Polymer Bulletin 26, 39–46 (1991)

Polymer Bulletin

Graft-copolymerization of PVC with polymerizable UV absorbers

A. Al-Mobasher, S. Attari, H. Pasch*, K. F. Shuhaibar, and F. A. Rasoul

Materials Application Department Petroleum, Petrochemicals and Materials Division,
Kuwait Institute for Scientific Research, P.O. Box 24885, Safat 13109, Kuwait

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.

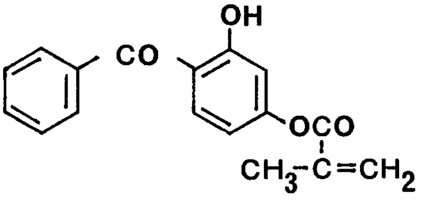
The latter approach, i.e., the graft copolymerization of a monomeric UV absorber onto a preformed polymer chain, was used to stabilize polyolefins. Munteanu (1,2) stabilized LDPE, HDPE and PP by melt grafting with polymerizable benzophenones, whereas Vogl et al. (3) carried out the grafting reaction 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).

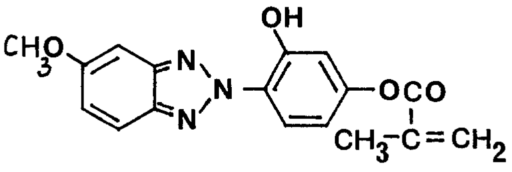
---

*Permanent address: Central Institute of Organic Chemistry, Academy of Sciences, Rudower Chaussee 5, O-1199 Berlin, FRG

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).



I



II

EXPERIMENTAL

PVC powder was obtained from Enichem Polimeri 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, 10^3 and 10^4 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.

The graft copolymerization of DHPVC with I and II was carried out as follows:

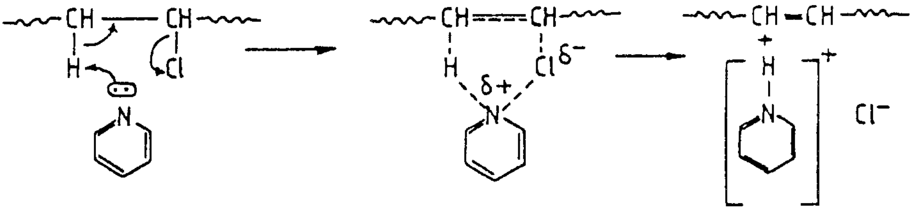
In a 100 ml capacity beaker equipped with a magnetic stirrer, 2 g of DHPVC was dissolved in 50 ml freshly distilled dry THF; 0.1 g of UV absorber and 0.001 g of AIBN initiator were then added to the reaction mixture and transferred to a 100 ml long necked, round bottomed flask equipped with a magnetic stirrer. The flask was then connected to a vacuum line and the mixture was degassed trice in freeze-thaw cycles before sealing. The sealed flask was cooled to room temperature and then heated in a water bath at 60-65°C with stirring for 48 h. After approximately 40 h of heating, the color of the reaction mixture changed from a reddish brown to a yellowish color. The grafted copolymer was obtained by precipitating the reaction mixture into 250 ml of petroleum ether (40-60°C). The white precipitate was then filtered off and vacuum dried. The grafted copolymer was purified by dissolving it in 50 ml THF and reprecipitated in petroleum ether (40-60°C). Then the grafted copolymer was washed with methylene chloride to separate the monomer and homopolymer of the UV absorber and then vacuum dried at 50°C till constant weight.

RESULTS AND DISCUSSION

The dehydrochlorination of PVC was carried out in an inert atmosphere to avoid the presence of oxygen, leading to secondary reactions. It is accompanied by the discoloration of the polymer due to the formation of polyene sequences.

Several mechanisms of PVC dehydrochlorination in nonoxygen atmosphere have been proposed but never the less it has not been conclusively established.

Mukherjee and Gupta (4,5) suggest a mechanism, where the interaction between pyridine and the polymer leads to the formation of an intermediate, this intermediate facilitates the elimination of HCl. The latter is eliminated as pyridine-hydrochloride rather than the free acid.



