

## Photochemical Effect of Azocompounds Acrylates Grafted in Different Polymeric Matrices

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### Summary

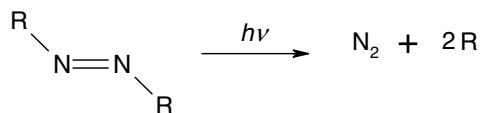
Acrylate side chains containing a photocromic azobenzene group (Disperse Red 1, DR1) grafted onto different polymer matrices: polypropylene (PP), low density polyethylene (PE), polyethyleneterephthalate (PET) and polycarbonate CR-39 (PC), were prepared by gamma radiation of polymer films in toluene solutions of acryloyl chloride in Pyrex ampoules sealed in vacuum, and then esterified with DR1 in presence of triethylamine. Comparison of photochemical properties of the different systems, as well as thermal stability and surface morphology were studied.

### Introduction

Optically active methacrylic homopolymers with side-chain azobenzene chromophores have been studied in solution, and kinetics of the trans-cis photoisomerization of the azo-aromatic double bond has been measured by Angiolini [1], photochromic side chain liquid crystalline polymethacrylates containing paranitroazobenzene group were synthesized and characterized by Zhang [2]. Polymers containing azobenzene chromophores possessing interesting properties such as the possibility of direct formation of surface relief gratings among others, have attracted considerable attention in the last decade [3-5]. Some azo polymers have been synthesized in recent years and they were studied for the photo-fabrication of surface relief gratings (SRG) [6-9]. He [10] synthesized a novel polymer containing azobenzene chromophores in the main and side chains and studied the thermal and photochemical properties. The effect of photobleaching in polymer films containing azo dyes was studied by different authors [11-14]. Hattori [14] reported that the absorption band at around 485 nm from the DR1 molecule in the film of PMMA decreased under exposure to UV light in function of time and completely disappeared after 7 h, and a new band appeared at around 370 nm which corresponds to a molecule of p-nitroaniline which means that the decomposition of the azo group of DR1 molecule occurs during UV light exposure.

The general reaction of photobleaching with UV radiation is shown in scheme 1.

The purpose of this paper is to show that azocompounds grafted in polymeric systems are photosensitive as small azocompounds in solutions or polymers containing this group. Liquid systems of azocompounds present instability to UV light and grafted



Scheme 1. Photobleaching of azo compounds.

copolymers have the advantages that we can choose the mechanic properties such as transparency, flexibility and other mechanical properties, without modifying photosensitivity with change of the polymer matrix, and their stability is larger than that of compound alone or in solution. We also studied the possibility to use those systems as a photochemical dosimeter (actinometer), and also as a UV solar atmospheric dosimeter in open spaces like deserts and beaches, because of the proportional decay absorbance intensity in a limited range of UV irradiation. In this way, the field of applications could be wider.

## Experimental

### Materials

Films of polypropylene (PP), thickness of 0.07 mm, with molecular weight of 39,000 ( $\overline{M}_n$ ), 179,000 ( $\overline{M}_w$ ), density of 0.902 g/ml and crystallinity of 88%; low density polyethylene (PE) thickness of 0.07 mm, from PEMEX, Mexico with a density of 0.92 g/ml and crystallinity of 62%; polyethyleneterephthalate (PET) from Good Fellow UK, thickness 0.25 mm, molecular weight of 52,500 and crystallinity of 82.5%; and polydiethylenglicol bis allyldicarbonate CR-39, (PC) from Pershore UK, thickness 0.25 mm, were washed in methanol for two hours, and then dried under vacuum. The Disperse Red 1 (1,2-[4-4-nitrophenylazo)-N-ethylphenylamino]ethanol) (DR1) and triethylamine were supplied by Aldrich Chemical Co. Acryloyl chloride obtained from Aldrich was purified by distillation at a reduced atmospheric pressure. Toluene, methanol and dichloromethane were supplied by Baker.

