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N-Vinylcarbazole: An Additive for Free Radical Promoted Cationic Polymerization upon Visible Light

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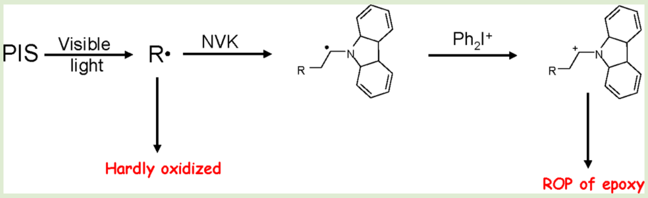
Supporting Information

ABSTRACT: *N*-Vinylcarbazole is proposed as an additive for epoxy ring-opening polymerization ROP upon visible light exposure. This compound can convert hardly oxidizable radicals to carbon centered radicals by an addition process onto the *N*-vinylcarbazole double bond. The generated radicals can be further easily oxidized by an iodonium salt thereby leading to efficient initiating cations for the ROP of epoxides. Different visible light photoinitiating systems have been investigated: Type I photoinitiators (derived from phosphine oxides) and dye/iodonium salt couples. The underlying chemical mechanisms are investigated by electron spin resonance (ESR) experiments.



Cationic photoinitiators for ring-opening polymerization (ROP), such as, for example, onium salts, required UV light irradiation. Typically, UV-C and UV-B (or A) lights must be used with iodonium and sulfonium salts, respectively, the respective maximal absorption wavelengths being, for example, 227 and 300 nm for Ph_2I^+ and $Ph\text{-}S\text{-}Ph\text{-}S^+Ph_2$.[1,2] The epoxy ROP under visible lights remains an exciting research topic: indeed, a large amount of the visible light emitted by the conventional lamps is lost and the potential use of visible LEDs or laser beams for different applications (laser imaging, holographic recording, etc.) is ruled out.

Among others, a well-known strategy adopted to develop systems absorbing at long wavelengths is based on the use of various radical sources sensitive to visible lights through an elegant process usually called *free radical promoted cationic polymerization* FRPCP and already achieved for more than two decades (see refs 3−8 and references herein). This approach consists of producing a radical $R^•$ (from a photoinitiating system PIS) that can be easily oxidized by an iodonium salt (e.g., Ph_2I^+). The resulting cation R^+ (reaction 1, Scheme 1) corresponds to the ring-opening polymerization initiating structure. However, the nature of the primary radicals produced from the PIS is crucial for getting a high polymerization efficiency as they should be characterized by excellent oxidation properties; moreover, the resulting cations must be efficient structures for the ROP reaction.[9] Even if a lot of systems have been developed in the last years,[9,10] the search for novel additives being able to improve the FRPCP process still appears as a challenge.

In the present paper, *N*-vinylcarbazole (NVK) is used as an additive for FRPCP of an epoxide upon visible light exposure (EPOX, Scheme 2) under air. Different visible light-sensitive PISs have been investigated (Scheme 2): (i) Type I photoinitiators (phosphine oxides TPO and BAPO) generating benzoyl and phosphinoyl radicals[1,2,11] and (ii) dye/Ph_2I^+ couples generating phenyl radicals (where the dye is acridine orange (AO) and Eosin Y (Eo), Scheme 2).[1] The EPOX ring-opening polymerization efficiency is evaluated, and the underlying chemical mechanisms are investigated by ESR experiments.

Phosphine Oxide/NVK/Ph_2I^+ Initiating Systems: Using the phosphine oxide/Ph_2I^+ systems, the EPOX polymerization under halogen lamp irradiation under air is not efficient, that is, final conversions ~10% with BAPO/Ph_2I^+ (Figure 1, curve 2) and <5% with TPO/Ph_2I^+ (Figure 2, curve 1). Interestingly, the addition of NVK strongly improves the polymerization profiles, that is, both the polymerization rates and the final conversions are higher in the presence of NVK (for BAPO: see Figure 1, curve 3 vs curve 2; for TPO: see Figure 2A, curve 3 vs curve 1). An increase in the NVK content leads to an increase of the polymerization initiating ability of the three-component system (Figure 2A, curve 3 vs curve 2). BAPO is better than TPO in these three-component initiating systems in line with the better visible light absorption properties of this compound (Figure 2 in SI).

No polymerization occurs with the NVK/Ph_2I^+ system in the same irradiation conditions (Figure 1, curve 1), that is, the phosphine oxide (TPO or BAPO) is required, as expected, for an efficient process as NVK and Ph_2I^+ only absorb in the UV range (Figure 2 in SI).

