual controlling agent trapped within the matrix. When alkoxyamine **3** is used at 120 °C with a targeted M_n of 20,000 g.mol⁻¹ (Figure 1b), good control was still obtained, but it must be noted that the molecular weight distributions were slightly broadened ($\bar{D} = 1.3$ at 60 % conversion). The evolution of M_n versus conversion presents the typical non-zero molecular weight at low conversion due to the conversion occurring before the establishment of the main equilibrium.^{27, 28} The presence of extra free nitroxide is required to have a better agreement of M_n versus conversion at low conversion.^{27, 28} This is consistent with acrylate polymerizations mediated by nitroxides where small amounts of side reactions (such as chain transfer, etc) are known to decrease somewhat the control of the polymerization process, particularly at high conversions.²⁹ As already reported, alkoxyamines analogous to **2** demonstrated good control over the polymerization of

styrene, it must be noted that the control is more difficult to achieve when acrylates are polymerized.¹⁷ Indeed, the high k_p value of acrylate derivatives typically requires the addition of excess free nitroxide in the medium to obtain a high degree of polymerization control.²⁷ In the case of 2,2-dimethyl-4-phenyl-3-azapentane-3-oxyl nitroxide, the presence of only one methyl group on the carbon linked to the aminoxyl function led to a nitroxide that is not persistent and as such could not be isolated.¹⁷ Grubbs and co-workers¹⁷ presented an elegant procedure that consists of a pre-heating of the alkoxyamine without any monomer to generate in situ the excess nitroxide. The addition of *n*-butyl acrylate and its polymerization was in that case living and controlled with dispersities close to 1.4 at 90 % conversion.¹⁷

conversion, although the M_n was higher than the theoretical value due to the fact that a low amount of the starting alkoxyamine decomposed during the pre-heating step at 80 °C. The dispersities are quite high compared to polymers obtained with alkoxyamine **3** but are lower than without pre-heating (\bar{D} close to 3, data not shown). Thus, the pre-heating strategy allowed us to obtain a rather good controlled polymerization of isobornyl acrylate.

In conclusion, we have demonstrated that alkoxyamines **2** and **3** allow efficient thermally induced NMP of styrene and isobornyl acrylate.

Photochemically Induced Polymerization.

In this study, only acrylate derivatives were used for photopolymerization experiments since high k_p values are required to polymerize at room temperature in a relatively short reaction time. The nitroxide mediated photopolymerization (NMP2) of *n*-butyl acrylate with alkoxyamine **2** has been described previously, but with a different experimental set-up.¹² The experimental set-up is known to influence photochemical processes with sample to irradiation source distance, and sample volume ratio being two key variables amongst several factors.

Photopolymerization of isobornyl acrylate with alkoxyamine **2** was then performed using a Rayonet reactor for 5 min. Similar results were obtained compared to those already published,¹² showing an increase of M_n versus conversion with experimental M_n above the theoretical value and an increase of \bar{D} with conversion (Figure 2).