The ultraviolet spectrum of DHPVC (see Figure 1) consists of a broad absorption band, exhibiting a local absorption maximum at about 280 nm and ranging to about 320 nm at the higher wavelength side. Experimental data for the relationship between the wavelength of the absorption peak and the polyene sequence length (9) indicate that the DHPVC contains mostly short polyene sequences of 3 to 5 double bonds.

The molar masses of all resulting products were determined by GPC using the refractive index detector. It was found, that the starting PVC had a number average molar mass of about 39.000. After dehydrochlorination a product was obtained (DHPVC), having a molar mass of about 7.300, which is remarkably lower than $\bar{M}n$ of the starting material. Obviously, the dehydrochlorination results not only double bonds along the polymer chain, but to a certain extent chain-scission takes place. This is in agreement with Mukherjee and Gupta's observation that in thermal dehydrochlorination of PVC in pyridine chain scission as well as crosslinking can take place (4,5).

During graft copolymerization the color of the reaction mixture changed from reddish brown to light yellow which indicates the reaction of the double bonds either with the UV absorber or by recombining of the DHPVC to form PVC molecules. The absorption spectra of the resulting products, DHPVC-g-I and DHPVC-g-II, after reprecipitation are presented in Figure 1.

They show absorption peaks at 330 and 345 nm, characteristically for the UV absorber moieties I and II respectively. From the intensity of these absorption peaks it was

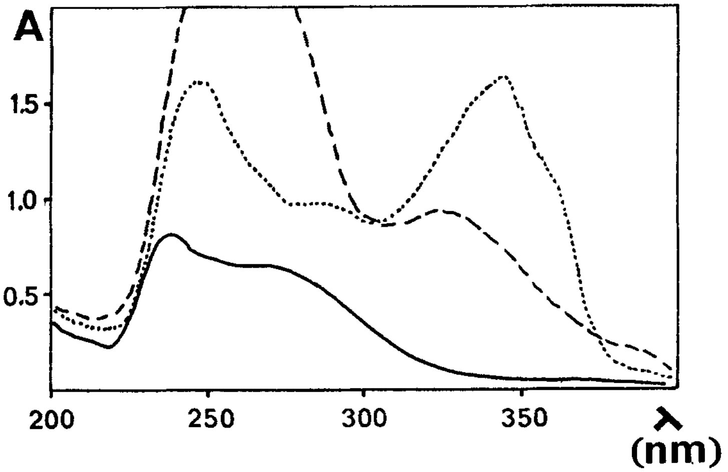


Figure 1. UV spectra of DHPVC (_____), 2.8 g/l; DHPVC-g-I (----), 2.4 g/l; and DHPVC-g-II (....), 1.5 g/l in THF.

possible to calculate the amount of incorporated UV absorber and it was found that DHPVC-g-I contains 3.5 wt % of UV absorber and DHPVC-g-II contains 1.7 wt % of UV absorber, instead of the initial 4.8 wt %. The rest of the (obviously unreacted) UV absorbers was separated from the products during the reprecipitation process.

In addition to the reprecipitation the products were washed with methylene chloride to remove residual monomers. The resulting products together with the unwashed samples were subjected to GPC and the results are presented in Table 1.

Table 1. Molar Masses and Polydispersities of PVC, DHPVC and Grafted DHPVC (Calibration Based on Polystyrene)

Sample	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
PVC	38.700	140.400	3.6
DHPVC	7.300	19.100	2.6
DHPVC-g-I			
before washing	12.800	28.200	2.2
after washing	14.700	37.900	2.6
DHPVC-g-II			
before washing	18.000	37.500	2.1
after washing	29.000	49.000	1.7
Filtrate	main peak	⟶	monomers

The molar masses of the products after the grafting reaction are significantly higher than the molar mass of the initial DHPVC. From the low amount of incorporated UV absorber this strong increase in the molar mass can not be expected. It is therefore, likely that to a certain extent recombination of DHPVC molecules takes place.

