

Polymer Chemistry

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Polymer Chemistry

ARTICLE

Polymers synthesized by RAFT as versatile macrophotoinitiators

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An exploitation of the generally unwanted sensitivity to light of chain-end functions in polymers synthesized by reversible addition-fragmentation chain transfer (RAFT) is proposed. This reactivity can be purposely enhanced through the simple introduction of a strongly absorbing chromophore on the terminal monomer unit. The concept was validated on RAFT polymers with a xanthate chain-end function and a terminal monomer unit derived from *N*-vinylcarbazole (NVC). We demonstrate that such compounds can be considered as efficient and versatile macrophotoinitiators, being able to initiate both free radical and radical promoted cationic polymerizations under UV irradiation.

Introduction

Considering the outstanding advances that they have brought towards a better controllability of macromolecular structures, as well as the ensuing miscellaneous synthetic possibilities that they have offered in the field of macromolecular engineering,¹ it cannot be denied that the industrial exploitation of reversible deactivation radical polymerizations (RDRPs),² more commonly called “controlled radical polymerizations”, has remained extremely limited.³ This observation is mostly ascribable to the fact that RDRPs are significantly more expensive to carry out than conventional radical polymerizations, due to the extra cost generated by the added control agent, the longer reaction time needed to reach either similar conversions or molar masses, and in some cases higher temperatures or necessary purification steps. These limitations have probably definitely ruled out the realistic industrial application of RDRPs to the synthesis of commodity polymers, for which cheaper and well-established procedures have been used for a long time. For these reasons, the renewal of the industrial interest into RDRPs necessarily implies innovative valorization strategies, in which derived polymers would be considered exclusively as new high-added-value specialty products.

The goal of this contribution comes within this framework, focusing on polymers synthesized using a RDRP mechanism mediated by reversible addition-fragmentation chain transfer (RAFT).⁴ Discovered in the late 90s, the RAFT mechanism appears now as one of the most versatile RDRPs in terms of

compatible monomers and procedures.⁵ However, the same thiocarbonylthio chain-end functions having ensured the control of the polymerization may become a real issue in the final products due to the unwanted features that they can induce, such as a marked coloration of the polymers or their potential sensitivity to heat or light. Their removal implies necessarily an additional synthetic step.⁶ This flip side to the advantages brought by the RAFT mechanism inevitably hinders the interest in the derived products from an industrial point of view. However, the appeal of polymers synthesized by RAFT can be totally renewed if these remaining chain-end functions are no longer considered as a drawback, but on the contrary as key functions that can be made use of in the subsequent applications of these products. In this view, the modification of terminal functions in polymers synthesized by RAFT has been already broadly investigated.⁷

Considering the reactivity of these functions, it is well-known that several thiocarbonylthio compounds were already commonly used as photoinitiators or photoiniferters before the discovery of RAFT, and especially dithiocarbamates⁸ and xanthates.⁹ This observation strongly suggests that the aforementioned sensitivity of the chain-end functions to light can be exploited advantageously. In this contribution, we focused on polymers synthesized by RAFT and exhibiting structures in which the photodissociation efficiency of the thiocarbonylthio end-groups is enhanced. In this approach, the RAFT mechanism can be viewed as a versatile synthetic platform for the design of tailor-made macrophotoinitiators. In RAFT polymers, an enhanced photodissociation efficiency of the C-S bond between the main chain and the thiocarbonylthio function can be expected if a chromophore resulting in an intense light absorption is purposely introduced at its vicinity. Two possibilities can be thus considered: either the thiocarbonylthio function itself, through a specific Z group, or a side function that would be directly present on the terminal