### Grafting

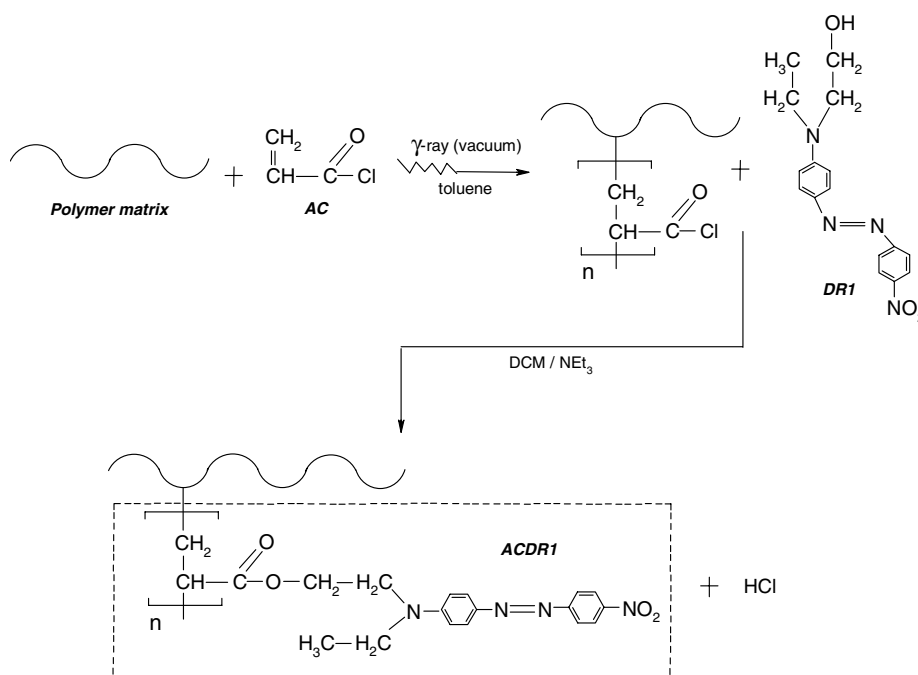
Polymer films were placed in glass ampoules which contained acryloyl chloride in toluene solutions at different monomer concentrations; the ampoules deaerated under vacuum by repeated freezing and thawing method, then they were sealed and irradiated with a  $^{60}\text{Co}$   $\gamma$  source (Gammabeam 651 PT, Nordion International Inc.) at different dose rates and radiation doses depending of the optimum conditions of each system studied. AC was grafted onto PE films in a solution of 50 % in toluene v/v, and at dose rate of 4.1 kGy/h; PP was grafted from 70 % AC in toluene at a dose rate of 4 kGy/h; PC with 30 % of AC in toluene and dose rate of 4.4 kGy/h; and PET from 70 % AC in toluene and at dose rate of 3.2 kGy/h. To extract the residual homopolymer formed by irradiation and occluded in the films during the irradiation, the grafted samples were stirred with toluene for 2 h in a closed flask and then stirred for 24 h with DR1, in dichloromethane (DCM) with concentrations from 0.01 to 0.03 M, in order to esterify the grafted polymers with the chromophore, triethylamine (nucleophilic catalyst) was added. Then the samples were washed with methanol to remove the unreacted DR1 until this solvent was colorless, and also for conversion of

the remaining chloride group to the methyl ester. Grafting percentage was calculated by the equation (1):

$$\text{Grafting}(\%) = [(W - W_0) \times 100] / W_0 \quad (1)$$

where  $W_0$  is the initial weight and  $W$  the final weight of the sample. The amount of DR1 bonded to the film was estimated by elemental analysis (Desert Analytics, Tucson AZ) of nitrogen contents of the films [16, 17]. Optimum conditions of the AC grafting onto PC, PP and PET were published by Aliev [15], and Bucio [16, 17] respectively.

Route of synthesis of azo compounds onto different polymer matrix by gamma irradiation shows in the scheme 2.



Scheme 2. Copolymer with azo compounds.