The distribution of the U.V. absorber units along different polymer fractions can be visualized using the U.V. detector at a wavelength of 313 nm, where only the UV absorber but not the PVC backbone gives a response. It can be seen from the GPC profiles that in all cases a part of the U.V. absorber units is located in the polymer bulk. A second part is located in the oligomer and monomer region, obviously as unreacted U.V. absorber molecules. When the reaction product is washed with a solvent, which only dissolves in the U.V. absorber monomer, this second part disappears. It is noteworthy that the ratio between the amount of U.V. absorber in the first and the second part differ significantly, depending on the U.V. absorber. Comparing Figures 2 and 3 it can be seen, that the amount of unreacted UV absorber, locating in the low molar mass region of the chromatogram, is much lower in the case of the benzophenone (I) compared to the phenylbenzotriazole (II).

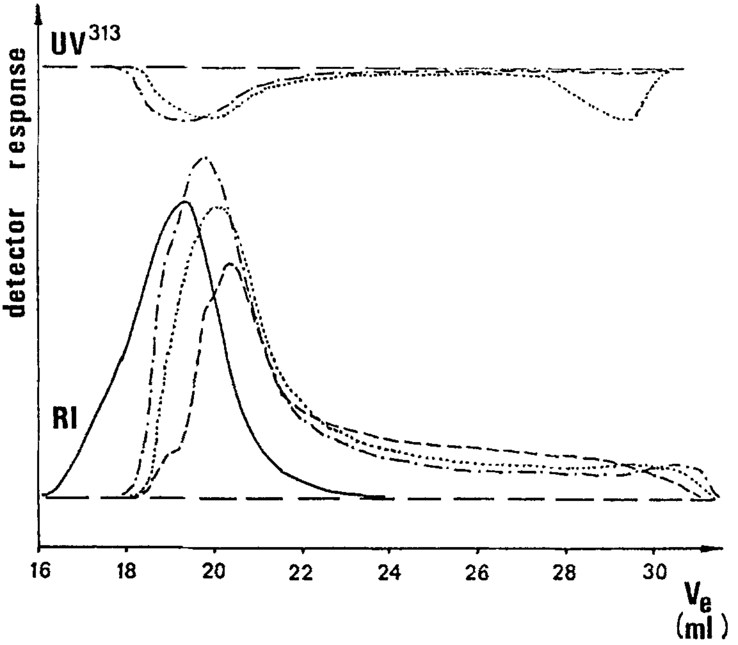


Figure 2. GPC chromatograms of PVC (——), DHPVC (- - -), DHPVC-g-I before (...) and after washing (_._.).

Because in all cases the same DHPVC and the same amount of U.V. absorber were used, it can be concluded, that the reactivity towards grafting changes in the order benzophenone > phenylbenzotriazole.

As it was mentioned above, besides grafting recombination of the polymer molecules takes place. It can be seen from the molar mass values (see Table 1), that the molar mass of the reaction products changes in the order phenylbenzotriazole > benzophenone.

If we consider that in all cases DHPVC has an equal number of reactive sides, then these reactive sides can react either with a U.V. absorber monomer in a grafting reaction or with a second polymer molecule in a recombination reaction. These reactions are competitive and therefore the reactivity of the monomeric U.V. absorber is responsible for the degree of grafting and the resulting molar mass.