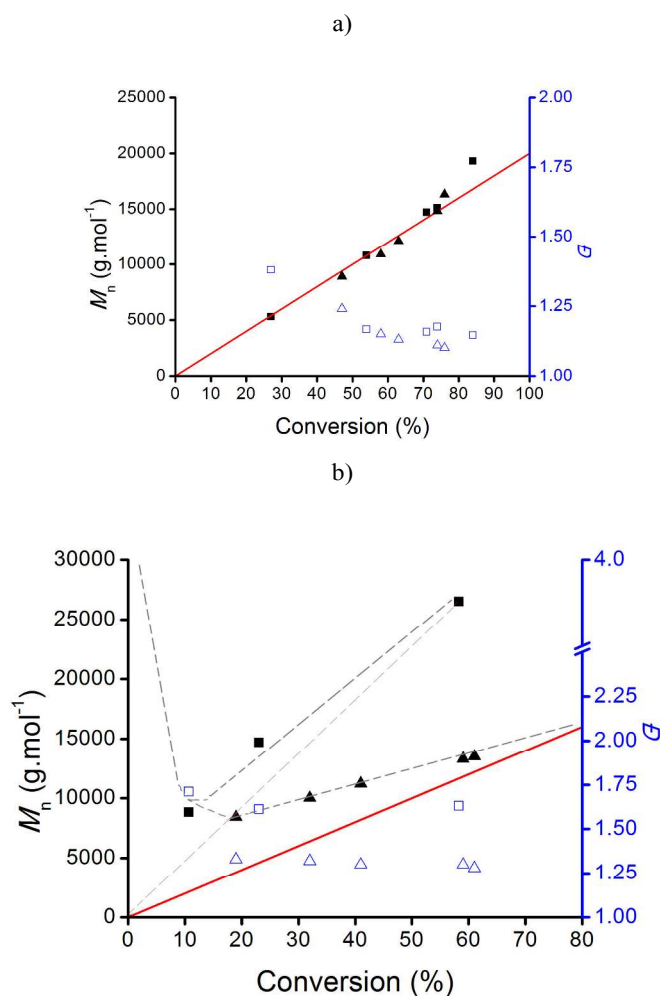


Figure 1. a) Evolution of number-average molar mass (M_n full symbols) and dispersity (\bar{D} empty symbols) vs conversion for the bulk styrene polymerization ($[S]_0 : [\text{Alkoxyamine}]_0 = 200:1$). The solid line corresponds to the theoretical M_n . (■) styrene initiated by **2**; (▲) styrene initiated by **3**. b) Evolution of number-average molar mass (M_n full symbols) and dispersity (\bar{D} empty symbols) vs conversion for the bulk isobornyl acrylate polymerization ($[\text{iBA}]_0 : [\text{Alkoxyamine}]_0 = 200:1$). The solid line corresponds to the theoretical M_n . (■) iBA initiated by **2**; (▲) iBA initiated by **3**. The grey dotted lines are guides for the eyes only.

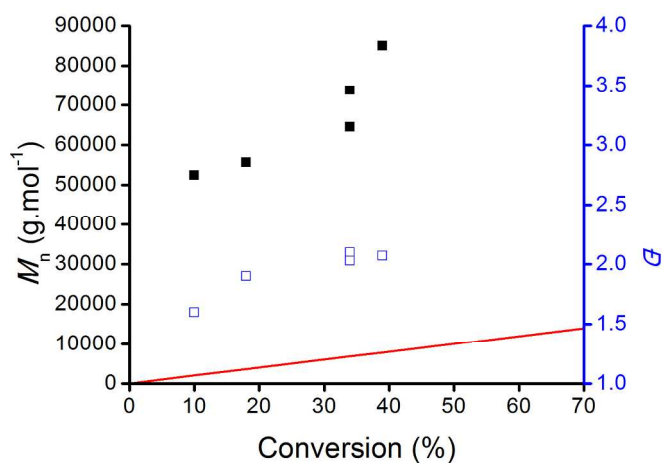


Figure 2. Evolution of number-average molar mass (M_n full symbols) and dispersity (\bar{D} empty symbols) vs conversion for the bulk isobornyl acrylate photopolymerization in a Rayonet reactor ($[\text{iBA}]_0 : [\mathbf{2}]_0 = 200:1$). The solid line corresponds to the theoretical M_n .

Following this procedure, we performed the polymerization of isobornyl acrylate and obtained a linear evolution of M_n versus

It is important to note that whilst bulk polymerizations of isobornyl acrylate under thermal conditions benefit from thermal solubilisation, the photochemical process takes place at room temperature with polymer precipitation occurring, even at low conversion. Moreover, due to the gradient effect, whereby

the light intensity diminishes with increasing penetration of the irradiated sample, polymer precipitation occurs at the vial-acrylate interface, radiating inwards with increasing conversion. This phenomenon enhances the likelihood of side reactions as the precipitated polymer generates an artificial high conversion environment.

Since it was already reported that no nitroxide was produced under UV irradiation of alkoxyamine **3**,¹⁴ photopolymerization experiments were performed using a conventional type II photoinitiator system, *i. e.* a benzophenone derivatives (**3** in this work) in combination with an amine as hydrogen donor.

In laser flash photolysis experiments, the triplet state of **3** is strongly quenched by triethylamine with a rate constant of reaction of $4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The lifetime of the triplet state of **3** is 50 ns in the presence of 0.0067 M of amine vs. 2.2 μs in the absence of amine (Figure 3a). The ketyl radical is also clearly observed at 545 nm with an intense persistent residual absorption as usually observed for the benzophenone ketyl radical.³⁰

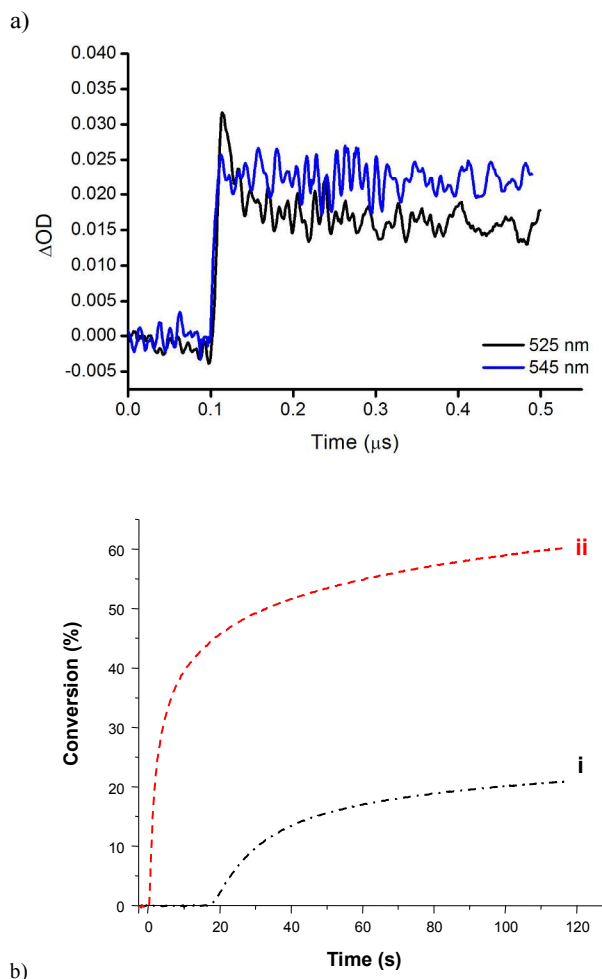
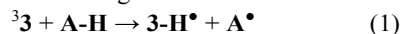


