

Article Type (Communication.)

Visible Light Induced Cationic Polymerization of Epoxides by Using Multi-walled Carbon Nanotubes

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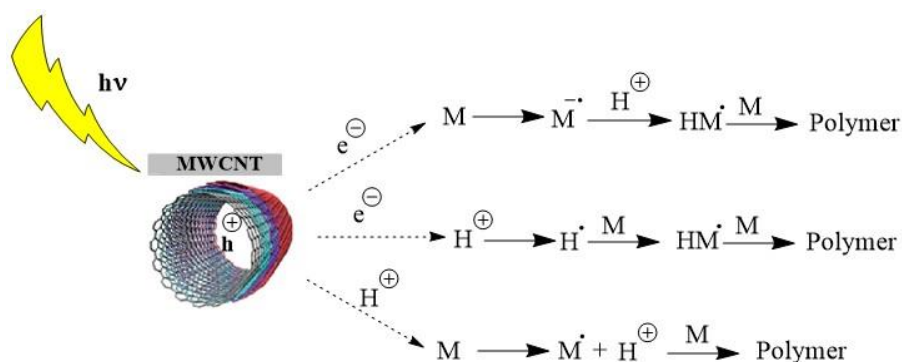
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Visible light induced cationic polymerization of epoxides can be achieved by means of MWCNTs that act as visible light photoinitiator via a radical induced cationic photopolymerization process. When MWCNTs are irradiated with longer wavelengths (above 400 nm), they generate carbon-radicals by hydrogen abstraction from the epoxy monomer; these radicals are oxidized, in the presence of an iodonium salt, to carbocation reactive enough to start the cationic ring-opening polymerization of epoxy monomer. These mechanisms have been supported by EPR analysis



1. Introduction

Photoinitiated polymerization processes continue to attract interest due to their potential applications in coatings, adhesives, inks, printing plates, optical wave-guides, and microelectronics^[1]. By applying a large variety of photoinitiating systems and combination of different monomers, various complex polymer architectures such as block and graft copolymers² and hyperbranched polymers^[3,4] can be prepared. Quite recently, new photochemical methodologies to obtain polymers with controlled molecular weight, structure and functionality have been developed^[5,6]. Photopolymerizations can be initiated by various ways, such as radical, cationic or even anionic processes. Many photoinitiating system acting at UV, visible^[7] and even near IR region^[8-12] have been developed. Because of the fact that UV wavelength requires higher energy and can cause skin and eye damages^[13], there is tremendous interest to extend photoactivation of polymerizations into the visible range. Although photoinitiated free radical polymerization is in more advanced state, much effort has been made to develop visible light photoinitiating for the cationic mode as well, since many industrially important monomers such as epoxides and vinyl ethers can only be polymerized by a cationic mechanism which is insensitive to oxygen inhibition.

General strategies to conduct cationic polymerization at the visible range involve oxidation^[14] of free radicals by onium salts (also called as free radical promoted cationic polymerization), formation of charge transfer complexes^[15], and electron transfer reaction^[16] within the exciplexes of polynuclear aromatic compounds and onium salts. Lallevee and coworkers have also shown that various dyes^[17], silanes^[18], and polythiophenes^[19] were efficiently induce reduction of onium salts even at visible range.

Carbon nanotubes, discovered by Iijima^[20] are nano-objects characterized by peculiar electronic properties as a function of their structure^[21]. In particular, the change in chirality can transform the CNTs into a semiconductor with a large gap electronic properties^[22]. The nature as a semiconductor could be exploit in photochemistry in order to produce an

electronic hole pair or an exciton during the irradiation of multi-walled carbon nanotube (MWCNT).

It has already been reported in literature that ultra-small semiconductor particles^[23] as well as magnetite nanoparticles^[24] are able to generate radicals upon photoexcitation which can start radical polymerization of vinyl monomers. In a more recent paper, we have reported the use of CNTs as radical generators upon UV-irradiation. The high efficiency of the photoinitiating system was evidenced^[25] by very fast acrylic double bond conversion achieved even in the presence of the carbon filler. The initiation mechanism is based on the reactions of electrons and holes generated in conduction (cb) and valance (vb), respectively in analogy to the general behaviour of CNTs. The overall mechanism is presented in **Scheme 1A**. Both electrons and holes can participate in the generation of initiating radicals. Conceptually similar visible light photoinitiated radical polymerization based on the generation of electrons and holes by using mesoporous carbon nitride was also described.