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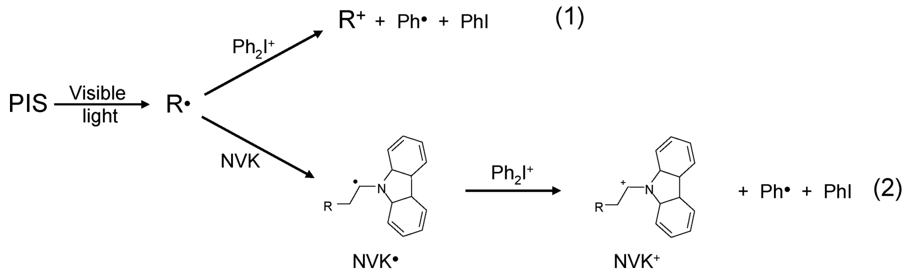
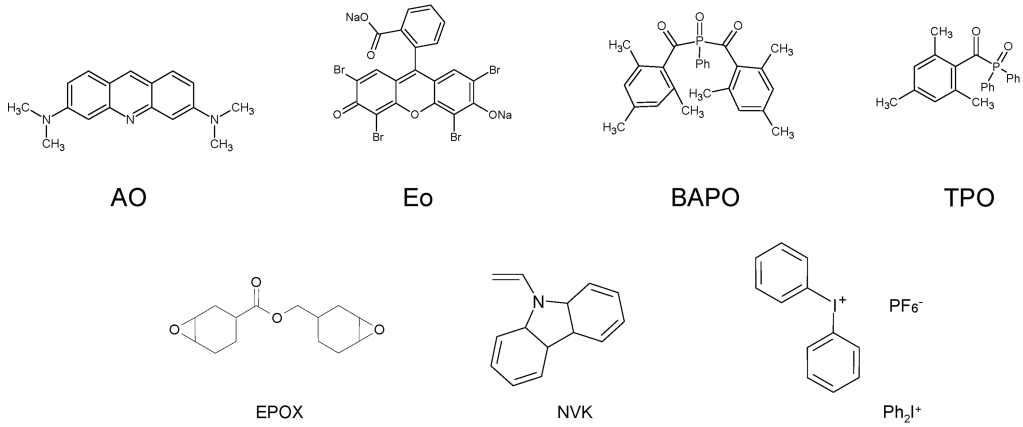
Scheme 1



Scheme 2



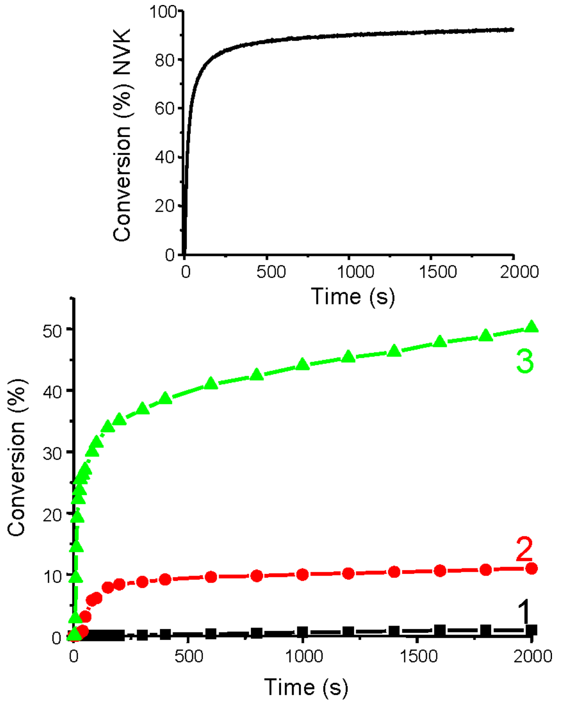


Figure 1. Polymerization profiles of EPOX using different photoinitiating systems: (1) NVK/Ph$_2$I$^+$ (3%/ 2% w/w); (2) BAPO/Ph$_2$I$^+$ (1%/ 2% w/w); (3) BAPO/NVK/Ph$_2$I$^+$ (1%/3%/2% w/w); under air, halogen lamp irradiation. Inset: consumption of the vinyl function of NVK in the BAPO/NVK/Ph$_2$I$^+$ photoinitiating system as continuously followed by real time FTIR spectroscopy at 1640 cm^{-1}.

