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UV-ACTIVATED FRONTAL POLYMERIZATION OF GLASS FIBRE REINFORCED EPOXY COMPOSITES

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ABSTRACT:

In this paper we report, for the very first time, the possibility to UV-crosslink a glass fibre reinforced epoxy composites. We have demonstrated that the crosslinking reaction proceeds via a radical induced cationic frontal polymerization (RICFP), where the UV-surface activation of cationic ring opening polymerization is able to promote the heat front that will activate a thermal initiator in the deeper layers. Because of the very high velocity of the reaction we could obtain quickly epoxy composites maintaining the good thermo-mechanical properties.

Keywords: Photopolymerization, UV-light, epoxy, Glass Fibre Reinforced Polymers (GFRPs) composites.

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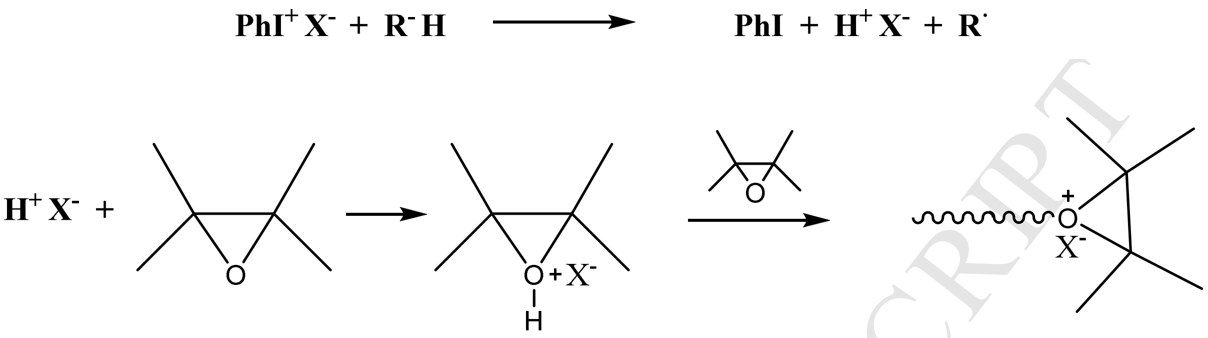
1. Introduction

Epoxy resins are by far the most used material in composites, applied in different field varying from sport, automotive, marine and aviation industry [1-3]. Usually epoxy-glass fibre composites are produced by thermal polymerization in the presence of amine or anhydride as a hardener.