### Characterization

FTIR-ATR spectra were taken using a Paragon 500 (Perking-Elmer) spectrophotometer. ZnSe glass was used for contact with the samples surfaces, and the IR radiation penetrated into samples to depth of 5-6  $\mu\text{m}$ . The X-ray diffraction patterns of the films were obtained by an X-ray diffractometer Bruker-AXS D8-Advance. The observation of surface of the films was made using an atomic force microscope (AFM) Autoprobe-CP, Park Scientific Instruments, with 10  $\mu\text{m}$  scanner (contact mode) and an autocalibration by Scanner Master. Differential Scanning

Calorimetry was performed using a DSC 2010 calorimeter (TA instruments), measured at 10 °C/min. A Varian Cary Model 100 UV-visible spectrophotometer (Varian Associates) was used to observe the UV absorbance decay of the azobenzene group in films. A 200 Watt medium pressure mercury lamp of Ace Glass was used to irradiate the films; the well known liquid phase potassium ferrioxalate actinometer system has been used to determine the intensity of the UV lamp [18, 19], we found an intensity of  $3.1 \times 10^{14}$  quanta  $\text{cm}^{-3} \text{s}^{-1}$ .

## Results and Discussion

### Grafting

The graft percentage increases with the irradiation dose, this behavior is normal for radiation induced grafting. Figure 1 shows the optimum results on grafting of the ACDR1 in all polymers studied.

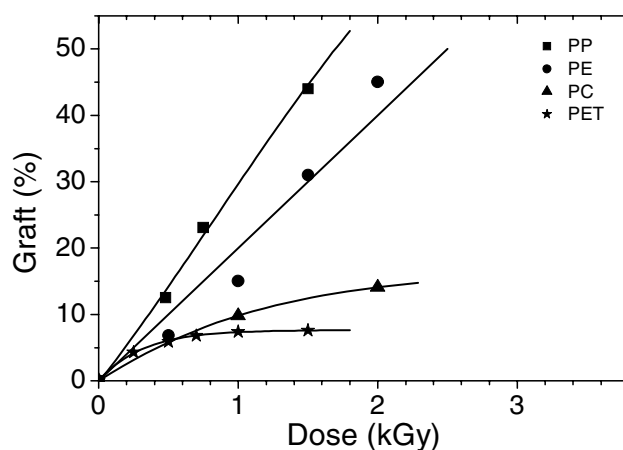


Figure 1. Graft (%) of ACDR1 onto different polymer matrix, as a function of radiation dose.

In the case of PP films we obtained the highest grafting percentages, but higher ones could be obtained with further dose increase [16]; PE films have also high graft percentages, near to those of PP. The maximum grafting obtained for the PC films was 18 % at 4.4 kGy/h, this yield decrease with dose rate (7 % at 0.4 kGy/h) [15]; and the lowest grafting yield was found for the PET films. The low grafting yield obtained in PET films, is due to the chemical structure with an aromatic group which absorb part of the gamma ray energy by the resonance of the benzene ring, and because of the highest Tg of all the studied polymer matrix, of about 76 °C; PC is another polymer with a Tg of 59 °C; on the contrary, polyolefines like PP and PE have a Tg below zero, then the mobility of the molecules enhance the efficiency of grafting. Radiation grafting on polymers that do not swells in the monomer solutions, has been investigated earlier by many researchers [20-22], and similar observations were made of a rapid increase in grafting at the beginning, and a level off at higher doses, it is expected by their observations that with less than 30 % of grafting, there will be

insignificant or no change in the thickness of the grafted region with a surface grafting. As grafting increase beyond 30 %, the thickness and the area of the grafted region should continue to increase and the monomer diffuses into the grafted layers through the film, at doses about 100 %, bulk grafting was obtained. In this paper the thickness of the film did not change, and the grafting is localized in the surface, due to low graft samples studied, less than 10 %.