Interestingly, when using the BAPO (or TPO)/NVK/Ph$_2$I$^+$ initiating system, a complete consumption of the vinyl function of NVK is observed during the EPOX polymerization (inset of Figure 1, this consumption is easily followed from the associated FTIR band at 1640 cm^{-1}). This is consistent with an addition of the Ph$_2$P(=O)$^•$ radical to the NVK double bond and the formation of NVK$^•$ radicals (reaction 2, Scheme 1) that are easily oxidized by an iodonium salt, thereby leading to NVK$^+$.[13,14] NVK$^•$ is characterized by a very low ionization potential (Table 1); this is fully consistent with the associated fast oxidation process. On the opposite, the Ph$_2$P(=O)$^•$ can hardly be oxidized by iodonium salt ($k_{ox} < 1.0 \times 10^6$ M^{-1} s^{-1}[19a]), in agreement with a higher ionization potential (6.6 eV, Table 1). The NVK$^+$ cation being a highly efficient initiating structure for the ROP of an epoxy,[3a,13−15] it is not surprising that an efficient polymerization is found in the presence of NVK. Therefore, the NVK additive effect is based on a conversion of hardly oxidizable radical generated from the excited PIS into easily oxidizable NVK$^•$, that is, in Table 1, the different benzoyl or phosphinoyl derived radicals generated from BAPO or TPO are characterized by higher ionization potentials than NVK$^•$. This process leads to an efficiency increase of PIS/NVK compared to PIS alone.

This conversion reaction is well supported by ESR experiments. Upon irradiation of a TPO solution with the halogen lamp in ESR-spin trapping experiments, the nitroxide corresponding to the addition of Ph$_2$P(=O)$^•$ onto PBN is observed with hyperfine coupling (*hfc*) constants $a_N \sim 14.2$ G; $a_H \sim 2.9$ G; $a_P = 19.2$ G (Figure 3A) in full agreement with known data.[16] In the presence of NVK, a new PBN radical adduct ($a_N \sim 14.2$ G; $a_H \sim 1.8$ G) corresponding to the addition of NVK$^•$ to PBN is detected as a result of the Ph$_2$P(=O)$^•$ addition to NVK (Figure 3B). For αN-radical like NVK$^•$, a very high oxidation rate constant by iodonium salt is expected, that is, for aminoalkyl radicals derived from aliphatic or aromatic amines, almost diffusion rate constants were measured.[9a] For benzoyl (generated for TPO and BAPO

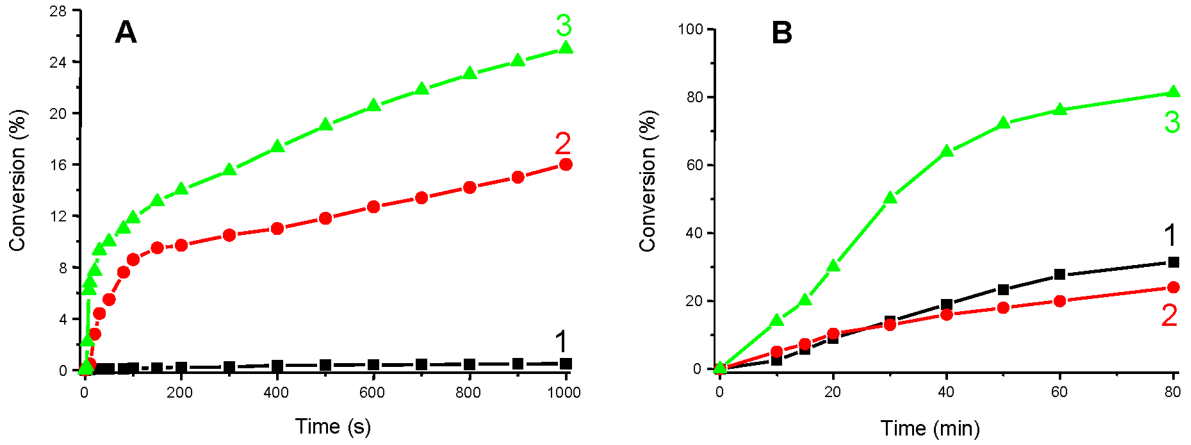
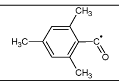
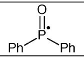
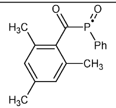
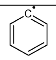
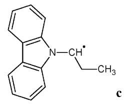


Figure 2. Polymerization profiles of EPOX using different photoinitiating systems: (A) (1) TPO/Ph_2I^+ (1%/2% w/w); (2) TPO/NVK/Ph_2I^+ (1%/1%/2% w/w); (3) TPO/NVK/Ph_2I^+ (1%/3%/2% w/w), under air, halogen lamp irradiation; (B) (1) NVK/Ph_2I^+ (3%/2% w/w); (2) BAPO/Ph_2I^+ (1%/2% w/w); (3) BAPO/NVK/Ph_2I^+ (1%/3%/2% w/w), under air, sunlight irradiation, Mulhouse April 2012.

