Photodecarboxylation in UV-curable Water-borne Coating

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Abstract

The attractive UV-curable water-borne coating, a kink of environment-friendly coating, could be simultaneously improved in water resistance after UV cured with the photodecarboxylation technique. In present research, the inter-molecular photodecarboxylation mechanism between alpha-carboxyl thioether and type II photoinitiator was revealed with GC-MS. Monomethyl thioether (CH_3-S-R) and thioethylene ether (R-S-CH_2CH_2-S-R) were found to be the primary photodecarboxylation products. An acrylated oligomer with alpha-carboxyl thioether was synthesized and formulated into UV-curable water-borne coating, in which ITX was employed as photoinitiator and photodecarboxylation accelerator. With the UV curing of the water-borne coating, the thiomethyl carboxyl group pended on the backbone was cut-off and water-resistance of the cured film was thus improved.

Introdcution

Decarboxylation, a chemical reaction in which a carboxyl group (-COOH) is split off from a compound as carbon dioxide, is attractive in the field of medicine research and has been extensively investigated in traditional organic chemistry, such as photodecarboxylation of ketoprofen and specific amino acids. Photoinduced decarboxylation, namely photodecarboxylation, usually undergoes with UV irradiation and stops if turning off the UV light. The controllability of decarboxylation can be improved greatly in contrast to thermal decarboxylation. In other words, the storage stability of the carboxyl group and its scission efficiency may be perfectly balanced with actinic irradiation[1]. Side reactions may be avoided or relieved. Furthermore, efficiently controlled photodecarboxylation can be potentially applied in many science and technology fields, such as the development of photodegradation of flocculating agent for waste water treatment and pesticide with low residual toxicity. Lots of surfactants can be potentially designed with photodecarboxylation property and may be employed for smart fabrication of micro-/nano-structures and controllable surface conversion from hydrophilicity to hydrophobicity[2]. The potential application of photodecarboxylation could be demonstrated in **Figure 1**.

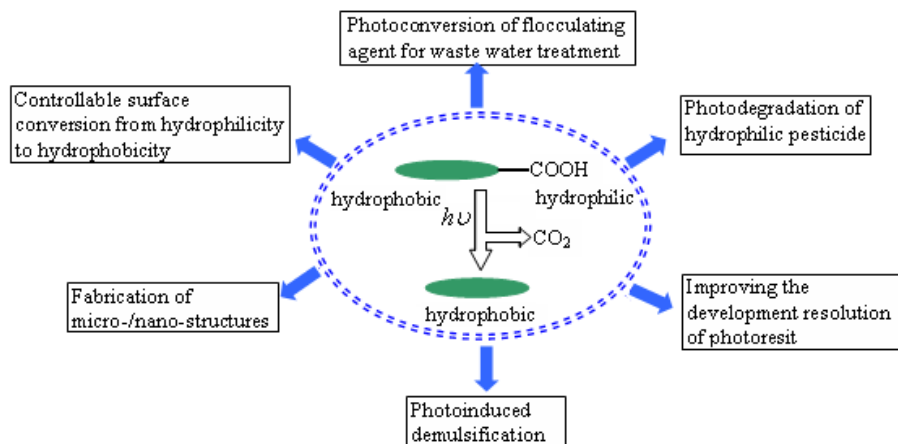* Corresponding to Jianwen Yang, PhD, E-mail: cesyjw@mail.sysu.edu.cn

Figure 1.   Potential application of photodecarboxylation

Photodecarboxylation efficiency is closely dependent on the structure of substrates. Lots of aromatic group connected aliphatic carboxylic acids (Ar-R-COOH) have been found to undergo photodecarboxylation with poor efficiency[3, 4, 5]. The aromatic moieties, acting as chromophores, could absorb UV photons to initiate the decarboxylation intra-molecularly. Thioether and tertiary amine moieties contained in the aromatic aliphatic acids have been found to improve the decarboxylation efficiency[6, 7, 8, 9]. In order to develop the application of photodecarboxylation in functional materials, thioether containing carboxylic acid and chromophore were separated; the mechanism and kinetics for the inter-molecular photodecarboxylation were investigated.