As cationic polymerizations can successfully initiated by the redox process involving photochemically generated radicals and iodonium salts^[26], it seemed appropriate to trigger cationic polymerization epoxy by using MWCTs.

Herein, we describe a novel methodology for cationic polymerization of epoxides through visible light generated electrons and holes from MWCTs followed by electron transfer reactions with iodonium salt. The proposed mechanism has been evaluated and confirmed by EPR analysis. The crosslinked film were characterized by thermo-mechanical properties.

2. Experimental Section

2.1 Materials

The monomer (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate) (EEC, Aldrich) p(octyloxyphenyl)phenyliodonium hexafluoroantimonate (**PI**, ABCR). The

multiwall carbon nanotubes (MWCNT's) NC 7000, were purchased by Nanocyl S.A. and employed without further purification.

2.2 Samples preparation

The CNT's filler were dispersed in the ratio between 0.05 to 0.3 wt% in the epoxy resin and mixed with a high-shear homogenizer (Ultra-Turrax, IKA) at 30000 rpm for 5 minutes. After mixing, the iodonium salt photo-initiator agent were added at 3 wt.% in each formulation. The different formulations were coated by a wire-wound applicator (film thickness 100 μm) on a polypropylene substrate. The films were cured with a visible lamp (Hamamatsu LC8 with visible bulb and a cut-off filter below 400 nm equipped with 8mm light guide) under nitrogen.

2.3 Characterization

The photopolymerization process was followed by measuring the epoxy group conversion by FTIR spectroscopy during irradiation, employing a Thermo-Nicolet 5700 instrument. The total epoxy conversion was calculated by monitoring the decrease in the absorbance of the epoxy group between 780-820 cm^{-1} . The formulations were coated on SiC (film thickness 25 μm) and FTIR spectra were collected before and after irradiation. The films were cured with a visible lamp (Hamamatsu LC8 with visible bulb and a cut-off filter below 400 nm equipped with 8mm light guide).

Electron Paramagnetic Resonance (EPR) analysis²⁷ were performed at room temperature on a Bruker ESR 300E spectrophotometer in the presence of the spin-trap DMPO (5,5-dimethyl-1-pyrroline-N-oxide). MWCNT's were irradiated 60 min with visible light, then 17 mM DMPO was added. The reaction mixture was irradiated again for 2 min and the EPR spectrum was recorded immediately after the end of irradiation. Measurements were carried out in quartz capillary tubes and the following parameters were used: microwave frequency 9.78 GHz,

power 5 mW, modulation frequency 100 kHz, modulation amplitude 0.4 Gauss, time constant 40 ms. Simulated spectra were obtained by means of the WinSim software²⁸.

DMTA on the photocured samples was performed on a MK III Rheometrics Scientific Instrument at 4 Hz frequency in the tensile configuration with 5 K/min. The storage modulus, E' , and the loss factor, $\tan \delta$, were measured from room temperature up to the temperature at which the rubbery state was attained. The T_g value was assumed as the maximum of the loss factor curve ($\tan \delta$).

3. Results and Discussion

In this work, we have investigated the efficiency of MWCNT's to act as visible light photoinitiator for cationic photopolymerization of an epoxy monomer, namely 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (EEC) through a radical induced cationic polymerization mechanism. Because of the two epoxy groups, this monomer in suitable conditions can readily crosslinks and ultimately forms networks.

The epoxy formulation containing MWCNT at 0.05, 0.1 and 0.3 wt% were added with 3 wt% of iodonium salt as cationic oxidant and irradiated with visible light at above 400 nm; at this irradiation wavelength the iodonium salt is transparent. Upon irradiation, the formulations containing the CNT, however, rapidly cross-linked and formed solid tack-free film confirming promoting effect of MWCNT.

Conversion during irradiation was evaluated by FT-IR analysis, following the broad peak at $815\text{-}780\text{ cm}^{-1}$ belonging to epoxy group, which decreased after 30 min of irradiation with an overall conversion of 75% of epoxy group. The lowered conversions attained high concentration of MWCNT (**Table 1**) may be due to the screening effect or favored coupling of the radicals thus formed.