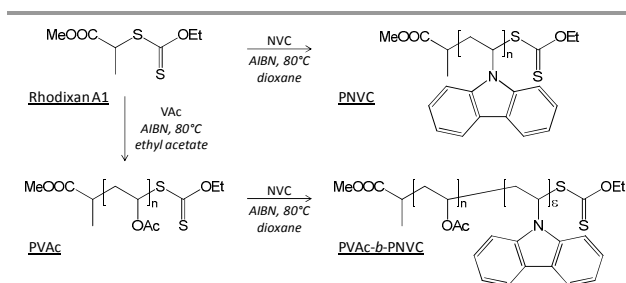
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monomer unit. Both of them are worth being investigated from a fundamental point of view. The first one would imply chain-transfer agents (CTA) exhibiting significantly improved photodissociation efficiency compared to usual CTAs. To this regard, thiocarbonylthio compounds with a *N*-carbazole Z group could be especially adapted, since it was demonstrated that such compounds are both excellent photoinitiators¹⁰ and CTAs.¹¹ However, such compounds would imply necessarily their preliminary custom synthesis, which inevitably restricts the relevance of this approach regarding our scope. On the contrary, simple synthetic schemes based on usual monomers and CTAs, being either commercially or industrially available, can be imagined in the framework of the second approach, which seems therefore more promisingly applicable.

In this contribution, we used "Rhodixan A1" (Scheme 1), namely methyl 2-[(ethoxycarbonothioyl)sulfanyl]propanoate, which is a xanthate developed industrially by Rhodia, now Solvay, as a classical RAFT agent especially suitable for vinyl esters and monomers of similar reactivity.¹² An efficient photodissociation of chain-end functions in the derived polymers synthesized by RAFT can be expected, since xanthates were already well-known photoinitiators. However, this reactivity needs to be exacerbated in order to develop products being competitive macrophotoinitiators. We decided therefore to focus on polymers with a strongly absorbing chromophore on the terminal unit and resulting directly from the structure of the polymerized monomer. Taking into account the necessary compatibility of this monomer with the xanthate regarding the control of its polymerization by RAFT, *N*-vinylcarbazole (NVC) appeared as an excellent choice. This monomer combines indeed the features needed to validate the concept. First of all, the carbazole chromophore will induce an intense light absorption in the near UV range, expected to result in an easier dissociation of the C-S bond under irradiation. Then, the control of the polymerization of NVC by RAFT can be efficiently achieved using xanthates,¹³ although an even better control was obtained recently using trithiocarbonates.¹⁴ Finally, NVC is commercially available.



Scheme 1. Structures of the (co)polymers synthesized by RAFT and studied in this contribution.

Experimental section

Materials

Vinyl acetate (VAc; Sigma-Aldrich; $\geq 99\%$), ethyl acetate (Carlo Erba; 99.8 %) and dioxane (Sigma-Aldrich; 99.5 %), were distilled under reduced pressure over CaH_2 prior to use. Azobisisobutyronitrile (AIBN; Sigma-Aldrich; 98 %) was recrystallized twice from methanol prior to use. *N*-vinylcarbazole (NVC; Sigma-Aldrich; 98 %), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO; Alfa-Aesar; 98 %) and diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$; Alfa-Aesar; 98 %) were used as received. Methyl 2-[(ethoxycarbonothioyl)sulfanyl]propanoate ("Rhodixan A1"; Xa) was provided by Rhodia and used as received. Trimethylolpropane triacrylate (TMPTA) and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EPOX) were provided by Allnex and used as received.

Synthesis of PVAc

18.5 mg of AIBN (0.5 eq.), 47.0 mg of Xa (2.26×10^{-1} mmol, 1 eq.), 971.1 mg of VAc (50 eq.) and ethyl acetate (5.00 mL) were added in this order into a dried Schlenk flask. The solution was thoroughly deoxygenated by five freeze-pump-thaw cycles. The flask was filled with nitrogen gas and placed in an oil bath maintained at 80 °C for 24 h under magnetic stirring. Solvent was then evaporated under vacuum and the conversion α of vinyl functions was determined by gravimetry during this step: $\alpha = 97.3\%$. The polymer was then dissolved in a small volume of THF, precipitated in a large excess of cyclohexane and dried under reduced pressure. Characterization by SEC: $M_n = 4.28 \cdot 10^3$ g/mol; $M_w/M_n = 1.15$.