Figure 3. a) Kinetics observed at 525 nm and 545 nm for **3**/triethylamine in acetonitrile ([triethylamine] = 0.0067 M), laser shot at $t=0.1 \mu\text{s}$. b) Polymerization profiles for TMPTA in laminate upon a UV light exposure for different initiating systems: (i) **3** (1% w/w) and (ii) **3**/triethylamine (1%/1% w/w).

From the respective optical densities of the benzophenone chromophore triplet state at 525 nm and the ketyl radical at 545 nm, the quantum yield in ketyl radical (Φ_K) for reaction (1) can be calculated according to established procedures.³⁰ It was determined that Φ_K is close to 1 (0.95) in full agreement with a quantitative reaction process between the **3** and the triethylamine. A polymerization initiating aminoalkyl radical (A^\bullet) is generated as well as 3-H^\bullet a scavenger of macroradical; ketyl radicals are known as poor initiating but excellent terminating radicals.³¹



In agreement with reaction (1), it could be observed that **3**/triethylamine is an excellent photoinitiating system for the polymerization of trifunctional acrylate (TMPTA) in films (Figure 3b). In the absence of amine almost no polymerization occurs albeit a very efficient initiating system is obtained in the presence of the amine (Figure 3b curve i vs. curve ii).

After 5 min of irradiation inside the Rayonet reactor, a polymer of $M_n = 15,500 \text{ g}\cdot\text{mol}^{-1}$ and $D = 3.5$ was obtained with a conversion of 83 %. The purified polymer was subsequently analysed by ESR to ensure that the alkoxyamine moiety was incorporated within the polymer backbone through the trapping of the macroradical by the ketyl radical (Scheme 3).

The appearance of the characteristic signal of the SG1 nitroxide upon heating within the ESR cavity (Figure 4) is evidence that the alkoxyamine moiety is covalently bound to the polymer. The presence of SG1 bound to the polymer enables the combination of the thermally and UV-induced polymerization modes with alkoxyamine **3**.

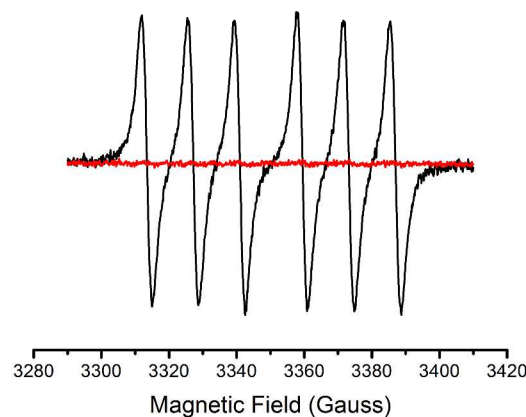


Figure 4. ESR spectra of the purified P(iBA) obtained by UV-induced polymerization of iBA initiated with **3** before (red line) and after (black line) heating at 120°C in the ESR cavity.

Advanced Macromolecular Architectures.

ALKOXYAMINE **2**

Having demonstrated the ability for alkoxyamine **2** to mediate both the thermal polymerizations of styrene and isobornyl acrylate as well as the photopolymerization of isobornyl acrylate, we then tested the combination of these two processes for the synthesis of block copolymers.

The first block copolymer examined was prepared through the photopolymerization of isobornyl acrylate which reached 12 % conversion after one minute of UV irradiation to afford poly(isobornyl acrylate) (PiBA) with a M_n of 38,400 $\text{g}\cdot\text{mol}^{-1}$ ($D = 2.0$). After precipitation of the PiBA block in cold methanol and removal of residual solvent *in vacuo*, the PiBA macroinitiator was heated at 120 °C in the presence of styrene to afford the PiBA-*b*-PS block copolymer (Figure 5).

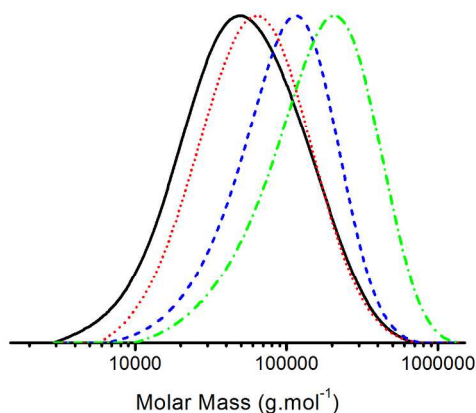


Figure 5. Molar Mass Distribution obtained from the bulk styrene polymerization initiated with the PiBA macroinitiator obtained by the photopolymerization of iBA initiated by **2** (M_n of 38,400 $\text{g}\cdot\text{mol}^{-1}$, $D = 2.0$). (black solid line: macroinitiator); (red dotted line 8 % conversion); (blue dashed line 28 % conversion); (green dotted dashed line 40 % conversion).

