Polymer Bulletin 52, 73–82 (2004)
DOI 10.1007/s00289-004-0250-8

Polymer Bulletin

Immobilization of disperse red 1 onto polydiethyleneglycol-bis-allylcarbonate (CR-39) radiation grafted with poly(acryloyl chloride)

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Received: 15 April 2004/Accepted: 20 April 2004

Abstract

Acryloyl chloride (AC) was radiation grafted from 30% solution of monomer in toluene onto polydiethyleneglycol-bis-allylcarbonate (CR-39) by their simultaneous γ-irradiation. The grafting process was more efficient at dose rate of 4.4 kGy/h as compared with 0.4 kGy/h, and grafting values of 15-18% were achieved at 2.2-5.5 kGy. Subsequent immobilization of disperse red 1 (DR1) onto the grafted polymer was carried out from 0.02 M solution of this dye in dichloroethane, and the immobilized DR1 yield increased with the grafted polyAC value. Surfaces of the starting and modifed CR-39 were characterized with the FTIR-ATR spectroscopy and atomic force microscopy. An essential difference in chemical structure and topography of the CR-39 surface before and after the DR1 immobilization has been shown. The colourless plates of CR-39 became red after the DR1 immobilization, and the color intensity increased with the dye content. Changes in visible absorption spectra of the immobilzed DR1 caused by the photoinduced trans-cis isomerization of this dye were discussed.

Introduction

At present, there is an essential interest in developing polymeric materials with second order nonlinear optical (NLO) properties, and a special attention is paid to these materials synthesis and characterization [1,2]. Disperse red 1 (DR1) is a well known nonlinear chromophore, and it is widely used for binding to some optically transparent polymers with good mechanical durability and thermal stability like polystyrene [3-6], poly(methyl methacrylate) [3,7-12] and polycarbonate [3,13]. Changes in optical properties of the obtained compositions due to the photo-induced trans-cis isomerization of this azo dye have been shown [9,10,12].

Polydiethyleneglycol-bis-allylcarbonate (CR-39®) is a thermoset plastic that combines excelent optical clarity with good mechanical properties. CR-39 is used in the optical industry as a casting resin to produce lenses, rods, tubes and flat sheets of high quality [14]. But it seem to be no data on coupling of CR-39 with DR1.

Radiation graft polymerization is widely used for polymers modification and, in particular, for immobilization of different compounds, mainly, biomolecules (enzymes, proteins etc) [15,16]. Radiation grafting is used also to improve a dyeability of polymers [17-19], but apparently this method has never been applied before for a subsequent immobilization of dyes with the NLO properties. As to the DR1, recently a synthesis of a new polymer surface bearing this grafted dye was reported [20]. But in this case, DR1 was transformed into an acrylic monomer and then grafted onto a polypropylene surface modified with a cold carbon dioxide-plasma treatment, and optical properties of this composition were not studied.

Radiation grafting of acryloyl chloride (AC) from liquid or vapor phase of this monomer onto polyethylene, polypropylene and polytetrafluoroethylene was investigated earlier [21-23]. An efficient grafting by the direct method, when the polymers were irradiated in contact with the AC, was observed, and the polyAC grafting values of 8-30% were achieved at the doses range of 0.5-2 kGy, i.e. under relatively mild irradiation conditions. Besides, it has been shown [21] that chloroanhydride groups, which are sensitive to hydrolysis, transformed slowly to carboxyl groups in the presence of atmospheric moisture, and this process was completed after samples keeping in open air for 100-120 h. The grafted polyAC was used successfully as the acylation agent in reactions with benzylamine, heparine [21], methanol [22,23] and tolane-containing alcohols [22].

It is known that polycarbonates (PC) are radiation degradable polymers, and, for example, γ-irradiation of bisphenol-A PC was accompanied by formation of different gaseous product, including carbon oxides due to this polymer chain breaking through carbonate bond rupture [24]. Carbon dioxide formation was also detected by the CR-39 γ-irradiation, and this gas yield was investigated at the doses range of 130-950 kGy [25]. It should be noted that essential deterioration of optical and mechanical properties of polycarbonates, caused by their degradation, occurs at high absorbed doses more than 10^3 kGy [26].

There are a few publications concerning radiation grafting onto CR-39. Earlier we studied radiation grafting of N,N-dimethylaminoethylmethacrylate (DMAEMA) from its 50% solution in chloroform onto CR-39 by the method of this polymer preirradiation in air, and the polyDMAEMA grafting achieved value of 20% [27]. Besides, grafting of N-isopropylacrylamide and acryloyl-l-proline methyl ester was carried out onto surface of pores produced in the CR-39 by this polymer irradiation with heavy ion beams [28].

In the present study, radiation grafting of AC onto CR-39 followed by the DR1 immobilization on the modified polymer as well as some characterizations of the compositions obtained are reported.

Experimental

Plates of CR-39 (Pershore Mouldings Limited, England) with a thickness of 0.25 mm and size of 1x5 cm were washed in methanol, and then dried under vacuum to a constant weight. AC, DR1, toluene, dichloroetane, chloroform and methanol were supplied by Aldrich Chemical Co. AC and solvents were purified by distillation at a reduced and atmospheric pressure, respectively. After purification, the CR-39 plates, monomer and solvents were stored in desiccator over $CaCl_2$ to avoid their contact with atmospheric moisture.

For the swelling to be characterized, the CR-39 plates were immersed in 30 vol % solution of AC in toluene or chloroform at room temperature until equilibrium swelling was reached. Then samples were taken out from this solution, and the excess solution deposited on the film surface was removed quickly with blotting paper, and the samples were weighed. The swelling degree was calculated by the equation: swelling (%) = $(W - W_0)100/W_0$, where W and W_0 are the weights of swollen and dry samples, respectively.

