Graft-copolymerization of PVC with polymerizable UV absorbers


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Summary

Polyvinyl chloride has been grafted with two different monofunctional polymerizable ultraviolet (UV) absorbers, 4-methacryloyloxy-2-hydroxybenzophenone and 2(2-hydroxy-4-methacryloyloxyphenyl) 2H-5-methoxy-benzotriazole. PVC was activated by dehydrochlorinating it in pyridine and subsequently grafted with the monomeric UV absorbers in tetrahydrofuran by free radical polymerization. The molar masses of the resulting grafted polymers and the distribution of the UV absorber moieties along different molar mass fractions were determined by GPC. It was shown that in addition to the grafting reaction, recombination of the DHPVC and homopolymerization of the UV absorber molecules take place.

INTRODUCTION

Polyvinyl chloride is a widely applicable polymer. However, under the normal conditions of processing, storage, or utilization, PVC undergoes degradation, resulting in the deterioration of its useful properties.

In order to overcome the photodegradation of PVC certain ultraviolet (UV) absorbers are added, which can absorb most of the harmful radiation and reemit it in a non-harmful form. The UV absorber must be effective over a longer period of time, therefore it must not be degradable, volatilize from the polymer, leached out by solvents. Also the additive must be evenly distributed which requires that it be compatible with the polymer. UV absorbers can be introduced to the polymer by either adding it in low percentage to the polymer mix during polymer processing or hooked to the polymer chain by copolymerization or graft copolymerization, which requires a polymerizable UV absorber, containing vinyl or allyl group in its side chain.

The latter approach, i.e., the graft copolymerization of a monomeric UV absorber onto a preformed polymer chain, was used to stabilize polyolefins. Munteanu (1,2) stabilized LDPE, HDPE and PP by melt grafting with polymerizable benzophenones, whereas Vogl et al. (3) carried out the grafting reaction of a vinyl benzotriazole onto atactic PP in chlorobenzene solution. In all cases, organic peroxides were used as grafting initiators.

To our knowledge the graft polymerization approach was not applied so far to the photostabilization of PVC. In order to photostabilize PVC the polymer chains must be activated by creating conjugated or random double bonds. These active sides can be obtained by removing the active chlorine atoms using a weak base such as pyridine (4,5). The resulting dehydrochlorinated PVC (DHPVC) can be graft copolymerized free radically with any suitable monomer, as was done with styrene to prepare poly(vinylchloride–g–styrene) (6).
The present work is aimed at grafting two UV absorbers, 4-methacryloyloxy-2-hydroxy-benzophenone I and 2(2-hydroxy-4-methacryloyloxyphenyl) 2H-5-methoxy-benzotriazole II to DHPVC and characterizing the grafted polymer by UV spectroscopy and Gel Permeation Chromatography (GPC).

![Chemical structures of UV absorbers](image)

**EXPERIMENTAL**

PVC powder was obtained from Enichem Polymeri S.P.A. Company. The UV absorber monomers I and II were prepared in our laboratory using published procedures (7,8).

HPLC grade tetrahydrofuran (THF) was kept over sodium metal overnight, then it was distilled under nitrogen over fresh sodium metal. AR grade pyridine was purified by keeping it over sodium hydroxide pellets overnight, then distilling it under nitrogen over fresh sodium hydroxide pellets. AR grade methanol and petroleum ether (40–60°C) were used without further purification. AR grade 2,2'-azobisisobutyronitrile (AIBN) initiator was obtained from KODAK Company and twice recrystallized from methanol.

The absorption spectra were recorded in purified THF using a SHIMADZU spectrophotometer UV-160.

The GPC measurements were conducted on a WATERS High Performance Gel Permeation Chromatograph LC 244, equipped with refractive index and ultraviolet detectors. 50–200 µl of 2% polymer solutions in tetrahydrofuran were injected via an automated sampling system WISP 710B (WATERS). The mobile phase was HPLC grade tetrahydrofuran.

The determination of the molar masses was carried out using a column system consisting of WATERS ULTRASTYRAGEL 500, 10³ and 10⁴ Å, 30 cm x 7.8 mm I.D. and a flow rate of 0.8 ml/min. A calibration was used based on narrow distributed polystyrene calibration samples (WATERS).

For the determination of the amount of UV absorber units bonded to different molar mass fractions, a column system was used, consisting of WATERS ULTRASTYRAGEL 500 Å and linear, 30 cm x 7.8 mm I.D., and a flow rate of 1.0 ml/min. In this case the UV detector signal at a wavelength of 340 nm was recorded.

The dehydrochlorination was carried out in a 2 L, three necked, round bottomed flask equipped with a mechanical stirrer, thermometer and nitrogen gas inlet in which 41.7 g of virgin dry PVC was dissolved in 1 L of dry freshly distilled pyridine under nitrogen. After all the PVC polymer was dissolved, the reaction mixture was heated in an oil bath at 120°C for 3 hours under nitrogen atmosphere. The reaction mixture started to develop a reddish brown color gradually from colorless to yellow, orange and red as heating continued. Then the reaction mixture was cooled to room temperature and precipitated in 2 L of methanol. The produced dehydrochlorinated PVC (DHPVC) which is pink in color was filtered, washed several times with water then methanol and dried in a vacuum oven at 50°C till constant weight. The obtained DHPVC product was further purified by dissolving it in freshly distilled dried THF and precipitated in petroleum ether (40–60°C). The purified DHPVC was vacuum dried at 50°C.