The re-initiation experiment was followed by SEC and a clear shift in the molecular weight distribution to a higher molecular weight with increasing conversion was observed. After heating at 120 °C for one hour, 8 % conversion of styrene was attained with an associated increase in the M_n to 44,000 $\text{g}\cdot\text{mol}^{-1}$ ($D = 1.89$). This increased to 62,600 ($D = 1.76$) and 70,600 $\text{g}\cdot\text{mol}^{-1}$ ($D = 1.73$) at 28 and 40 % conversion after heating for two and three hours respectively. Combined with the disappearance of the peak corresponding to the first block polymer, the increasing M_n with conversion gives evidence for the successful re-initiation of the PiBA block and formation of the expected PiBA-*b*-PS block copolymer. Moreover, the decreased dispersity obtained during the re-initiation test demonstrated the controlled polymerization of the second block and confirmed the living character of the previously prepared PiBA.

After the successful formation of the first block copolymer, we sought to examine the possibility of reversing the order of block copolymer formation. In a pure thermal process, it is well known that such block order lead to significant amount of dead chains and large PDIs due to unfavorable kinetic parameters. This was illustrated with TEMPO, TIPNO and SG1 both in homogeneous and aqueous dispersed media.^{32, 33} In this work

the two blocks are prepared using different polymerization modes. Accordingly, the first block was prepared through the thermal polymerization of styrene at 120 °C for 4.25 hours to afford PS with a M_n of 8,000 $\text{g}\cdot\text{mol}^{-1}$ at 49 % conversion ($D = 1.24$). After precipitation of the PS block in cold methanol and removal of residual solvent *in vacuo*, re-initiation of the PS block under UV irradiation in the presence of iBA then afforded the PS-*b*-PiBA block copolymer.

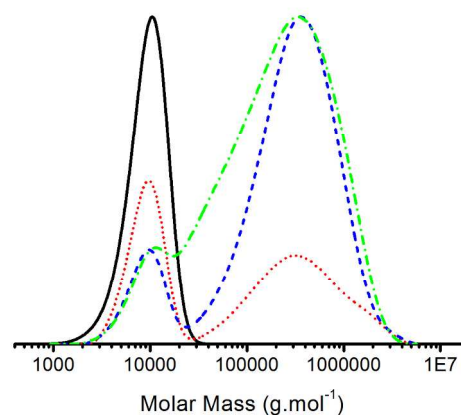


Figure 6. Molar Mass Distribution obtained from the bulk iBA photopolymerization initiated with the PS macroinitiator obtained by the thermal polymerization of S initiated by **2** (M_n of 8,000 $\text{g}\cdot\text{mol}^{-1}$, $D = 1.24$). (black solid line: macroinitiator); (red dotted line 8 % conversion); (blue dashed line 28 % conversion); (green dotted dashed line 40 % conversion).

Following reinitiation, a reduction of the peak corresponding to the first block polymer was apparent, with an increase of the M_n with conversion demonstrating successful re-initiation and formation of the PiBA-*b*-PS block copolymer (Figure 6). However, it must be noticed that a proportion of lower molecular weight chains remained following re-initiation, originating either from dead chains during the synthesis of the first block or the early stages of the second block copolymer synthesis. Furthermore, a broadening of the molecular weight distribution was observed at high conversions. This is consistent with the increased propensity for side reactions at high conversion of acrylate polymerizations as previously discussed.

ALKOXYAMINE **3**

Alkoxyamine **3** demonstrated the ability to independently mediate the thermal polymerizations of styrene and isobornyl acrylate, as well as act as a type II photoinitiator for the photopolymerization of iBA. Accordingly, the prospect of combining these processes to determine whether alkoxyamine **3** could function as a dual initiator for the preparation of block copolymers was of interest.

To examine the potential of alkoxyamine **3** as a dual initiator for the synthesis of block copolymers, this compound was first used to mediate the thermal polymerization of styrene at 120 °C for 0.5 hours to afford PS with a M_n of 8,600 $\text{g}\cdot\text{mol}^{-1}$ at 40 %

conversion ($D = 1.28$). Similarly, the thermal polymerization of isobornyl acrylate at 120 °C for 1.5 hours afforded PiBA macro-photoinitiator with a M_n of 8,000 $\text{g}\cdot\text{mol}^{-1}$ at 41 % conversion ($D = 1.33$).