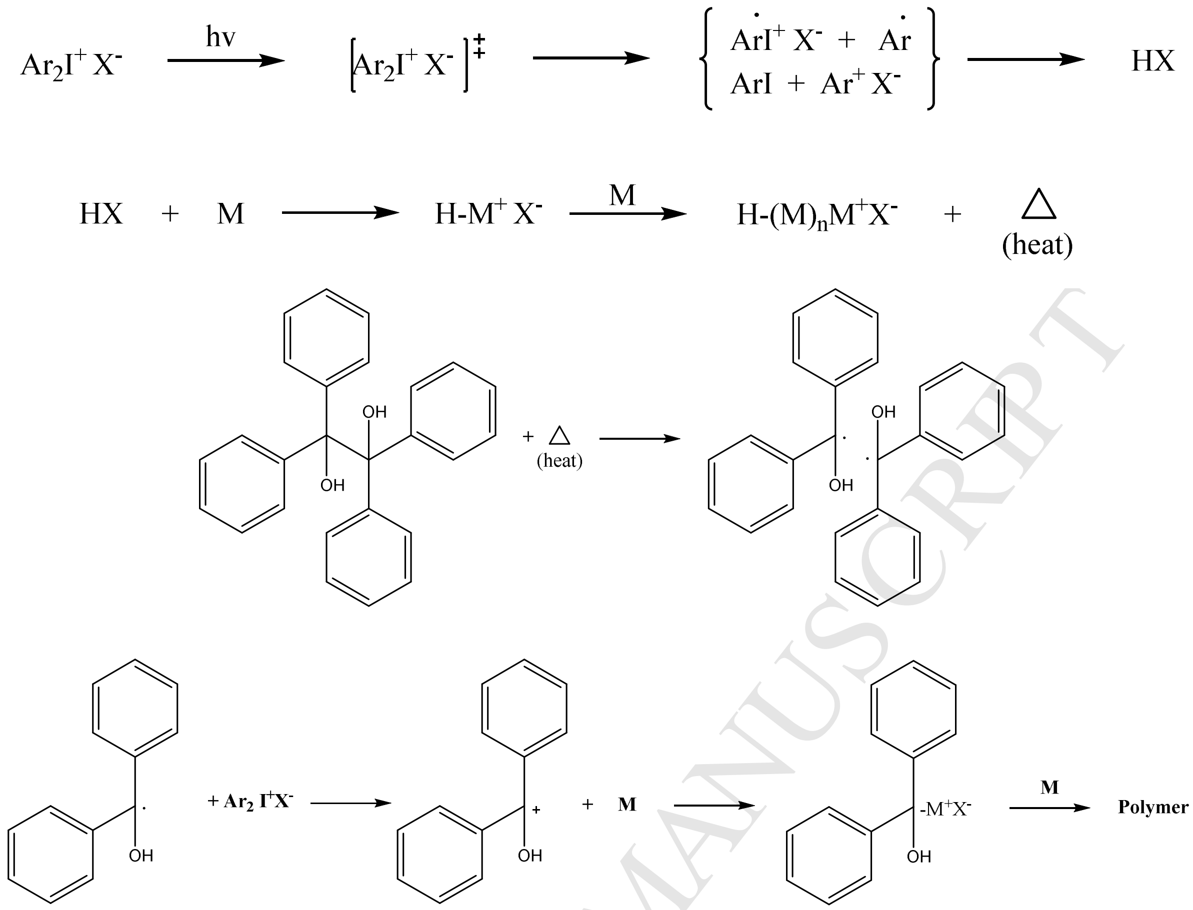
It is very well known that photo-induced polymerization can be used to activate epoxy curing in the presence of a suitable cationic photoinitiator [4-6], as an interesting alternative to thermal curing. The UV-activation is particularly attractive since the crosslinkable formulations are solvent free, the production rates are high and the energy required is much less than thermal curing [7]. Typically onium salts, either triarylsulfonium or diaryliodonium salts, are considered as photo-acid generator under UV-irradiation. The strong photo-acid generated is able to promote cationic ring-opening polymerization of an epoxy resin (reaction reported in Scheme 1).



Scheme 1: representation of diaryliodonium salt activation under UV-light and epoxy ring opening polymerization

Nevertheless, the photoinduced epoxy chain-growth polymerization is limited to a thin epoxy layer film (100-200 µm) because of a low penetration depth of UV-light. Furthermore, the presence of fillers or fibres could hinder the light penetration to deeper layers. For this reason, UV-Curing was never reported to be used for glass-fibres epoxy composites fabrication.

In recent years different authors reported the feasibility to activate the polymerization of thicker layer of epoxy resin [8-11].This was possible thanks to the Radical Induced Cationic Frontal Polymerization (RICFP). Frontal Polymerization (FP) can be activated by the dissociation of a radical thermal initiator promoted by the heat released by the surface UV-activated cationic ring opening polymerization. Subsequently, the carbon-centered radical can be oxidized by the diaryliodonium salts forming a reactive carbocation which is able to start the cationic ring-opening polymerization (see Scheme 2).



Scheme 2: representation of diarylonium salt activation under UV-light and following radical induced cationic frontal polymerization

In a more recent paper we have demonstrated the success of epoxy composites fabrication starting from an epoxy formulation containing SiO_2 particle which was crosslinked via RICFP [11]. A bisphenol-A-diglycidyl ether was used as crosslinkable resin and the influence of filler content on frontal propagation was examined. The presence of SiO_2 particles influenced the generation of a stable front with a retarding propagation which was attributed to the low thermal conductivity of this filler. Although propagation was decelerated in the presence of silica, stable front was observed and successful UV-induced RICFP was achieved.

Taking these data into consideration, we tried to use RICFP for the crosslinking of epoxy-glass fibres composites. The FP can be exploited if the amount of dissipated heat is not too high, then a sufficient heat is available to induce epoxy curing close to the hot zone. As a result the formation of a hot polymerization front would be able to crosslink the epoxy-glass fibres composites.

In this paper we report for the first time, the UV-induced polymerization of an epoxy-glass fibres composite. The epoxy formulation contained a diaryliodonium hexafluoroantimonate salt, as photoacid generator, and tetraphenylendiol (benzopinacol) as thermal initiator. Hand-made GFRPs composites containing 2 glass-fibres layers deposited at 90° were prepared and photocrosslinked via RICFP. The properties of the crosslinked composite were compared with the same composite thermally cured.