In the process, the radicals formed upon irradiation of MWCNT can abstract hydrogen from the epoxy ring of the monomer to generate oxidizable radicals as demonstrated by Crivello^[29].

These electron donating radicals can readily be oxidized by iodonium salts to generate corresponding cationic species capable of further propagating to essentially yield networks due to the bifunctional nature of the monomer (**Scheme 1B**).

In order to gain more insight into the mechanism, EPR studies were conducted (EPR spectra reported in **Figure 1**). Thus, a water suspension of MWCNT's irradiated with visible-light in the presence of DMPO, led both to the formation of typical DMPO-OH radical species, previously observed by Wu et al.^[30] after UV irradiation of MWCNT's, and the C-centred radical characterized^[31] by a six-line pattern with $a_N = 15.7$ Gs and $a_H = 23.2$ Gs.

The effect of the amount of MWCNT on the thermomechanical properties was also investigated by DMTA. As can be seen from **Figure 2**, as the content of the MWCNT is increased, a significant decrease of T_g with a shift of the maximum of $\tan\delta$ curves towards lower temperature. This observation arising from the lower crosslink density, in complete agreement with FT-IR analysis (wide ante).

4. Conclusions

We have demonstrated the ability of MWCNT to act as visible light photoinitiator via a radical induced cationic photopolymerization of epoxy monomers. We have shown that when MWCNT's are irradiated with longer wavelengths (above 400 nm), they generate carbon-radicals by hydrogen abstraction from the epoxy monomer; these radicals are oxidized, in the presence of an iodonium salt, to carbocation reactive enough to start the cationic ring-opening polymerization of epoxy monomer. These mechanism has been supported by EPR analysis and it was shown that by increasing the MWCNT's content there is a possible shielding effect which induced a decrease of epoxy group conversion with a consequent decrease of crosslinking density and T_g of the cured films

Acknowledgements

This research was supported in part by a Marie Skłodowska-Curie Research and Innovation Staff Exchange (RISE) Fellowship (Mat4Treat, proposal no. 645551) within the H2020- MSCARISE-2014 European Community Call.

Received: Month XX, XXXX; Revised: Month XX, XXXX; Published online:

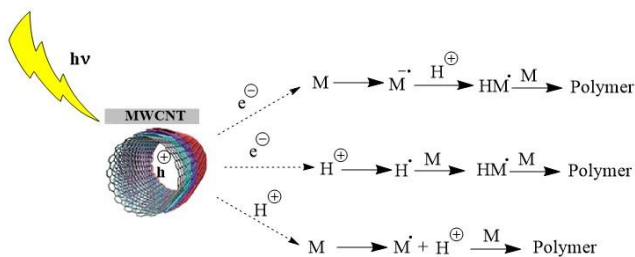
((For PPP, use “Accepted: Month XX, XXXX” instead of “Published online”)); DOI: 10.1002/marc.((insert number)) ((or ppap., mabi., macp., mame., mren., mats.))

Keywords: visible light cationic photopolymerization, MWCNTs, epoxy monomer

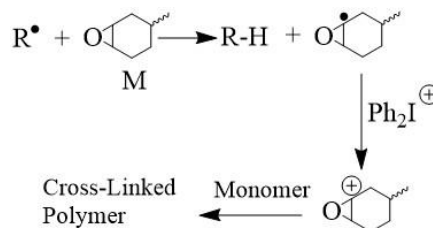
1. Y. Yagci, S. Jockusch, N.J. Turro, *Macromolecules*, **2010**, 43(15), 6245-6260.
2. Y. Yagci, W. Schnabel, *Prog. Polym. Sci.*, **1990**:15(4):551-601.
3. C. Aydogan, M. Ciftci, V. Kumbaraci, N. Talinli, Y. Yagci Y., *Macromol. Chem. Phys.*, **2017**, 218, 1700045.
4. C. Aydogan, G. Yilmaz, Y. Yagci, *Macromolecules*, **2017**, 50, 9115–9120.
5. S. Dadashi-Silab, M.A. Tasdelen, Y. Yagci, *J. Polym. Sci. Part A: Polym. Chem.*, **2014**, 52(20), 2878-2888.
6. N. Corrigan, J. Xu, C.A. Boyer, *Macromolecules*, **2016**, 49 (9), 3274–3285.
7. J.P. Fouassier, X. Allonas, D. Burget, *Prog. Organ. Coat.*, **2003**, 47, 16–36.
8. J. Shao, Y. Huang, Q. Fan, *Polym. Chem.*, **2014**, 5, 4195-4210.
9. B. Strehmel, T. Bromme, C. Schmitz, K. Reiner, S. Ernst, D. Keil, *Polym. Sci.* **2015**, 213–249.
10. T. Karatsu, M. Yanai, S. Yagai, J. Mizukami, T. Urano, A. Kitamura, *J. Photochem. Photob. A.*, **2005**, 170(2), 123–129.