#### *FTIR spectra*

The IR spectra of the starting and modified polymer matrix surfaces with the grafted poly AC reveal new peaks as compared with the starting polymer, the absorptions at  $1750\text{ cm}^{-1}$  and  $970\text{-}940\text{ cm}^{-1}$  attributed to the COCl groups of the grafted AC. Besides, a broad band at  $3300\text{-}2500\text{ cm}^{-1}$  responsible for the O-H stretching vibrations in carboxylic groups was not found that indicated absence of the COCl groups hydrolysis. Spectrum of polymer composition with the immobilized DR1 contained 4 new peaks at  $1600$ ,  $1500$ ,  $1430$  and  $1328\text{ cm}^{-1}$  due to aromatic rings, -N=N- and  $\text{NO}_2$  groups stretching vibrations, respectively, and some displacement of peak near  $1400\text{ cm}^{-1}$  to a long-wave region can be explained by the poly(methyl acrylate) formation after treatment of the remaining chloride with methanol.

#### *Crystallinity*

The crystallinity of films decreased as the grafting percentage increases. In case of the PP from 88 % to 31 % when the films were grafted from 0 to 240 %, PE present a decrease of crystallinity from 62 % without grafting to 8.4 % at 263 % graft, PET crystallinity of 82.5 % decrease to 79.4 % at 4.3 % grafted film, because at this low graft percentage, the ACDR1 is in the surface of the sample. At grafting percentages of this paper, lower than 10 %, there are not important changes in crystallinity, in all the polymer matrix.

#### *DSC thermograms*

The melting point ( $T_m$ ) of PP and PE decrease with the grafting of ACDR1. Melting point of PP film at 101 % graft decrease from 170 to 159 °C. PP and PE films with graft percentage of about 200 % show two bands because of the effect of DR1 mesophase. Table 1 shows thermal transitions of graft copolymers; on cooling we observe only one  $T_m$  peak, this mesophase is not reversible. PC has a  $T_g$  of 52 °C, this  $T_g$  decrease to 40 °C in films with 18 % graft, there are not significantly change in PET systems.

Table 1.  $T_m$  and  $T_g$  (°C) of different polymers studied and grafted with DR1 acrylate

Polymer	$T_m$ of polymer, °C	$T_m$ of grafted film, °C	Graft (%)
PP	170	114 and 174	237
PE	112	76 and 114	262
PET	250	249, ( $T_g$ ) 76	7.3
PC	( $T_g$ ) 52	106 and 218, ( $T_g$ ) 41	18
DR1 alone		142 and 163	

### AFM and SEM

AFM observations show heterogeneous surfaces at low graft percentages with small dispersed globules with size of few  $\mu\text{m}$ , and surface more homogeneous at higher doses, with one aligned shape. The necessary percentage of grafting to get an homogeneous surface is different, depending on the studied system AC-g-polymer. In the PP system [16] the film surface present an average roughness of 17.5  $\text{\AA}$ ; at 32.5% graft the surface present many lumps and the average roughness increase to 1330  $\text{\AA}$ , and at 18 % graft , the surface became aligned, smooth and regular, and the average roughness decrease to 486  $\text{\AA}$ . In PC system [15], at low graft ACDR1-g-PC surfaces (11 %), an heterogeneous roughness surface with small dispersed globules was observed, but at higher percentages of about 17 %, we observed a more homogeneous surface with almost no small globules. SEM characterization of ACDR1-g-PE and ACDR1-g-PP showed a surface layer at low graft % and bulk graft at higher graft %, in the cryogenic transversal fracture [15, 16].

### UV irradiation

The photochemical effect was studied in all cases in samples with low grafting percentages due to saturation of the absorbance in the UV spectrophotometer. Figure 2 shows the absorption changes of the UV-VIS spectra of the PE film grafted with DR1 after irradiation with UV lamp at room temperature.