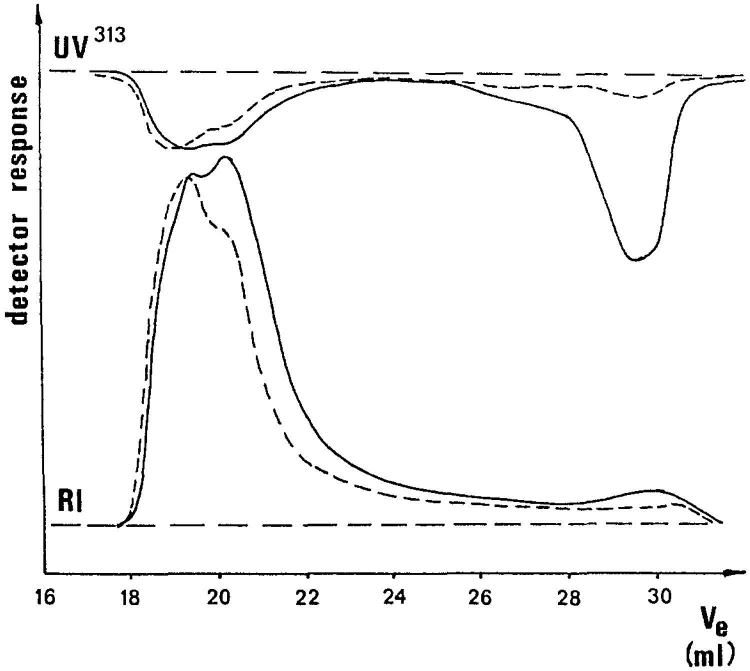
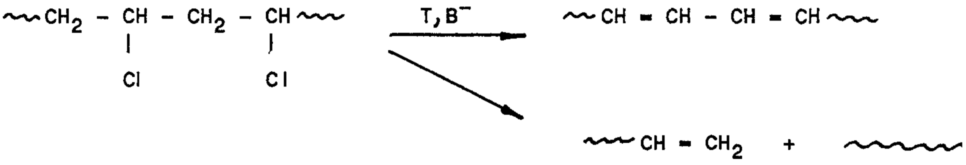


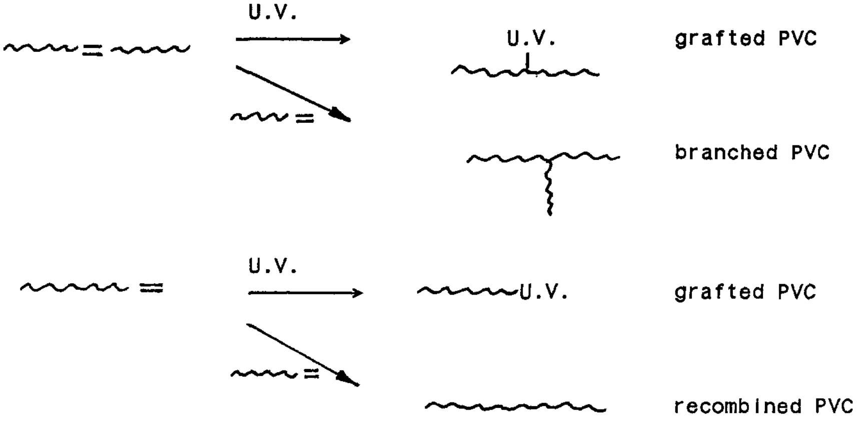
Figure 3. GPC chromatograms of DHPVC-g-II before (——) and after washing (- - -).

The following reaction mechanism can be assumed:

1. Dehydrochlorination



2. Grafting



In order to give a more detailed information about the distribution of the UV absorber units along different molar mass fractions we repeated some of the GPC measurements using the UV detector and not the RI detector in the calculation mode. To enhance the resolution a column combination of waters Ultrastyragel linear and Ultrastyragel 500 Å was used. The sensitivity of the detection was improved by using a detector wavelength of 340 nm, which corresponds to the absorption maximum of the UV absorber units. The obtained chromatograms are presented in Figure 4.