11. C. Schmitz, A. Halbhuber, D. Keil, B. Strehmel, *Prog. Org. Coat.*, **2016**, 100,32–46.
12. A. Kocaarslan, S. Tabanlı, G. Eryurek, Y. Yagci, *Angew. Chem. Int. Ed.*, **2017**, 56, 14507-14510.
13. H. Moseley, *Phys. Med. Biol.* **1994**, 39(11), 1765-1770.
14. F.A.M. Abdulrasoul, A. Ledwith, Y. Yagci, *Polymer*, **1978**, 19(10), 1219-1222.
15. G. Hizal, Y. Yagci, W. Schnabel, *Polymer*, **1994**, 35(11), 2428-2431.
16. D. Dossow, Q.Q. Zhu, G. Hizal, Y. Yagci, W. Schnabel, **1996**, 37(13):2821-2826.
17. J. Lalevee, F. Dumur, M.A. Tehfe, A. Zein-Fakih, D. Gigmes, F. Morlet-Savary, B. Graff, J.P. Fouassier, *Polymer* **2012**, 53 (22), 4947–4954.
18. J. Lalevee, N. Blanchard, M. Tehfe, J.P. Fouassier, *Macromol. Rapid Commun.* **2014**, 32 (11), 838–843.
19. J. Zhang, M. Frigoli, F. Dumur, P. Xiao, L. Ronchi, B. Graff, F. Morlet-Savary, J.P. Fouassier, D. Gigmes, J. Lalevee, *Macromolecules*, **2014**, 47 (9), 2811–2819.
20. S. Iijima, *Nature*, **1991**, 354, 56-68.
21. S.C. Tjong, *Mat. Sci. Eng.*, **2006**, R53, 73-85.
22. M. Knupfer, *Surf. Sci. Rep.*, **2001**, 42, 1-9.
23. A.J. Hoffman, H. Yee, G. Mills, M.R. Hoffmann, *J. Phys. Chem.*, **1992**, 96, 5540-5553
24. M. Sangermano, L. Vescovo, N. Pepino, A. Chiolerio, P. Allia, P. Tiberto, M. Coisson, L. Suber, G. Marchigiani, *Macromol. Chem. Phys.*, **2010**, 211, 2530-2537.
25. M. Sangermano, F. Marino, M. Reuel, M.S. Strano, *Macromol. Chem. Phys.*, **2011**, 212, 1469-1473.
26. A. Mariani, S. Bidali, S. Fiori, M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, 42, 2066-2075.
27. L.F. Velasco, V. Maurino, E. Laurenti, C. Ania, *Applied Catalysis A: General*, **2013**, 453, 310-318.

28. D.R. Duling, *J. Magn. Res. Series B*, **1994**, 104, 105-109.
29. J.V. Crivello, *J. Polym. Sci., Part A: Polym. Chem.*, **1999**; 37, 4241-4253.
30. B. Wu, , D. Zhu, S. Zhang, , W. Lin, , G. Wu, , B. Pan, *J. Coll. Int. Sci.* **2015**, 439, 98-107.
31. I. Roppolo, A. Chiappone, S. Porro, M. Castellino, E. Laurenti, *New J. Chem.*, **2015**, 39, 2966-2973.



(Scheme 1A)



(Scheme 1B)

Scheme 1A: Visible Light Initiated Radical Polymerization by Using MWCNTs. **Scheme 1B:** Oxidation of the radicals formed by visible light irradiation of MWCNT followed hydrogen abstraction

Table 1. The Effect of MWCNT Concentration on the Visible Light Initiated Cationic Polymerization of EEC at $\lambda > 400$ nm.