As shown in **Scheme 1**, two aliphatic sulfur-containing carboxyl acids (SCCA) were prepared: methyl 3-(carboxymethylthio) propionate (MCP) $CH_3O-CO-CH_2CH_2SCH_2COOH$ though Michael addition of mercaptoacetic acid and methyl acrylate and Trimethylolpropane mono-3-(carboxymethylthio) propyl ether (TMCPE) $CH_3C(CH_2OH)_2CH_2OCH_2CH_2CH_2SCH_2COOH$ through free radical thermal addition of mercaptoacetic acid and Trimethylolpropane monoallyl ether (TMPME).
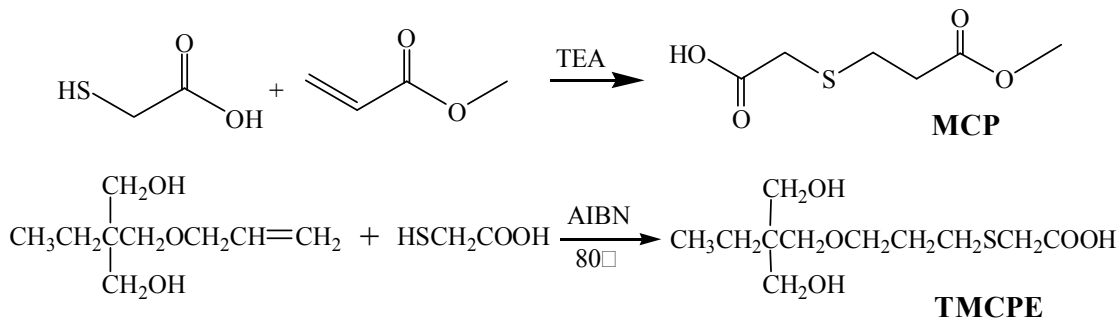
Scheme 1   The synthesis of MCP and TMCPE

After exposed to UV radiation ranging from 320 – 400 nm with the light intensity of 4.2 mW/cm^2, the photoreactions of MCP in the presence of different photoinitiators (2-hydroxy-1-[4-(2-hydroxy-ethoxy)phenyl]-2-methylpropan- 1-one (Darocur 2959), isopropyl

thioxanthone (ITX) and benzophenone (BP)) was measured with ^{1}H NMR, respectively. It was found that the photodecarboxylation of MCP could be efficiently induced by the type II photoinitiator BP and ITX other than the type photoinitiator Darocur 2959. The rate of decarboxylation of MCP with ITX was greater than that with BP. However, the ITX was found to deplete slowly during photodecarboxylation due to the possible dismutation of ketyl radical/anion and regeneration of ITX (**Figure 2**). It was implied that the photoinduced electron transfer (PET) from carboxylmethyl thioether to aromatic ketones was indispensable to the intermolecular photodecarboxylation.
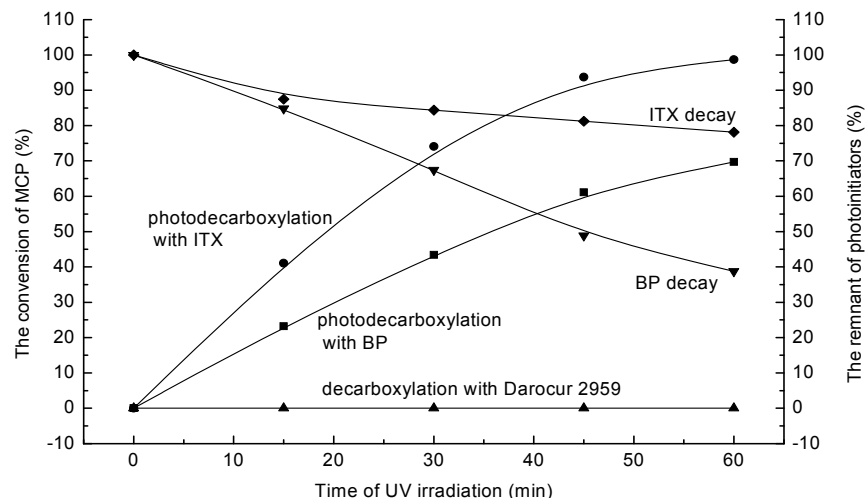