Synthesis of PNVC

3.4 mg of AIBN (0.2 eq.), 21.5 mg of Xa (1.03×10^{-1} mmol, 1 eq.), 999.1 mg of NVC (50 eq.) and dioxane (2.00 mL) were added in this order into a dried Schlenk flask. The solution was thoroughly deoxygenated by three freeze-pump-thaw cycles. The flask was filled with nitrogen gas and placed in an oil bath maintained at 80 °C for 24 h under magnetic stirring. Solvent was then evaporated under vacuum and the conversion α of vinyl functions was determined using the UV detector at 360 nm, by comparing the respective areas of the peaks corresponding to the polymer and to the residual monomer: $\alpha = 96.4\%$. Characterization by SEC: $M_n = 5.16 \cdot 10^3$ g/mol; $M_w/M_n = 1.25$.

Synthesis of PVAc-*b*-PNVC

4.2 mg of AIBN (0.5 eq.), 466.6 mg of PVAc (2.26×10^{-1} mmol, 1 eq.), 99.9 mg of NVC (5 eq.) and dioxane (1.00 mL) were added in this order into a dried Schlenk flask. The solution was thoroughly deoxygenated by four freeze-pump-thaw cycles. The flask was filled with nitrogen gas and placed in an oil bath maintained at 80 °C for 24 h under magnetic stirring.

As expected, the respective reactivities of VAc and NVC implied that only a fraction of the PVAc underwent a chain-extension. This is visible on the SEC chromatogram, with a bimodal distribution of polymer products (ESI). It was possible to separate efficiently the chain-extended product from residual PVAc and monomer by two successive selective

precipitations: the product was dissolved in a small volume of THF and precipitated in a large excess of ethanol; PVAc-*b*-PNVC is insoluble in ethanol, contrary to PVAc and PNVC. Characterization by SEC (the UV detector at 360 nm was used additionally to confirm the length of the PNVC block): $M_n = 6.40 \cdot 10^3$ g/mol; $M_w/M_n = 1.33$. The length of the second block ($DP_n \approx 11$), higher than the targeted value (5) is consistent with the important fraction of PVAc homopolymer after the chain-extension experiment.

Photodissociation experiments

Solutions at $5.0 \cdot 10^{-4}$ mol/L in toluene containing 3 equivalents of TEMPO were prepared for each polymer. Each solution was transferred in an ESR tube in which it was deoxygenated by nitrogen bubbling during 30 min. For each tube, ESR spectra were recorded after predetermined irradiation durations using a Xe-Hg LC5 Hamamatsu lamp ($100 \text{ mW} \cdot \text{cm}^{-2}$).

Photopolymerization of TMPTA

A formulation containing 10 mg of PNVC in 1 g of TMPTA was prepared before being deposited (thickness: 35 μm) on a BaF_2 pellet in laminate conditions (the formulation is sandwiched between two polypropylene films). The conversion of the acrylate functions (band at 1630 cm^{-1}) occurring during the irradiation of the film was followed by real time Fourier Transform InfraRed spectroscopy (JASCO FTIR 4100 spectrometer). The light source was a Xe-Hg lamp (Hamamatsu LC8; $100 \text{ mW} \cdot \text{cm}^{-2}$). As a comparison, the same experiment was performed using a formulation in which the PNVC was replaced by the same quantity of PVAc.

Photopolymerization of EPOX

A formulation containing 10 mg of PNVC and 10 mg of $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in 1 g of EPOX was prepared. The procedure was the same as for TMPTA, except that the photopolymerization was performed in air with the formulation being directly deposited (thickness: 35 μm) on the BaF_2 pellet. The conversion of the epoxide functions was monitored following the evolution of the band at 790 cm^{-1} . As a comparison, the same experiment was performed using a formulation without PNVC.