MWCNT (wt%)	Oct-Ph ₂ I ⁺ PF ₆ ⁻ (wt%)	Irradiation Time (min)	Conversion ^a (%)
0.05	3	30	75
0.1	3	30	58
0.3	3	30	50

^aDetermined by IR spectral

Figure 1: EPR spectra of MCWNT's water suspension irradiated in solar simulator in the presence of DMPO (* indicate the lines attributable to the C-centred radical).

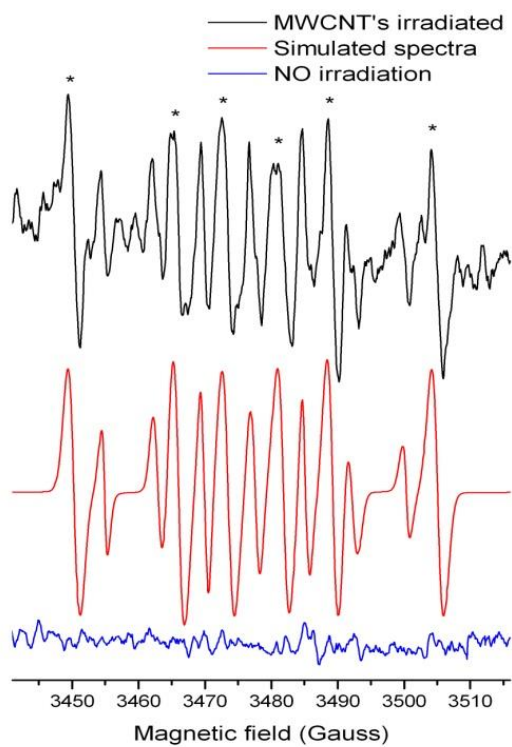
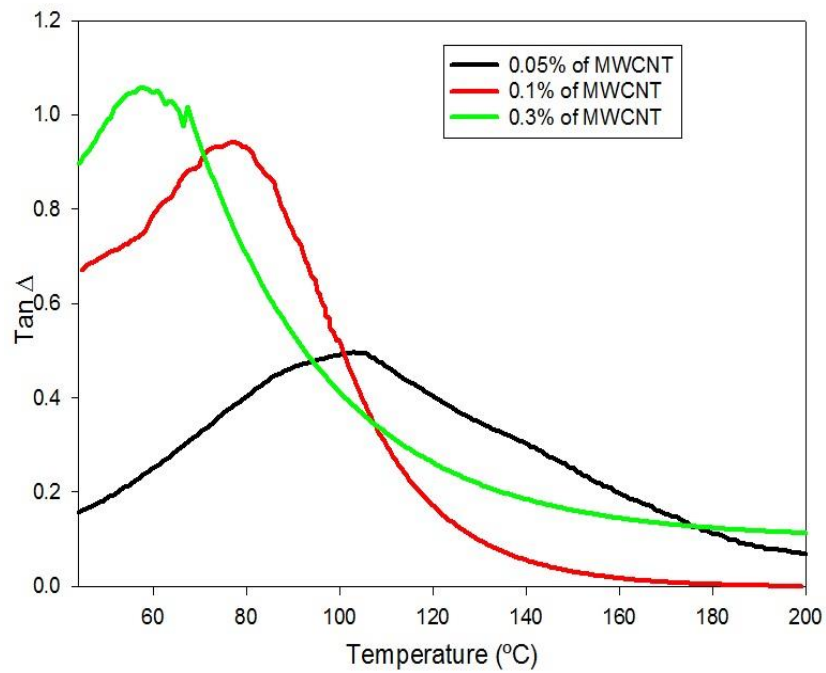


Figure 2: $\text{Tan}\delta$ curves registered by DMTA of the photocrosslinked epoxy films obtained from the formulations containing 0.05, 0.1 and 0.3 wt% of MWCNT's and 3 wt% of iodonium salt photoinitiator. The formulations were irradiated with visible light with a lamp with a cut-off at 400 nm.



Visible light induced cationic polymerization of epoxides can be achieved by means of MWCNTs via a radical induced cationic photopolymerization of epoxy monomers. The mechanism has been supported by EPR analysis and the crosslinked films fully characterized.

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