Figure 2 The rate of decarboxylation of MCP with different photoinitiators and the depletion of the photoinitiators

In present research, MCP, alpha-carboxyl thioether, was proposed to convert into the thioether free radical cation R-S$^{·+}$CH$_2$COOH after interacted with the BP in excited state and lost one of the n-electrons at sulfur atom. The PET decarboxylation process was shown in **Scheme 2**. With ^{1}H NMR and GC-MS, Monomethyl thioether (CH$_3$-S-R) and thioethylene ether (R-S-CH$_2$CH$_2$-S-R) were detected to be the primary photodecarboxylation products.
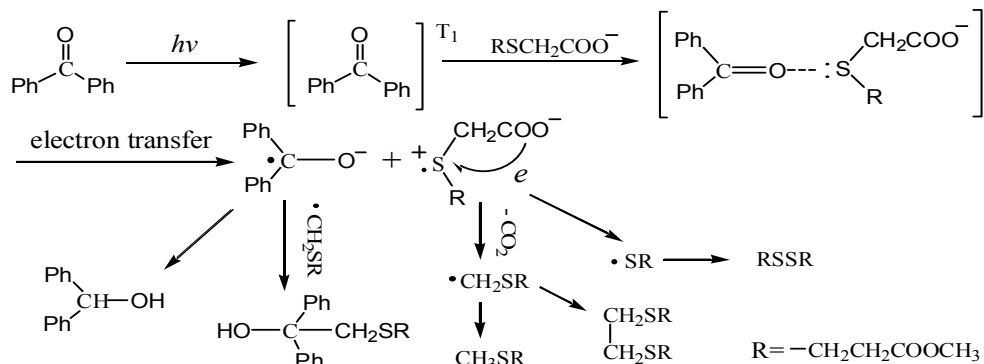
Scheme 2 The process of PET photodecarboxylation

In order to survey the influence of acid/base, organic acid trichloroactic acid (TCA), organic base triethylamine (TEA) and pyridine (Py) were added into the MCP/BP system (**Figure 3**). It was indicated that the acid impaired the photodecarboxylation possibly owing to the suppression of MCP dissociation by TCA. TEA and Py could certainly accelerate the dissociation of MCP and improve the concentration of carboxyl anion. Nevertheless, the photodecarboxylation of MCP was found to decrease in the presence of the amines. It should be ascribed to the efficient quenching of excited BP by TEA and Py. MCP, the substrate for decarboxylation, had to compete with the amines while donating electron to excited BP. It could be suggested that the alkalis, exhibiting strong tendency of electron donation, are better to be avoided while improving photodecarboxylation.
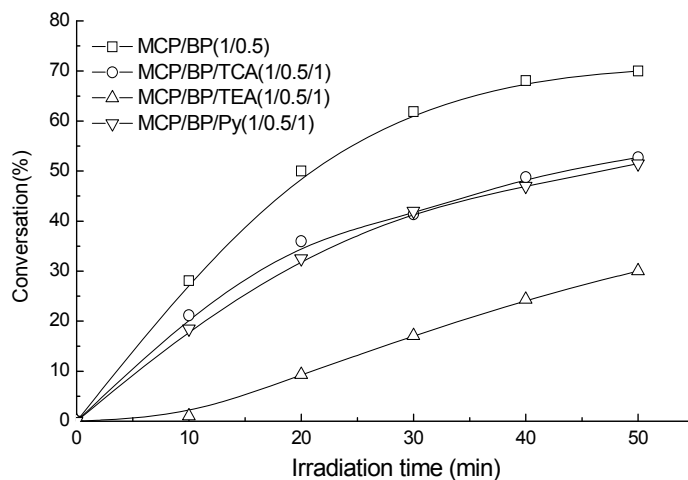