Characterizations

Size Exclusion Chromatography (SEC): Accurate molecular weights were determined by SEC in THF. Solutions of samples with precise concentrations around 5.00 mg/mL were prepared and filtered (PTFE membrane; 0.20 μm) before injection. The flow rate was 1.0 mL/min (35°C). The following Agilent 1260 Infinity series setup was used: a G1310B isocratic pump; a G1322A degasser; a G1329B auto-sampler; a G1316A thermostated column compartment equipped with set of Polymer Laboratories ResiPore columns (nominal particle size: 3 μm ; porosity: 2 μm) composed of a guard column (50 $\times$ 7.5 mm) and two columns (300 $\times$ 7.5 mm); a G1314B variable wavelength detector; a G7800A multidetector suite equipped with a MDS refractive index detector and a MDS viscosimeter

detector. Universal calibration was performed using a set of EasiVial polystyrene PS-M standards. Agilent GPC/SEC software and multi-detector upgrade were used to determine molar masses values and distributions.

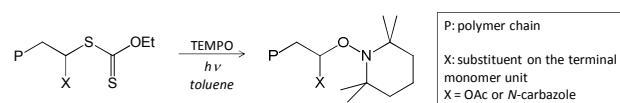
Nuclear Magnetic Resonance (NMR): ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solution at 300 MHz on a Varian Mercury spectrometer.

Electron Spin Resonance (ESR): ESR spin trap experiments were carried out using an X-Band spectrometer (Bruker EMX-plus).

Results and discussion

Photodissociation

In the case of a poly(*N*-vinylcarbazole) (PNVC) synthesized by RAFT, the carbazole chromophore will be bound directly to the C atom of the C-S dissociable bond. This effect of the nature of the terminal unit was first of all investigated by comparing the photodissociation efficiency of the xanthate chain-ends observed for a PNVC ($DP_n = 26$; $M_w/M_n = 1.25$) with the one observed for a poly(vinyl acetate) (PVAc) ($DP_n = 47$; $M_w/M_n = 1.15$) synthesized using the same CTA (Scheme 1). For this purpose, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was used as a spin-trap (Scheme 2). Two solutions in toluene, one of each polymer, were prepared at the same concentration ($C = 5.0 \cdot 10^{-4}$ mol/L) with 3 equivalents of TEMPO. The solutions were transferred in electron spin resonance (ESR) tubes and preliminary deoxygenated by nitrogen bubbling. For both of them, the photodissociation of xanthate chain-ends under UV irradiation (Xe-Hg lamp, $100 \text{ mW}/\text{cm}^2$), evidenced by the consumption of TEMPO, was directly followed *in situ* by ESR. A dramatic effect of the carbazole chromophore was observed, with a dissociation of xanthate chain-ends being 20 times faster in the case of PNVC, compared to PVAc (Figure 1). This result confirms that the well-known but relatively moderate photoinitiator behavior of xanthates can be greatly enhanced thanks to the introduction of a chromophore group at its vicinity. In both cases, we noticed that two molar equivalents of TEMPO were consumed when the ESR spectra reached their minimal intensities, indicating a complete photodissociation of the chain-ends. This is ascribable to the reactivity of the second radical which results from the photodissociation. A previous study by laser flash photolysis revealed indeed that the addition to TEMPO of this xanthate-derived sulfur-based radical is very fast.¹⁰



Scheme 2. Effect of the nature of the terminal monomer unit on the photodissociation efficiency of the xanthate terminal function using TEMPO as a spin-trap.

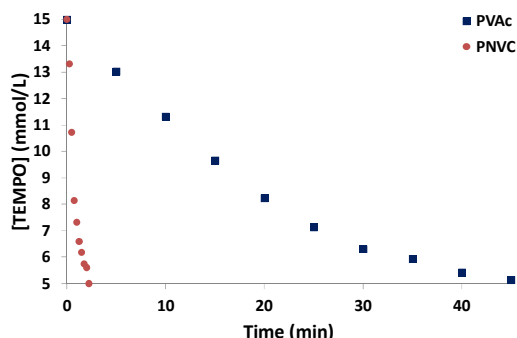


Figure 1. Effect of UV irradiation on the consumption of TEMPO in a deoxygenated solutions in toluene of TEMPO ($1.5 \cdot 10^{-3}$ mol/L) and: PVAc ($5.0 \cdot 10^{-4}$ mol/L; squares) or PNVC (5.0 mmol/L; dots).