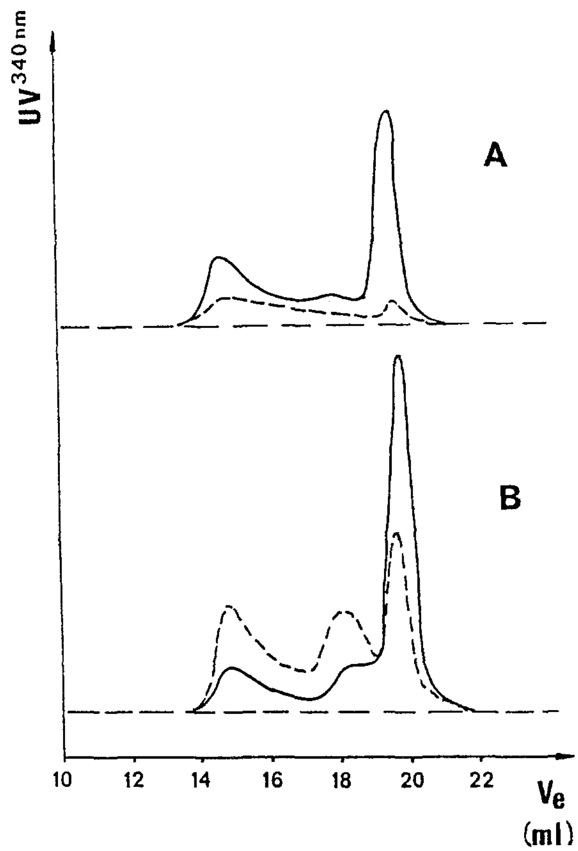


Figure 4. GPC chromatograms of DHPVC-g-I (A) and DHPVC-g-II (B) before (——) and after washing (-----).

With respect to the previous experiments for DHPVC a $\bar{M}_n$ value of 7.300 was determined. For comparison the same experiment was carried out on the new column system and a $\bar{M}n$ value of 7.200 was obtained, showing that both systems give the same molar mass values. Figure 4 shows that in the case of benzophenone two separate regions of high UV response were obtained, corresponding to the polymer bulk and the unreacted monomer. In the case of phenylbenzotriazole, a third region appeared, corresponding to a certain oligomer. The weight amounts of the fractions together with the corresponding molar masses are presented in Table 2.

As for the benzophenone about 50% of the UV absorber, incorporated into the product, was bound to the polymer backbone in the grafting reaction. In the consecutive washing

Table 2. Composition of Grafted DHPVC, Determined by GPC Using a UV$^{340\ nm}$ Detector

Sample	Polymer Fraction	Oligomer Fraction	Monomer Fraction
DHPC-g-I			
Before washing	M_p^1 = 16.300	--	M_p = 340
	A^2 = 49.2%		A = 50.8%
After washing	M_p = 14.000	--	M_p = 310
	A = 78.7%	--	A = 21.3%
DHPVC-g-II			
Before washing	M_p = 23.600	M_p = 760	M_p = 310
	A = 14.1%	A = 16.0%	A = 69.9%
After washing	M_p = 13.600	M_p = 770	M_p = 300
	A = 40.4%	A = 32.4%	A = 27.2%

(1) Molar mass at the peak maximum

(2) Amount of UV absorber units in mol. %

process a considerable amount of the unreacted monomer was removed, but extensive washing seems to be necessary to obtain a product free of unreacted monomer.

In the case of the phenylbenzotriazole the grafting efficiency was much lower and the reaction product contained about 70% of unreacted monomer. The high UV response of the oligomer fraction indicates, that this fraction mostly consists of homopolymerized UV absorber molecules. Therefore the efficiency in the grafting process is low compared to the benzophenone. In conclusion, it was demonstrated that PVC can be grafted with polymerizable UV absorbers. However, further efforts are necessary to optimize the procedure in order to increase the grafting efficiency.

ACKNOWLEDGEMENT

The financial support of the Kuwait Foundation for the Advancement of Sciences (KFAS) is greatly appreciated (Project Code No. 86-08-05).

REFERENCES

1. D. Munteanu, V. Aslan, C. Varin; Romanian Patent 60611 (1975).
2. D. Munteanu, I. Nanu; Rev. Roum. Chim. 22 (1977) 923.
3. W. Pradellok, O. Vogl, A. Gupta; J. Polym. Sci., Polym. Chem. Ed. 19(1981) 3307.
4. A.K. Mukherjee, A. Gupta; J. Macromol. Sci. Chem.; A16/4 (1981) 783.
5. A.K. Mukherjee, A. Gupta; J. Macromol. Sci. Rev.; C20/2 (1981) 309.
6. A.K. Mukherjee, A. Gupta; J. Appl. Polym. Sci., 28(1983) 1245.
7. R.A. Coleman; U.S. Patent 3.391.110 (1968).
8. F. Xi, W. Bassett, O. Vogl; Polymer Bull 11(1984) 329.
9. K.B. Abbas, E.M. Sorvik; J. Appl. Polym. Sci. 19(1975) 2991.

Accepted January 31, 1991 C