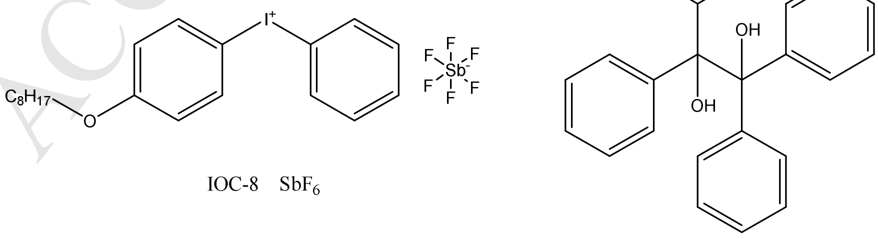
2. Materials and Methods

2.1 Materials

The epoxy resin and **Ampreg26** amine hardener was obtained by Gurit Switzerland. The epoxy resin consists of a blend of bisphenol A (50-100%), bisphenol F (25-50%) and 1,6 Hexanedioldiglycidylether (2.5-10%)) while the hardener is a blend of amines (polyoxyalkyleneamine (25-50%), 2,2'-dimethyl-4,4'methylenebis(cyclohexylamine) (10-25%), 4,4'-methylenebis(cyclohexylamine) (10-25%) and 2,2'iminodiethylamine (2.5-10%)).

The thermal initiator 1,1,2,2-tetraphenyl-1,2-ethandiol (**TPED)** was obtained from Alfa Aesar, the cationic photoinitiator (p-octyloxyphenyl)phenyliodonium hexafluoroantimonate (**PAG**) from ABCR. The E-CR glass fibres were obtained by Advantex. In Figure 1 the chemical structures of the initiators are reported.

Figure 1: Chemical formula of the initiators: **PAG** (p-(octyloxyphenyl)-phenyliodonium hexafluoroantimonate), (tetraphenylethandiol, **TPED**)



IOC-8 SbF$_6$

TPED

2.2 Glass Fibre Reinforced Epoxy Composites preparation and characterization

The composites was manufactured using E-CR glass fibres and the neat epoxy resin **Ampreg26** (without amine hardener) containing 1 wt% of TPED as thermal initiator and 2 wt% of the cationic photoinitiator . Two plies of glass fibre were disposed into a silicone mould with orientation of 0° and 90° with a sample dimension of 4.0 x 5,5 cm and with a thickness of 0,5 cm. Each ply was 0.9 g and 20 g of total epoxy formulation was added. The epoxy formulation was impregnated with the aid of vacuum for 5 hours. After impregnation the corner of the mould was irradiated with a UV-lamp, Lightning Cure^{TM} LC8, Hamamatsu, equipped with an optical fibre for 10 seconds, to activate the thermal front which allowed the completeness of polymerization in less than a minute.

As comparison, the same epoxy resin was added with the Ampreg26 amine hardener (epoxy/hardener ratio 100:33) and thermally cured at 80 °C for 5 hours.

The crosslinked GFRPs were characterized by Dynamic Mechanical Analysis (DMA) (Tryton Technology) and the morphology investigated by FESEM analysis on the surface fracture of the samples. Zwick z750 Load cell ID:0 WN:820133 50 kN machine was used to carry on the tensile test. Samples were disposed in the middle of holding grips with gauge length of 50 mm. Test speed was 2 mm/min with a maximum force of 450 N. The set up was performance following the ASTM D3039.