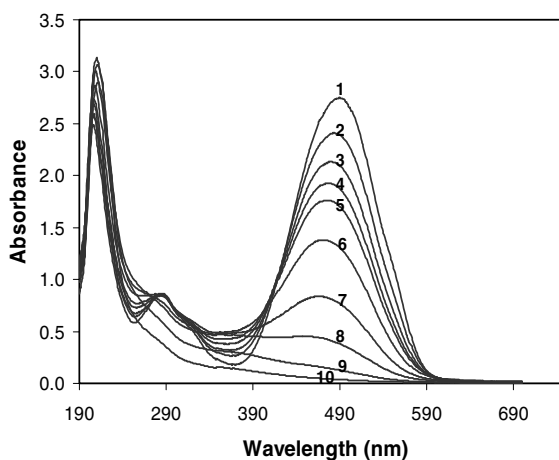


Figure 2. UV-VIS spectra of ACDR1-g-PE polymer films at different UV irradiation time: (1) No irradiation, (2) 30 min, (3) 60 min, (4) 90 min, (5) 120 min, (6) 210 min, (7) 420 min, (8) 600 min, (9) 885 min, (10) 1245 min.

In this paper, we did not studied trans-cis effect, because although azobenzene is a photochromic material, and has two isomers, cis-trans, that absorb at different wavelengths [23, 24]; when the azobenzene bearing donor-acceptor substituents, the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  bands absorbance become superimposed, these azobenzenes are not photochromic anymore, but photobleaching is present, with the study of this effect it could be possible to use the films as a photochemical dosimeter (actinometer). Irradiation of the samples with the light from the range of 350-370 nm results in

changes on the corresponding shape, intensity and position of the UV absorption bands, the intensity of UV band slight increases accompanied by high decrease of the visible band. Figure 2 system of, PE with DR1 show one band at 490 nm associate with increase of azo compounds decomposition (photobleaching) due to UV radiation.

Figure 3 shows normalized absorbance decay as a function of UV irradiation time in all system studied; PP systems decrease in absorbance until a clear transparent colorless film in a time of 480 min (8 h), with not reversible effect on heating, due to chemical degradation mainly in the azocompound. PE grafted films required about 1245 min (20 h) for bleaching, PC decay faster at about 3.5 h and PET system was the most stable, at 20 hours the decay is slightly and we do not obtain a clear transparent film. All systems studied present a linear behavior on decrease of absorbance as a function of radiation time, in a limited range of irradiation; this range could be utilized in the determination of the radiation dose received by a UV lamp or solar radiation in open spaces. We calculated the quantum yield for the ACRD1-g-PP film (9.6 %) as  $3.4 \times 10^{-3}$  molecule  $\text{foton}^{-1}$ .

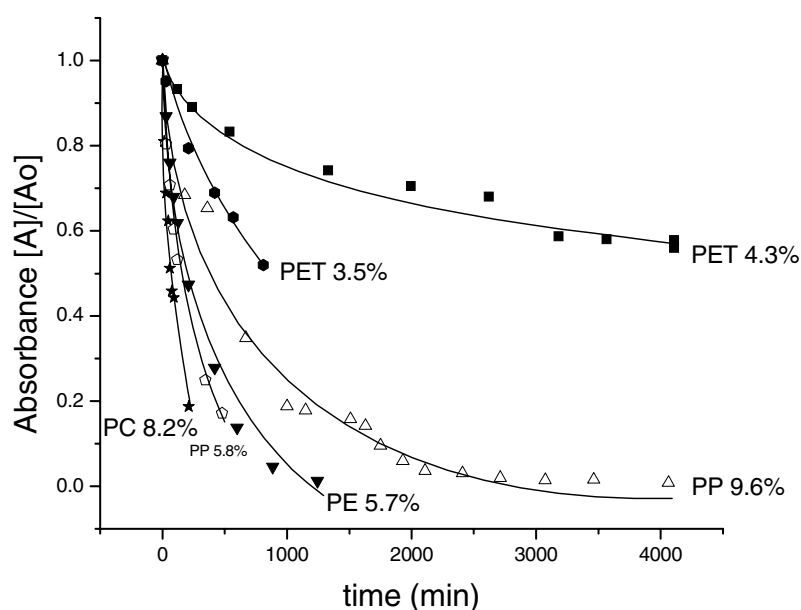


Figure 3. Decay of normalized UV absorbance  $A/A_0$  as a function of UV irradiation time in systems grafted onto different polymer matrix and graft percentages.