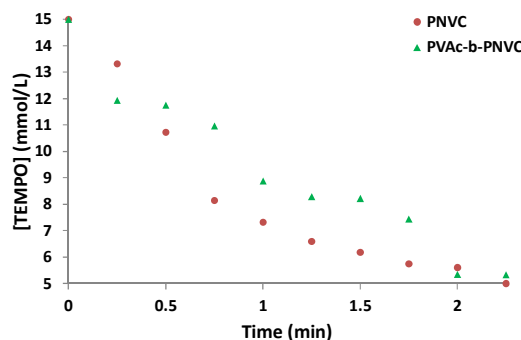


Figure 2. Effect of UV irradiation on the consumption of TEMPO in deoxygenated solutions in toluene of TEMPO ($1.5 \cdot 10^{-3}$ mol/L) and: PNVC ($5.0 \cdot 10^{-4}$ mol/L; dots) or PVAc-*b*-PNVC ($5.0 \cdot 10^{-4}$ mol/L; triangles).

PNVC was chosen here as a simple proof of concept compound. Of course, other chromophores or thiocarbonylthio end groups could be investigated in the same way. Besides, the chromophore is needed on the terminal monomer unit only. The efficiency of the photodissociation of chain-end functions is expected indeed to be enhanced in any RAFT polymer through the introduction of a terminal monomer unit bearing an appropriate chromophore. However, the modification of RAFT polymers with a single supplementary peculiar monomer unit could be very tricky and could result in a substantial fraction of unmodified polymers. The introduction of a short sequence consisting in a few supplementary monomer units, inspired from the strategies classically applied for the synthesis of block or gradient copolymers, appears far more realistic and adaptable.

In this view, the PVAc described previously was extended with a short oligo(NVC) block ($DP_n = 11$). It can be precised here that block copolymers based on VAc and NVC are preferably obtained when the PNVC block is synthesized first, since VAc is less activated than NVC.^{11d} In our case, the final sequence wanted imposed the order of polymerization and thus a significant proportion of residual PVAc precursor. However, the chain-extended product can be efficiently separated by selective precipitation. The kinetic monitoring of the photodissociation of xanthate chain-ends by ESR was then performed in the same conditions. Compared to the PVAc precursor, the impact of a terminal NVC unit is obvious, leading to a faster photodissociation efficiency being similar to the one observed for PNVC (Figure 2).

Of course, this chain-extension approach remains a simple proof of concept, since it implies supplementary synthetic and purification steps, prone to limit its interest from an industrial point of view. To this regard, very similar products could be obtained more simply if NVC was directly added during the xanthate-mediated RAFT polymerization of VAc, once VAc conversion would be almost complete. In this case, NVC would be preferably consumed thanks to the respective reactivity ratios of VAc and NVC.¹⁵ This would favor the formation of a second block composed predominantly of NVC and thus ensure the formation of copolymers with a NVC terminal unit as the major products, provided that the content of residual VAc would be kept negligible compared to the one of NVC.

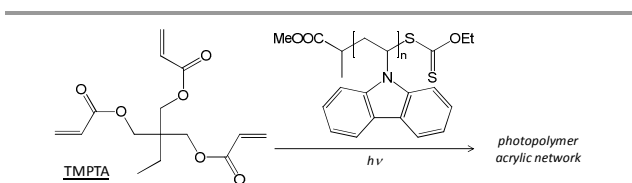
Photoinitiated radical crosslinking polymerization

After having demonstrated the high photodissociation efficiency of RAFT polymers terminated by a NVC-xanthate group, we studied the possibility to valorize such compounds as macrophotoinitiators. Their potential industrial development implies easily applicable processes. In this view, we focused on simple formulations classically implemented for the preparation of photopolymer coatings.