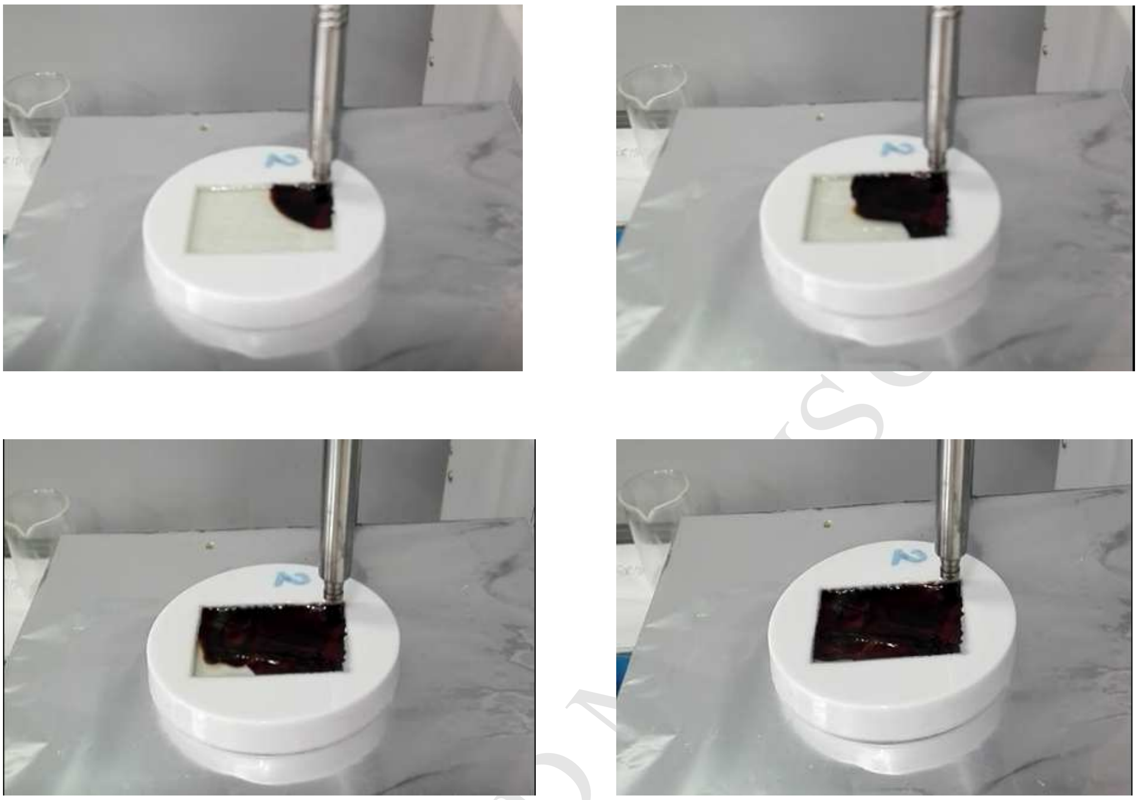
3. Results and discussion

The aim of this study was the achievement of epoxy-glass fibres crosslinking toward UV-irradiation, by RICFP process. The mechanism of polymerization has been explained in the introduction part and already demonstrated in our previous papers [8-11].

At the very beginning, we investigated the proper photoinitiator/thermal initiator ratio to obtain a self-sustaining heat front. It was possible to observe thermal front propagation in the presence of 1 wt% of TPED and 2 wt% of the cationic photoinitiator. In Figure 2 the pictures, extracted by a movie registered during the polymerization, are reported for the epoxy samples prepared with two plies of glass fibres disposed with orientation of 0° and 90°. The lamp was turn-on for 10 seconds. The heat front was propagating towards the entire composite very clearly and quickly. A fully crosslinked composite was obtained in less than a minute.

From the video the front starting time was calculated to be 10 seconds. This is why the mould was irradiated for 10 seconds with light. From the same video we could evaluate a front velocity of about 5 cm/min, so the entire sample contained in the mould was completely crosslinked in less than a minute.