Table 1. Ionization Potentials for the Different Investigated Radicals[a,b]

	Ionization Potential (eV)
	5.7
	6.6
	6.5
	8.3
 [c]	4.7

[a] The adiabatic ionization potentials (IP) were calculated at UB3LYP/6-31+G* level from the optimized radical and ion. This procedure was presented in ref 9a. [b] The electron affinity of Ph_2I^+ can hardly be calculated i.e. it is well-known that the associated reduced form is dissociative [1−2]. [c] A model NVK$^•$ with R = methyl in Scheme 1.

from C−P cleavage) or MesC(=O)-PPh(=O)$^•$ (generated from BAPO) radicals, a similar conversion process to NVK$^•$ can be expected.

Remarkably, the BAPO/NVK/Ph_2I^+ combination is also a very efficient initiating system under very soft irradiation conditions (e.g., sunlight): a final conversion >80% is obtained after 80 mn of sunlight irradiation. In these conditions, a low polymerization is observed with NVK/Ph_2I^+, that is, the small portion of UV light is absorbed by NVK which results in a photosensitization of the iodonium salt decomposition.[13]

Dye/NVK/Ph_2I^+ Initiating Systems: AO and Eo are characterized by strong absorption bands at 425 and 527 nm, respectively. The EPOX polymerization in the presence of the AO/Ph_2I^+ and Eo/Ph_2I^+ photoinitiating systems upon a halogen lamp irradiation under air are not efficient i.e. final conversions ~20% for AO (Figure 4A, curve 1) and <5% for Eo (Figure 4B, curve 1). The polymerization rates and the final conversions are better in the presence of NVK (Figures 4A and B, curve 2 vs curve 1). These dye/NVK/Ph_2I^+ initiating systems are also effective for diode laser irradiation (Figure 3 in SI).

A plausible mechanism is the following. As known,[1,2] a Ph$^•$ radical is generated in the *Dye/Ph_2I^+ interaction (reaction 3). These latter radicals can hardly be oxidized by an iodonium salt

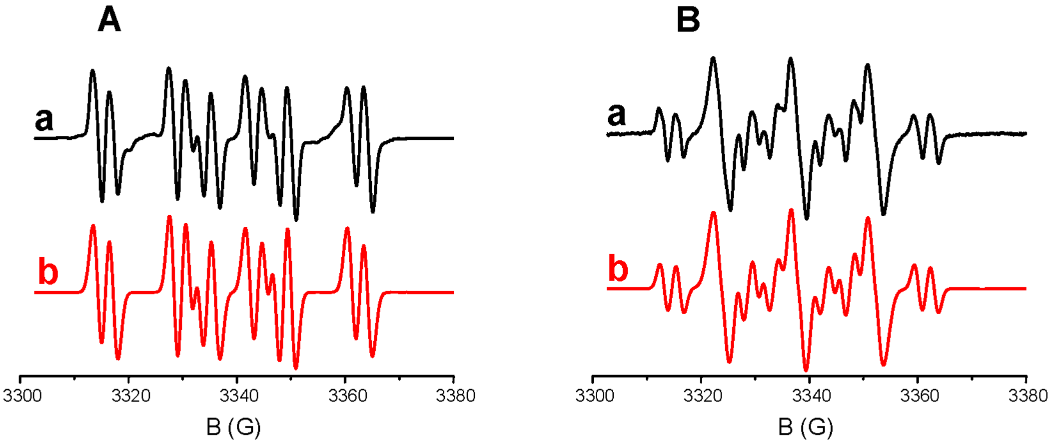


Figure 3. ESR-ST spectra obtained upon irradiation (halogen lamp) of (A) TPO and (B) TPO/NVK solutions: (a) experimental and (b) simulated ESR spectra. For (B), both phosphinoyls and NVK$^•$ are trapped (see text). PBN as a spin trap agent. In *tert*-butyl-benzene.