Figure 3   The rate of decarboxylation in presence of bases and acid

TMCPE, pale yellow viscous liquid, was perfectly compatible with acetone, but hardly soluble in water, dichloromethane and toluene. Strong hydrogen bonds between –OH and –COOH might reduce the solubility of TMCPE in water, dichloromethane and toluene. TMCPE could decarboxylate in the presence of ITX with UV irradiation just like MCP. As indicated in Figure 4, TMCPE in the lower layer is separated from toluene in the upper layer before UV exposure. The photogenerated carbon dioxide bubble was observed and migrated upward slowly in the viscous TMCPE phase while UV irradiation, but moved quickly upon entering into the upper toluene phase. Finally, the photodecarboxylation product eliminating carboxyl group got compatible with toluene and formed a homogeneous solution.
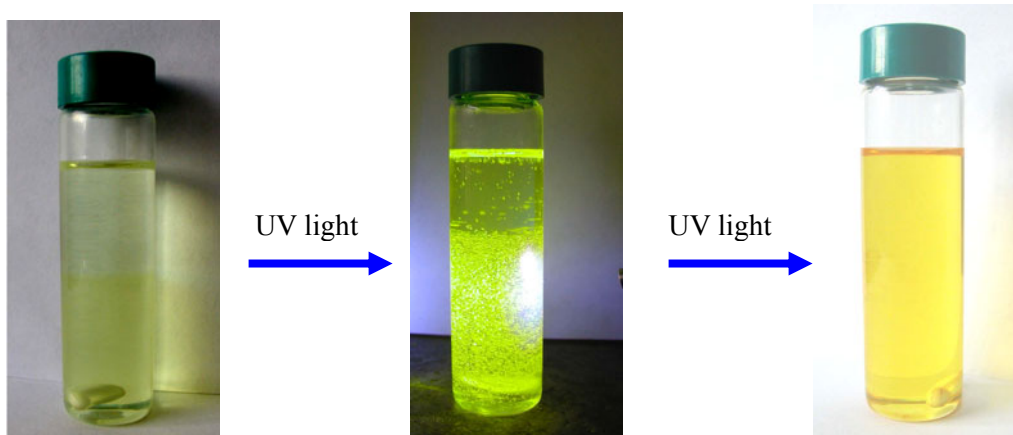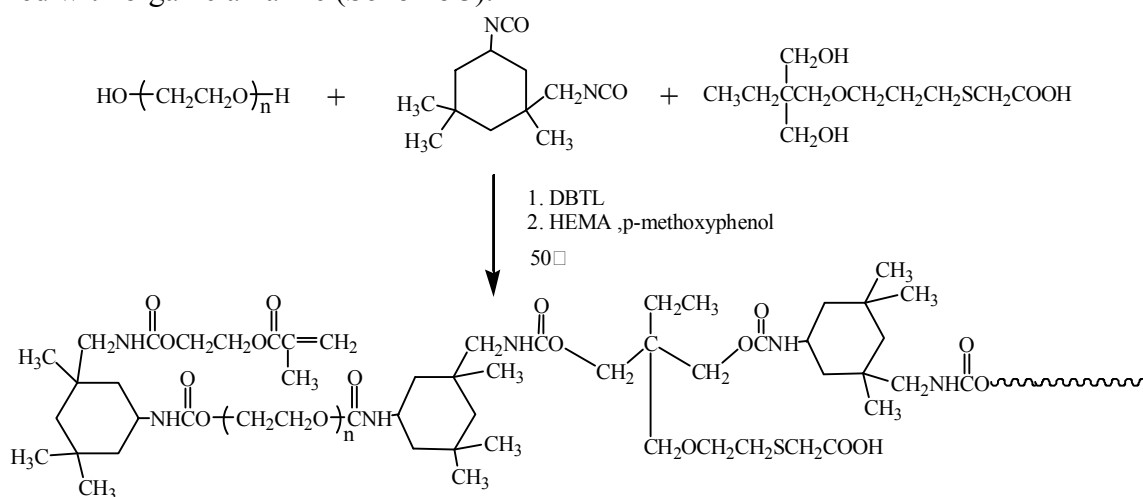
Figure 4   Transformation from heterogeneous phase to homogeneous phase after photodecarboxylation