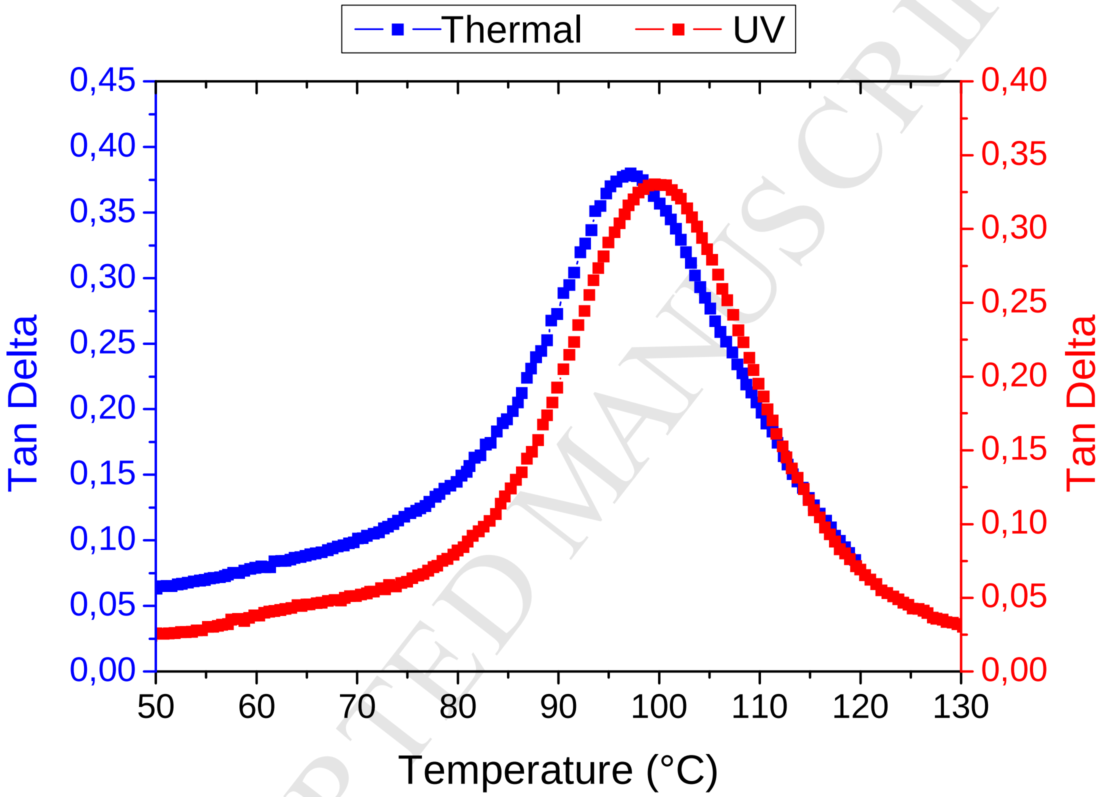
Figure 2: Pictures extracted by a movie registered during the polymerization of epoxy composites prepared with two plies of glass fibre disposed with orientation of 0° and 90°. Lamp turn-on for 10 seconds.



As comparison the Ampreg 26 epoxy resin containing two plies of glass fibre disposed with orientation of 0° and 90°, was thermally crosslinked in the presence of amine as hardner, at 80 °C for 5 hours, as previously reported [12]. The two composites were characterized by DMTA and analysis and tensile-test.

The tanδ curves obtained by DMTA curves are reported in Figure 3, respectively for the composites obtained by RICFP and the composite thermally cured. The composite obtained via UV-irradiation showed a slightly higher Tg, 105 °C, with respect to the thermal crosslinked epoxy composites which showed a Tg around 95 °C. The difference could be assigned to the formation of a different polymeric network. In fact, when the amine is used as a stoichiometric hardener, the flexibility of the epoxy network will be influenced significantly. When the composite is obtained by RICFP, the structure of the polymeric network is purely formed by the repeating epoxy resin unit, since the polymerization reaction occurs via a cationic ring-opening polymerization. Similar results were previously observed and reported in literature [8-10] and attributed both to the different network architecture as well as to a higher epoxy group conversion achieved by RICFP due to higher curing temperature because of the front-heat.

Figure 3: DMTA curves of the epoxy composites obtained by RICFP, after 10 seconds of irradiation and some minutes of frontal propagation (■ UV). Epoxy composites obtained by thermal curing at 80 °C for 5 hours (■ Thermal). The epoxy composites were prepared with two plies of glass fibre disposed with orientation of 0° and 90°.



The stress-strain curves allowed to measure the tensile strength and the modulus of the composites obtained via UV-induced polymerization compared with the same thermally cured. The data, collected in Table 1, showed that the UV-cured samples are characterized by a slightly higher mechanical performance, in accordance with the higher Tg recorded by DMTA.

Morphological investigation was performed on the epoxy composites obtained by RICFP. In Figure 4 the Field Emission Scanning Electron Microscopy (FESEM) images collected on the fracture surface of the crosslinked samples are reported. A strong adhesion of the glass fibres to the polymeric matrix is evident, which shows a good wettability of the glass-fibre surface.

Table 1: properties of the glass Fibres Reinforced Epoxy Composites

obtained by UV or Thermal curing

Sample	**Tg (°C)[1]**	**Tensile Strength (MPa)[2]**	**Tensile Modulus E (GPa)[3]**
UV-Cured	105	367±14	23.5±1.3
Thermally Cured	95	345±23	21.8±2.8