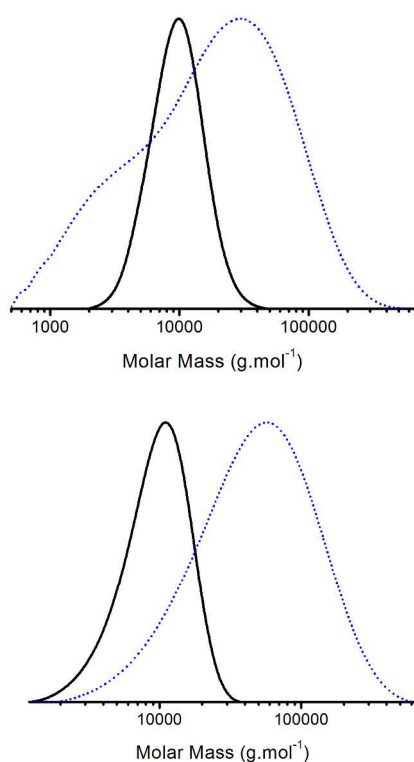


Figure 7. a) Molar Mass Distribution obtained from the bulk iBA polymerization initiated with the PS macroinitiator obtained by the polymerization of **5** initiated by **3** (M_n of 8,600 $\text{g}\cdot\text{mol}^{-1}$, $D = 1.28$). (black solid line: macroinitiator); (blue dotted line PS-*b*-PiBA M_n of 6,800 $\text{g}\cdot\text{mol}^{-1}$, $D = 5.14$). b) Molar Mass Distribution obtained from the bulk iBA polymerization initiated with the PiBA macroinitiator obtained by the polymerization of iBA initiated by **3** (M_n of 8,00 $\text{g}\cdot\text{mol}^{-1}$, $D = 1.33$). (black solid line: macroinitiator); (blue dotted line PiBA-*b*-PiBA M_n of 28,900 $\text{g}\cdot\text{mol}^{-1}$, $D = 2.44$).

As all polymeric chains were initiated by the alkyl fragment of alkoxyamine **3**, that possesses a benzophenone moiety, we therefore sought to examine the potential for the incorporated benzophenone moiety of the macroalkoxyamine to act as a type II photoinitiator.

Accordingly, after precipitation of the macroinitiator in cold methanol and removal of residual solvent in vacuo, the incorporated benzophenone moiety of the macroalkoxyamine was utilized as a type II photoinitiator in the presence of the sacrificial hydrogen donor triethylamine. Trapping of the propagating polymeric species by the benzophenone ketyl radical should then afford both the PS-*b*-PiBA and PiBA-*b*-PiBA block copolymers (Figure 7). In each case, after 5 minutes of UV irradiation, a clear shift in the molecular weight distribution to a higher molecular weight was apparent. This increase in the molecular weight distribution is evidence for the successful formation of the PS-*b*-PiBA block copolymer.

Nevertheless, different results were obtained depending on the nature of the macroinitiator. In the case of the PS macroinitiator, a proportion of lower molecular weight chains below the molecular weight of the PS block polymer were observed ($M_n = 6,800 \text{ g}\cdot\text{mol}^{-1}$, $D = 5.14$). When PiBA macroinitiator was used however, a clear shift in the molecular weight distribution to a higher molecular weight ($M_n = 28,900 \text{ g}\cdot\text{mol}^{-1}$, $D = 2.44$, at 89% conversion) was observed. The difference of reactivity may be attributed to the lower solubility of PS inside the iBA compared to the PiBA macroinitiator. Indeed, we could postulate that initiation occurred by the aminoalkyl radical coming from the triethylamine and that not all the chains are terminated by the PS-ketyl macroradical. This could lead to chains without the macroinitiator and chains bearing the PS moiety. As the incorporated benzophenone moiety of the nitroxide-capped PS block acts as a Type II photoinitiator, the polymerization therefore proceeds without controlling agent that moderate the reactivity of macroradicals.

In the final block copolymer examined, alkoxyamine **3** was utilized as a type II photoinitiator in the presence of iBA and the sacrificial hydrogen donor triethylamine. PiBA with a M_n of 15,500 $\text{g}\cdot\text{mol}^{-1}$ at 83% conversion ($D = 3.50$) was obtained after five minutes of UV irradiation. After precipitation of the PiBA block in cold methanol and removal of residual solvent in vacuo, thermal polymerization of styrene at 120 °C afforded the PiBA-*b*-PS block copolymer (Figure 8).

A clear shift in the molecular weight distribution to higher molecular weight was observed following re-initiation (Figure 8). At 9% conversion the M_n increased to 43,700 $\text{g}\cdot\text{mol}^{-1}$ ($D = 1.94$) and further increased to 70,000 $\text{g}\cdot\text{mol}^{-1}$ ($D = 3.13$) respectively at 9 and 37 % conversion.

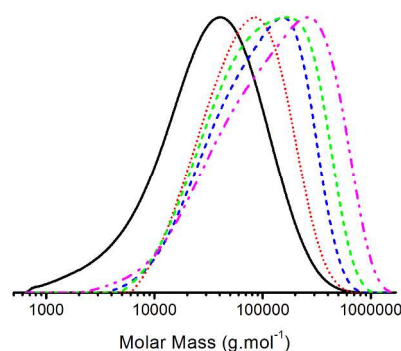


Figure 8. Molar Mass Distribution obtained from the thermal bulk S polymerization at 120 °C initiated with the PiBA macroinitiator obtained by the photo-polymerization of iBA initiated by **3** and NEt_3 (M_n of 15,500 $\text{g}\cdot\text{mol}^{-1}$, $D = 3.5$). (black solid line: macroinitiator); (red dotted line 9 % conversion, M_n of 43,700 $\text{g}\cdot\text{mol}^{-1}$, $D = 1.94$); (blue dashed line 16 % conversion M_n of 59,000 $\text{g}\cdot\text{mol}^{-1}$, $D = 2.16$); (green dotted dashed line 26 % conversion, M_n of 55,700 $\text{g}\cdot\text{mol}^{-1}$, $D = 2.62$); (magenta dotted dotted dashed line 37 % conversion, M_n of 70,000 $\text{g}\cdot\text{mol}^{-1}$, $D = 3.13$).