In a first experiment, the PNVC described previously was introduced (1 wt%) as a macrophotoinitiator in trimethylolpropane triacrylate (TMPTA) as a multifunctional acrylic monomer (Scheme 3). The formulation was irradiated (Xe-Hg lamp, 100 mW/cm^2) in laminated film conditions ($\sim 35 \mu\text{m}$ between 2 polypropylene films) without any particular precaution. The conversion was followed in situ by FT-IR (Figure 3). A very fast polymerization was observed, evidencing a very efficient photoinitiation process. More than 50% of the acrylate functions were converted in a few minutes, which is quite typical of the conversions usually observed for similar photopolymerizations.^{16,17} It is worth precising that this means a far higher monomer conversion, since TMPTA is a trifunctional monomer.

A comparative experiment was also performed, in which the PNVC was replaced by the aforementioned PVAc at the same molar fraction (Figure 3). A faster polymerization was observed when PNVC was used, in agreement with the faster

photodissociation evidenced previously and thus with a possible faster initiation. However, it can be noticed that the difference, though important, is not as marked as the one observed in the spin-trap experiment. This observation could be ascribable to differences in terms of diffusion for the macroradicals which are generated. Contrary to the photodissociation experiment, performed in solution, photopolymerization are performed in bulk for the photopolymerizations, meaning a viscous medium that is rapidly crosslinked. Therefore, a faster photodissociation could be partially counterbalanced by a slower diffusion. To this regard, PNVC and PVAc oligomers ($DP \approx 10$) as macrophotoinitiators were also compared with Xa as a photoinitiator used at the same molar concentration in TMPTA (ESI). The polymerization rate using Xa was really faster than the one relative to PVAc, but only slightly slower than the one observed with PNVC. This is in agreement with the possible balance described above between the photodissociation efficiency of the photoinitiator and the diffusion rate of the propagating species. Therefore, the modification of the nature of the terminal unit in order to favor the photodissociation of the chain-end could mitigate a decrease of photoinitiation efficiency due to a higher molecular weight. This can permit to combine the advantages of macrophotoinitiators, such as their low extractability, while maintaining or even enhancing the photoinitiation efficiency.



Scheme 3. Photoinitiated radical crosslinking polymerization of TMPTA using PNVC as a macrophotoinitiator.

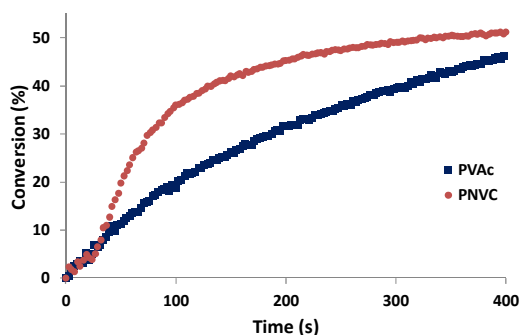
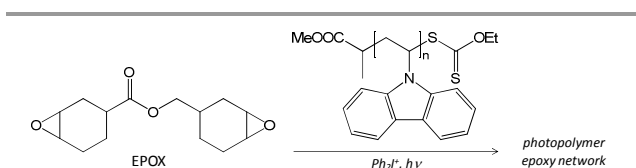


Figure 3. Conversion of acrylate functions followed by *in situ* FT-IR during the photoinitiated radical polymerization of TMPTA using PNVC (1 wt%) as a macrophotoinitiator (dots). In the comparative experiment (squares), PNVC is replaced by PVAc at the same molar fraction.