In the systems studied, grafting took place on the surface. In the cases of PP and PE which are not sensitive to UV light, the decrease tendencies of UV absorption spectra by UV irradiation, there is not significant difference if the grafting %, it is similar to each other (fig 3). In PET system, the polymer matrix is UV sensitive through the benzoyl group which exhibits a good UV light absorption and photochemical reactivity, and the PC is UV sensitive due to carbonyl groups, through Norish II photoscission process [25].

Figure 4 shows normalized UV absorbance decay ( $A/A_0$ ) as a function of photochemical UV and solar irradiation of the ACDR1-g-PP system, where  $A$  and  $A_0$  are the absorbance of films after and before irradiation, respectively. In both cases there a linear range of time that can be useful as a dosimeter after further studies.

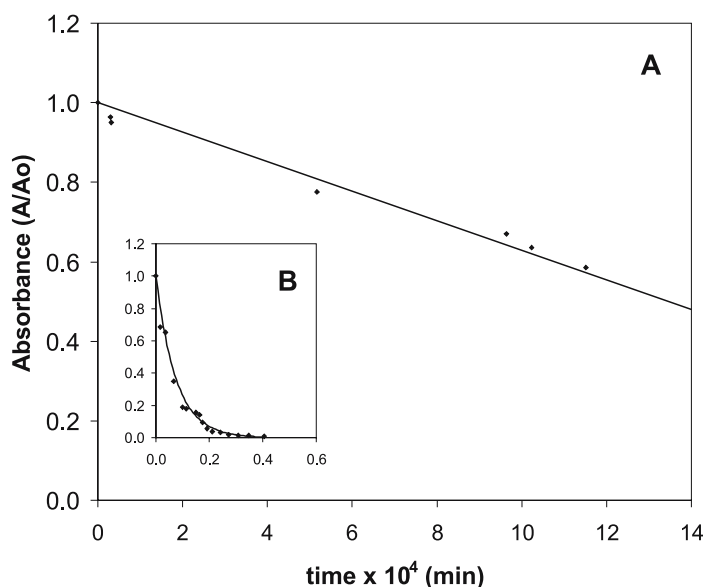


Figure 4. Normalized absorbance decay as a function of irradiation time; A) solar UV irradiation, B) UV lamp irradiation.

Table 2 shows the empirical equation found for the decay in each system studied with correspondent correlation factor.

Table 2. Mathematical expression of photochemical decay at different graft systems with DR1

Polymer	Graft (%)	Mathematic expression	Correlation ( $R^2$ )
PE	5.7	$y = 2.62 e^{-0.00330x}$	0.99694
PP	5.8	$y = 2.28 e^{-0.00337x}$	0.98421
PP	9.6	$y = 0.83 e^{-0.00140x}$	0.97678
PET	4.3	$y = 3.59 e^{-0.00010x}$	0.95790
PC	8.2	$y = 0.09 e^{-0.00923x}$	0.97974
PP*	9.6	$y = -4 \times 10^{-6x} + 1$	0.97974

\*Exposure to sun light.

Absorbance of UV decay was also observed by solar irradiation in the system of ACDR1-g-PP and this decay was thousand times slower than UV lamp irradiation. We observed approximately the similar mathematic expression for PP and PE with the similar graft % and decrease of the exponential factor with increase of graft % in the PP system.



## Conclusions

Different systems of Disperse Red 1 acrylate grafted in PE, PP, PC and PET were synthesized and characterized, UV absorption decay by irradiation with UV lamp was observed and this behavior studied to see if they could be applied as photochemistry dosimeter. Decay rate is different in all polymers studied, and it could be useful as dosimeters, depending of the radiation dose utilized with a lineal and proportional behavior in some range of irradiation. PET polymer matrix can be used for high irradiation doses.

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