These results demonstrate the successful formation of the PiBA-*b*-PS block copolymer. The evolution of the dispersity presented first a decrease that is due to the control of the

polymerization by the release of the SG1 nitroxide. Nevertheless the dispersity subsequently increases at higher conversion, which is attributed to dead chains arising from the uncontrolled polymerization of the first PiBA block that cannot be re-initiated.

PATTERNING AND SURFACE MODIFICATIONS

In the patterning field, one of the main drawbacks is the difficulty to combine both spatial and temporal control of the surface. If a polymer coating is prepared thermally using varying techniques such as SI-CRP, the temporal and post-functionalization process is achievable, however the spatial control has to be performed using complex printing techniques.³⁴ If photopolymerization is used for the polymer coatings, post-functionalization is rather difficult.³⁵ As the light sensitive alkoxyamines described in this study are both photo and thermal initiators, it should be possible to prepare a polymer coating that can be post-functionalized and where the spatial control is given by the UV mode and the temporal control (*i.e.* the living character) by the thermal mode.

As a proof of concept, we first prepared a polymer layer through the thermal polymerization of TMPTA in the presence of **3** (1% w/w). A conversion of 65% was obtained after 20 minutes of heating at 120 °C (gravimetric determination of the conversion). A second formulation containing only an amine (methyldiethanolamine – MDEA) in ebecryl 605 was then applied to the first layer obtained. The re-initiation of the polymerization was easily followed by FTIR spectroscopy at about 1630 cm⁻¹. The polymerization profile for this second layer is given in Figure 9; a good final conversion of ~ 60% was obtained after 300s of irradiation with a Xe-Hg lamp. The polymerization of the second layer results from a Type II initiation process between the BP chromophore of the first layer and the amine present in the second layer. Without the amine a poor degree of polymerization occurs with conversions typically being < 20% clearly showing the importance of the hydrogen abstraction reaction (1) for the re-initiation of the polymerization between layer 1 and layer 2.

A similar re-initiation procedure was also carried out with another monomer to highlight the prospects for surface property modification. Indeed, a contact angle (water/polymer) of 60° is found for a TMPTA surface indicating a significant hydrophilic character (Figure 10A). Employing the techniques described above, a second formulation can be coated on the top of the synthesized polymer (ethylidimethylaminobenzoate EDB in a fluoromonomer) allowing a re-initiation of the polymerization to generate a second layer under UV irradiation. Again the amine reacts with **3** upon light exposure to initiate the polymerization of the second layer *i.e.* after 5 minutes of irradiation a tack free surface is obtained. The contact angle for the modified surface was found to be 115° (Figure 10b), indicating a hydrophobic surface arising from the fluoro groups

present in the second layer. This re-initiation experiment clearly highlights the dual initiator behavior of **3**.

The re-initiation of the first layer is also supported by XPS analysis (Figure 10c). This technique provides information about the outermost surface of the sample in a range of 6-9 nm. This analysis supports the re-initiation of the second layer with the fluoromonomer. On the wide scan of the second layer, only carbon, fluorine and oxygen are detected on the surface and the atomic percentage of each species is 46.94, 39.72 and 13.34 respectively. Figure 10c highlights the re-initiation with the presence of fluorine in the F1s and C1s high resolution XPS spectra.