Photoinitiated radical promoted cationic crosslinking polymerization

Beyond their interest as macrophotoinitiators for free radical polymerization, these polymers terminated by a NVC-xanthate group can present an additional especially interesting feature, as suggested by two previous studies. In the case of the free radical polymerization of NVC, it was indeed demonstrated that the propagating radical can be easily oxidized into a carbocationic active center, enabling the initiation of the ring-opening cationic polymerization of cyclohexene oxide.¹⁸ Diphenyliodonium hexafluorophosphate (Ph_2I^+) was used as the oxidative species. In fact, this study comes within the scope of so-called radical promoted cationic polymerization, as a more general methodology enabling to switch from a radical propagation mechanism to a cationic one, for instance for the synthesis of original diblock copolymers.¹⁹ More recently, it was demonstrated that NVC can be used directly as an additive in order to convert hardly oxidable radicals into radicals based on a NVC unit, which can be then easily oxidized using Ph_2I^+ , enabling the initiation of a cationic polymerization.²⁰ The crosslinking ring-opening cationic polymerization of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EPOX) as a difunctional epoxide monomer was successfully promoted by radicals generated by usual photoinitiators. In this view, the possible additional behavior of NVC-xanthate terminated polymers as macrophotoinitiators for radical promoted cationic polymerization in the presence of Ph_2I^+ was also investigated. A formulation containing EPOX, the PNVC described previously (1 wt%) and Ph_2I^+ (1 wt%) was irradiated using the same lamp (thickness: 35 μm ; Scheme 4). The *in situ* monitoring of the reaction by FTIR evidenced here also a very fast polymerization, thanks to the combination of the efficient photodissociation of the chain-end function with the easy oxidation of the radical on the NVC terminal unit (Figure 4). No conversion was measured when the formulation contained the iodonium salt only. Both for TMPTA and EPOX, it was also possible to initiate the photopolymerization using LED lamps (ESI).



Scheme 4. Photoinitiated radical promoted cationic crosslinking polymerization of EPOX using PNVC as a macrophotoinitiator.

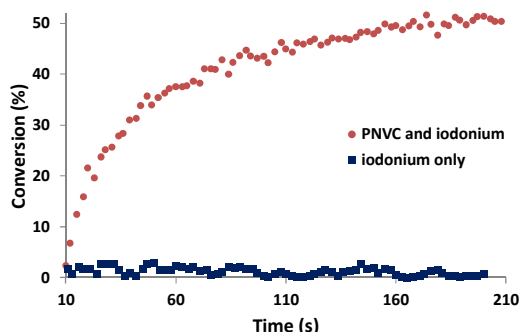


Figure 4. Conversion of epoxide functions followed by *in situ* FT-IR during the photoinitiated radical promoted cationic polymerization of EPOX using PNVC (1 wt%) as a macrophotoinitiator (dots) in the presence of the iodonium salt $\text{Ph}_2\text{I}^+\text{PF}_6^-$ (1 wt%). A comparative experiment (squares) was performed without PNVC.

Conclusions and perspectives

In conclusion, the well-known sensitivity to light of thiocarbonylthio chain-end functions in polymers synthesized by RAFT, often considered as a drawback from an industrial point of view, can be turned as an advantage. This reactivity can be indeed greatly enhanced when a chromophore is purposely introduced on the terminal unit as demonstrated in the present study using NVC and a xanthate. Such products can be thus considered as very efficient macrophotoinitiators. Moreover, the carbazole chromophore on the terminal monomer unit enables the easy subsequent oxidation of the radical active center resulting from the photodissociation. This makes these macrophotoinitiators especially versatile, allowing the initiation both of radical and radical promoted cationic polymerizations.

Regarding current industrial issues, the major advantage of macrophotoinitiators over photoinitiators of low molecular weight consists of their very limited extractability. However, a similar efficiency implies a similar molar content and thus a higher weight content in the case of macrophotoinitiators. This could have an impact on the final properties of the photopolymer film but we believe that this effect can be turned as an advantage. In the framework of the approach presented in this contribution, the RAFT mechanism becomes a synthetic platform for the design of tailor-made macrophotoinitiators. Therefore, their precisely controlled structure can be seen as a means to tune the final properties of the films, such as their thermal, mechanical or optical properties.

Beyond the purpose of this contribution, more directed towards potential applications, RAFT polymers especially designed so as to enhance the photodissociation efficiency of the chain-end functions appear very promising. This can be achieved by introducing a chromophore, such as the carbazole group, either on the terminal monomer unit or as the Z group in the thiocarbonylthio function. Both of them are worth being deeply investigated regarding the new synthetic methodologies that they can offer, such as the synthesis of

block copolymers that would combine RAFT and photoinitiated radical promoted cationic polymerization.

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