With TMCPE as functional monomer, a water miscible polyurethane acrylate oligomer, bearing photo-scissible carboxylmethyl thioether as pendant group, was synthesized and dispersed in water after neutralized with organic alkaline (**Scheme 3**).

Scheme 3   The synthesis of photodecarboxylatable waterborne polyurethane

Photoinitiator, Darcur 2959 and ITX, were dispersed in the self-emulsion of polyurethane acrylate, respectively. The oligomer micella was favorable for the dispersion of the photoinitiator even though ITX was insoluble in water. A cured film was obtained while the formulation was dispreaded over a piece of glass and exposed to UV irradiation after pre-drying. In contrast to the controlled determination, the cured films were post irradiated under the same UV lamp for 3 hours. The cured films were immersed in water as well as the post irradiated samples. The water uptake ratio of these films were measured with immersion time (**Figure 5**).
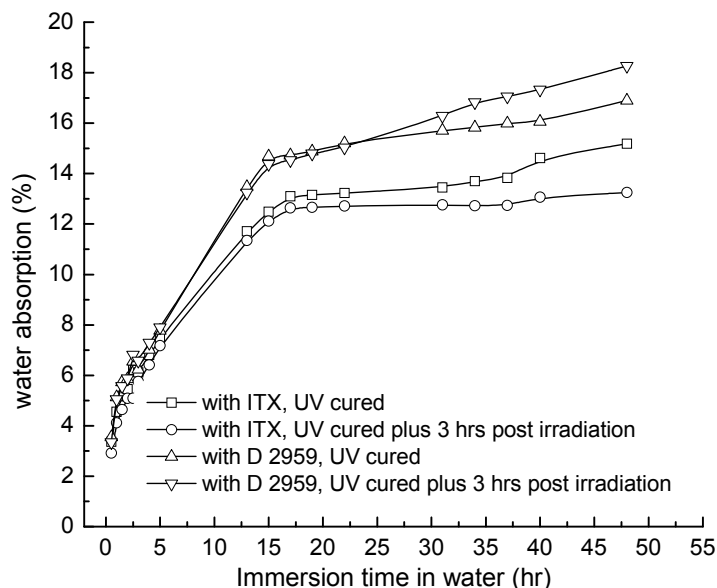
Figure 5. Water absorption of cured and post irradiated film with immersion time

According to the aforementioned investigation, tertiary amine used as neutralizer to the carboxylic oligomer might jeopardize the photodecarboxylation. Tetrabutyl ammonium hydroxide (TBAH), not active in the process of PET, was applied as neutralizing agent instead of TEA. It has been reported that TBAH could accelerate the photodecarboxylation of SCCA [10, 11]. The water resistance of the UV cured films, derived from water-borne formulations, could be predicted to improve if efficient decarboxylation occurred during photocrosslinking and/or post UV irradiation. In the aspect of photopolymerization extent, there was no significant difference between the cured film with D 2959 and that with ITX. The water resistance of the cured films was predominated by the hydrophilic carboxylic group in the film network. It was indicated in **Figure 5** that the photoinitiator employed in the formulation played an important role for the photodecarboxylation and water resistance of the cured films. ITX, as an efficient electron acceptor contrasted to D 2959, remarkably decreased the water absorption of the cured films by effective photodecarboxylation. On the other hand, It was also necessary to extend the UV irradiation after UV curing for improving the decarboxylation conversion. Post irradiation was found favorable for improving water resistance of the cured film.

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