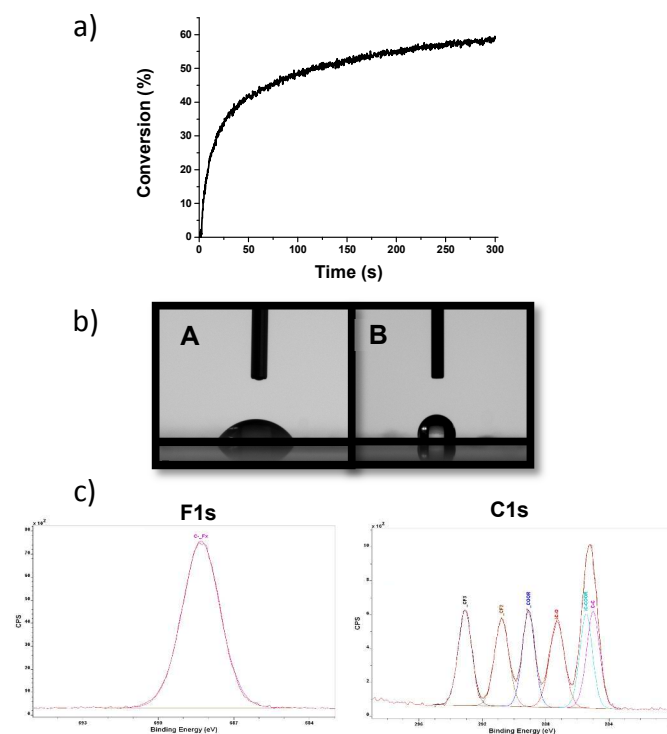


Figure 10. a) Photopolymerization profile upon a Xe-Hg lamp irradiation ($\lambda > 340$ nm) using MDEA (1% w/w) in Ebecryl 605; in laminate. The formulation is coated on the polymer synthesized through a thermal process. b) Contact angles for the polymer obtained for (A) the polymerization of TMPTA with **3** (1% w/w) -thermal polymerization at 120°; (B) After reinitiation upon a Xe-Hg lamp irradiation ($\lambda > 340$ nm) 1% of ethyldiaminobenzoate (EDB) with 2,2,3,3,3-pentafluoropropylacrylate. c) F1s and C1s high resolution XPS spectra after reinitiation with the fluoromonomer.

The initiation of the second layer as presented above can also be spatially controlled by the use of a mask. As a proof of concept, the experiments described previously were repeated for an irradiation through a mask (rectangular aperture: 0.6 mm - 4 mm). Notably even after 400s of irradiation; the polymerization restarts only in the irradiated area (Figure 11). A final thickness of ~100 μ m for the second layer was obtained in the irradiated area.

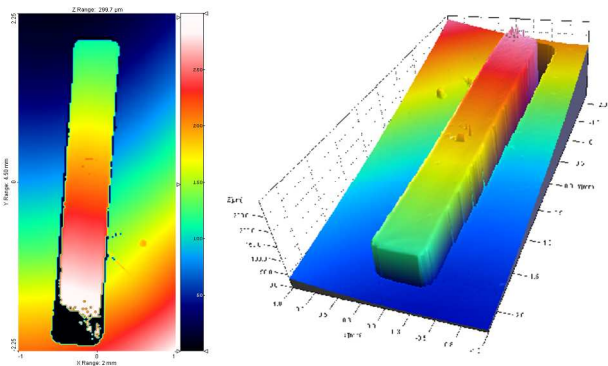
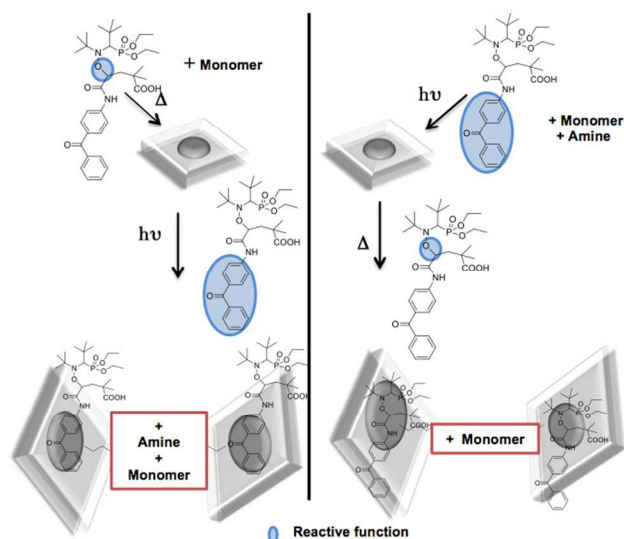


Figure 11. Profilometric profile of the second layer; irradiation through a mask for the photopolymerization of the second layer upon a Xe-Hg lamp irradiation ($\lambda > 340$ nm) using MDEA (1% w/w) in Ebecryl 605. The formulation is coated on the polymer synthesized through a thermal process

POLYMER BONDING

Figures 12A and 12C represent two polymer films obtained through thermal and UV polymerization, respectively. The aim of this experiment was to bind the two polymers together by combining thermal and UV polymerization (see Scheme 4). In the first example, two polymer films were produced through the thermal radical polymerization of an acrylate monomer (Ebecryl 605) using **3** as initiator at 120°C. These films were then successfully bound together upon UV light irradiation using an amine formulation in Ebecryl 605 (Figures 12A and 12B). In a second example, two other polymer films were prepared using **3** with MDEA in Ebecryl 605 through a radical photopolymerization, after 5 minutes of Xe-Hg lamp irradiation. Then Ebecryl 605 monomer was successfully used to bond the two polymer films together by thermal polymerization at 120°C over 20 minutes (Figures 12C and 12D).



Scheme 4. Use of dual photoinitiator for the linkage of two polymer films by combining UV and thermal polymerization in laminate.

As shown in Scheme 4, with a thermal polymerization the linkage is due to the NMP re-initiation of the polymerization. For the photochemical re-initiation, the initiating radicals are generated by the reaction of the benzophenone triplet state of the alkoxyamine with the amine.