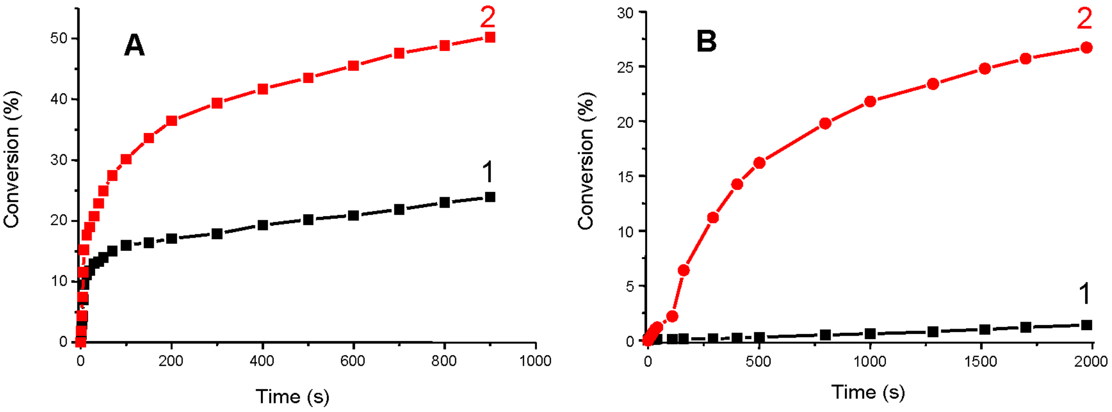


Figure 4. Polymerization profiles of EPOX using different photoinitiating systems: (A) (1) AO/Ph_2I^+ (0.1%/2% w/w); (2) AO/NVK/Ph_2I^+ (0.1%/3%/2% w/w), under air, halogen lamp irradiation; (B) (1) Eo/Ph_2I^+ (0.1%/2% w/w); (2) Eo/NVK/Ph_2I^+ (0.1%/3%/2% w/w), under air, halogen lamp.

(in Table 1, the ionization potential of $Ph^•$ is very high), that is, in these systems, $Dye^{•+}$ is assumed to be the initiating structure for the ROP of epoxy.[1,2] In the presence of NVK, the $Ph^•$ addition to NVK can be expected in agreement with the high consumption of the vinyl function of NVK in these systems during the EPOX polymerization. This is consistent with the formation of the easily oxidizable $NVK^•$ radicals (see Scheme 1, with $R^•$ = $Ph^•$) leading to a strong increase of the polymerization initiating ability.

$$\mathrm{Dye} \rightarrow {}^*\mathrm{Dye}(h\nu)$$

$$ {}^*\mathrm{Dye} + \mathrm{Ph_2I^+} \rightarrow \mathrm{Dye^{•+}} + \mathrm{Ph^•} + \mathrm{PhI} \qquad (3)$$

In the present paper, a conversion of hardly oxidizable radicals into more easily oxidizable αN-radicals by an addition process onto NVK is presented. This approach can be used to increase the polymerization initiating ability of different visible light sensitive systems. Excellent conversion versus time polymerization profiles are obtained even under sunlight irradiation. This approach could be used for applications in optics to increase the photosensitivity of cationic resins. Indeed, the development of cationic formulations can be highly useful in laser imaging or holographic recording applications to reduce the detrimental shrinkage observed with acrylate resins.

■ EXPERIMENTAL SECTION

Chemical Compounds: Acridine orange (AO), Eosin-Y (Eo), phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPO), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), diphenyl iodonium hexafluorophosphate (Ph_2I^+), and *N*-vinylcarbazole (NVK) were obtained from Aldrich and used with a purity >99%. (3,4-Epoxycyclohexane)-methyl 3,4-epoxycyclohexylcarboxylate (EPOX from Cytec; Uvacure 1500) was selected as a representative epoxy monomer (Scheme 2). Photopolymerization Procedures: For the epoxy ring-opening polymerization, the investigated photoinitiating systems are based on PIS/Ph_2I^+ or PIS/NVK/Ph_2I^+ with weight contents of 3 and 2% for NVK and iodonium salt, respectively. For PIS = (TPO or BAPO) and dye (AO or Eo), weight contents of 1 and 0.1% were used, respectively.

The EPOX films (25 μm thick) deposited on a BaF_2 pellet were irradiated under air inside the IR spectrometer cavity. The evolution of the epoxy content is continuously followed by real time FTIR spectroscopy (FTIR 4100, JASCO) at 790 cm^{-1}.[12] A halogen lamp [I = 8 mW/cm^2 for λ > 400 nm at the sample position (determined with a spectrometer for absolute irradiance measurement, Ocean optic); the emission spectrum is given in Figure 1 in Supporting Information (SI)] or sunlight (clear sky) was used for the irradiation of the films. ESR Experiments: ESR spin-trapping (ESR-ST) experiments were carried out using an X-Band EMX-plus spectrometer (Bruker Biospin). The radicals were produced at RT under a halogen lamp irradiation and trapped by phenyl-*N*-*t*-butylnitrone (PBN) according to a procedure described in detail in ref 12.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Emission spectrum of the halogen lamp; absorption spectra of BAPO; TPO and NVK in acetonitrile; polymerization profiles of EPOX using different photoinitiating systems, diode laser irradiation 457 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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