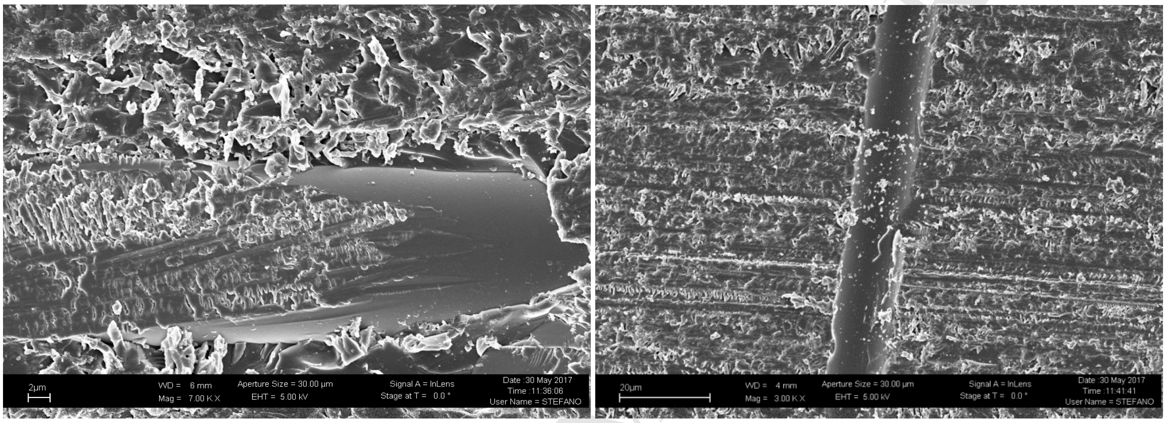


Figure 4: FESEM image of the fracture surface of the epoxy composites UV-cured by RICFP. The epoxy composites were prepared with two plies of glass fibre disposed with orientation of 0° and 90°.

4. Conclusions

In conclusion, for the very first time, here we report the possibility to crosslink a glass fibres epoxy composites by UV-irradiation in a very short time. We have demonstrated that the crosslinking reaction proceeds via a RICFP, where the UV-surface activation of cationic ring-opening epoxy polymerization is able to promote the heat front that will activate a thermal initiator in order to propagate the polymerization toward the thicker layer of the composite. When radicals are generated in the presence of a diaryliodonium salt, they are oxidized to carbocation able to activate a cationic ring-opening polymerization in the deeper layer. The propagation of the reaction is assured by the heat front propagation, in a frontal way. The crosslinked composite obtained by RICFP showed even slightly better properties by comparison with the same composite thermally cured. The important advantage of this crosslinking method is related to the very fast polymerization process compared with thermal curing, which allows to get high productivity maintaining the good thermo-mechanical properties of the epoxy composites.

Therefore, by RICFP of epoxy-glass fibres composites, we can have a high productivity because of the high velocity of curing reaction, maintaining the good thermo-mechanical properties typical for the epoxy composites.

References

1. Sangermano, M. “UV Cured nanostructured epoxy coatings” in “Epoxy polymers” new materials and innovations”, J.P. Pascault and R.J.J. Williams ed, Wiley, Weinheim, 2010.
2. Sangermano, M.; Roppolo, I.; Messori, M. “UV-Cured functional coatings”, in "Photocured Materials", Atul Tiwari ed., RSC, London, 121-133, 2014.
3. Periolatto, M.; Di Francia, E.; Sangermano, M.; Grassini, S.; Russo Spena, P. “Advanced Epoxy-Based Anticorrosion Coatings Containing Graphite Oxide” in L.F.M. da Silva (ed.), Materials Design and Applications, 135-155, 2017.
4. Sangermano M., Razza N., Crivello J.V., Macromol. Mat. Eng. 2014; 299: 775-793.
5. Sangermano M., Pure Appl. Chem. 2012; 84: 2089-2103.
6. Crivello J.V. , J. Polym. Sci. part A Polym. Chem. 2009;47: 866-875.
7. Crivello J. V. , Dietliker, K. "*Photoinitiators for Free Radical, Cationic and Anionic Polymerization*", 2nd ed., Wiley, New York, 1998, pp. 479.
8. Bomze D. , Knaack P. , Liska R., Polym. Chem. 2015; 6(47): 8161-8167.
9. Bomze D. , Knaack P. , Koch T. , Jin H. , Liska R., J. Polym. Sci. Part A: Polym. Chem. 2016; 54(23): 3751-3759.
10. Liska R. , Bomze D. , Kern W. , PCT Int. Appl. (2017), WO 2017035551 A1 20170309.
11. Klikovits N., Liska R., D'Anna A., Sangermano M., Macromo. Chem. Phys., in press.
12. Sangermano M., Tagliaferro A., Foix D., Castellino M., Celasco E., Macromol. Mat. Engin., 2014; 299: 757-763.