Conclusions

The use of light-sensitive alkoxyamines as bi-functional initiators for both thermally- and photo- induced radical polymerizations were investigated. The ability of alkoxyamines **2** and **3** to perform thermally driven nitroxide mediated polymerization was established as expected. Concerning the photopolymerization, the alkoxyamine **2** behaved as expected, undergoing an NMP2 process to generate polymers with a large dispersity but with a marked living character.

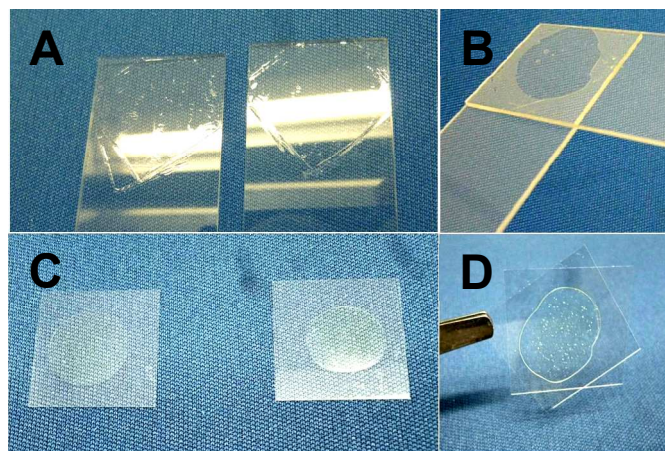


Figure 12. Polymerization of Ebecryl 605 monomer using: (A) alkoxyamine **3** (1% w/w) at 120°C; (B) MDEA (1% w/w) to bound the two polymer films of A upon a Xe-Hg lamp irradiation ($\lambda > 340$ nm); (C) alkoxyamine **3** + MDEA (1%/2% w/w) after Xe-Hg lamp irradiation ($\lambda > 340$ nm); (D) without initiator to bound two polymer films of C at 120°C.

The alkoxyamine **3** is found to be a good type II photoinitiator in combination with a hydrogen donor. This system has the advantage that the alkoxyamine functionality was inserted into the polymer backbone by the trapping of the ketyl radical on the polymer chain end. As all the polymers prepared by either thermal or UV-induced polymerization have a potential living character, their applications for block copolymer synthesis using two distinct polymerization modes were evaluated. Whatever the alkoxyamine structure and block copolymer polymerization mode order, block copolymers were always prepared with moderate to good control. These results showed the value of these alkoxyamines for the combination of both thermal- and UV- induced polymerization from a single substrate. This has potential applications in surface micro-patterning where thermally- or UV- induced coatings could be post-modified using another polymerization mode. To demonstrate this, an initial layer of TMPTA was formed by a thermal process and the contact angle of this surface was significantly modified using UV irradiation in the presence of another monomer. The same layer could also be modified by the addition of patterns also using UV irradiation and the

presence of photo-mask. Notably the two layers were covalently bound and no additional photoinitiators were added. Secondly the combination of these two alternative polymerisation processes could be used to bind polymer layers prepared by different polymerization modes. These two applications demonstrate the value of light-sensitive alkoxyamines that can exploit combinations of thermal and UV dissociation processes.

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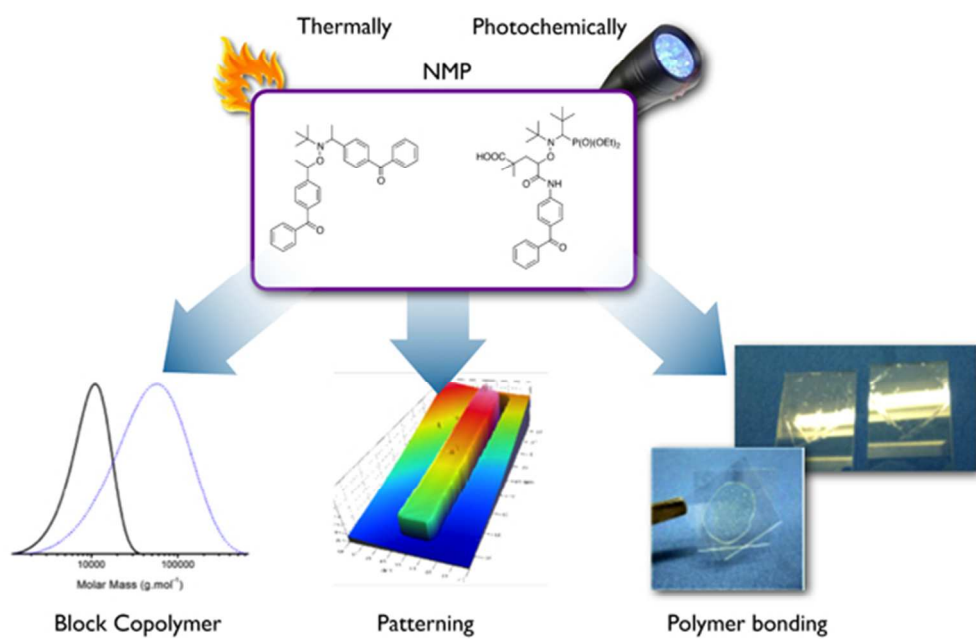
Notes and references

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