The CR-39 plates were placed in glass ampoules which contained 30% solution of AC in toluene. The ampoules were deaerated under vacuum by repeated freezing and thawing method, then they were sealed and irradiated with a ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) at the dose rates of 0.4 or 4.4 kGy/h and time from 1 to 6 h. To extract the residual monomer and polyAC homopolymer that could be formed and occluded in the films during the irradiation, the grafted samples were washed with dichloroethane for 12 h in a closed flask, then samples were dried under vacuum to a constant weight. The grafting yields were determined from weights increase in the modified CR-39 samples against the starting polymer.

Samples with different content of the grafted polyAC was placed immediately in dichloroetane solution of DR1 with concentrations from 0.01 to 0.03 M, triethylamine (nucleophilic catalyst) was added, and the DR1 acylation was carried out in a closed flask by stirring of the reactive volume for 24 h. Then, the samples were washed with methanol (in the presence of triethylamine) to remove the unreacted DR1 and for convertion of the remaining chloride to the methyl ester. Substitution of Cl atoms for OCH3 prevents a hydrolysis of the remaining chloride to carboxylic groups by the samples storage. After treatment with methanol, which became red in the presence of the unreacted DR1, the samples were dried under vacuum to a constant weight. This procedure was repeated untill the methanol colourlessness and the samples weights did not change. Yields of the immobilized DR1 were determined from weights increase in these compositions against the CR-39 grafted with polyAC.

FTIR-ATR spectra of the starting and modified CR-39 surfaces were obtained with the Perkin-Elmer (model Paragon 500) spectrometer. ZnSe glass was used for contact with the samples surfaces, and the IR radiation penetrated into samples to depth of 5-6 μm.

Examination of the the starting and the modified CR-39 surfaces was carried out using atomic force microscopy (AFM) with a NanoScope IIIa of Digital Instruments Inc, and images were recorded with contact mode at room temperature. The scan speed was 1.5 Hz, and low scanning forces (0.3 N/m) were used to avoid a surface damage.

Samples with the immobilized DR1 (17%) were subjected to irradiation with the 450 W medium pressure mercury lamp of the Ace Glass in the presence of argon to avoid the samples photooxidation, and the DR1 visible spectra were obtained with a Varian (model Cary 100) UV-visible spectrophotometer.

Results and discussion

Preliminary irradiation of the CR-39 plates up to 10 kGy did not result in any visible changes in their transparency and mechanical durability as compared with the starting ones.

The previous investigations on radiation grafting of AC onto different polymers [21-23] showed that reduced monomer concentrations were expedient to decrease its undesirable homopolymerization by irradiation of the polymer/monomer systems. It is known also that value of preliminary swelling of polymer in the monomer solution effects a distribution of the grafted chains in the polymer matrix. Under condition of good preliminary swelling of a starting polymer, an essential part of monomer penetrates in a polymer volume, and then grafted chains are formed, mainly, inside this polymer. But for the preferable surface grafting, non-swollen or partially swollen polymer-monomer systems are used [29]. Equilibrium swellings of CR-39 in 30% solutions of AC in chloroform and toluene were equal to 20% and 3%, respectively, and the AC/toluene solution was chosen for the grafting experiments.

Fig.1 shows a higher efficiency of the AC grafting at dose rate of 4.4 kGy/h as compared with the 0.4 kGy/h. It is known from theory and practice of radiation grafting that rate of this process increases with a dose rate, and linear kinetic dependences are observed, at least, at initial stages of grafting [29]. In our case, the grafting rate decceleration can be explained by competition of the monomer grafting and homopolymerization. The last process was controlled visually from a viscosity increase in monomer solutions at both dose rates. At 0.4 kGy/h, the partial AC homopolymerization was observed at 2.5 h of irradiation (1 kGy), then it increased essentially and hindered the grafting values obtaining more than 7-8%. But at 4.4 kGy/h, the monomer solution was practically liquid up to 0.25-05 h of irradiation (~1-2 kGy) that allowed to achieve 15% of grafting. Nevertheless, a further increase in grafting values was deccelerated because of the appreciable AC homopolymerization.

To find an optimal content of the immobilized DR1 in the CR-39 with grafted polyAC, the acylation process was performed from solutions with different concentration of this dye in dichloroethane, and the DR1 content increased with its concentration in solution (Fig.2). Concentration of 0.02 M was used to find dependence of the DR1 accumulation in the CR-39/polyAC compositions on the polyAC content (Fig.3). It is seen that yields of the immobilized DR1 were relatively low in spite of a big molecular weight of this dye. The calculations showed that DR1 content could reach 50%, against 17% in our case, if all Cl atoms of the polyAC would be substituted for this dye molecules. It means that only a little part (~1/3) of the grafted polyAC reacted with the DR1, and the remaining chloride formed the grafted poly(methyl acrylate). Determination of the DR1 content was done against the weight of CR-39 with grafted polyAC. If substitution of the remaining Cl atoms for OCH_3 groups practically did not change the grafted polymer weight, the DR1 immobilization was accompanied by the Cl atoms leaving from the polyAC that resulted in some decrease in weight of the grafted part estimated as 15% under condition that 1/3 of the Cl atoms were substituted for the DR1. In this case, a decrease in total weights of CR-39 with grafted polyAC was about of 2% due to relatively low contents of the grafted polyAC in these compositions. Thus, the error of the DR1 determination did not exceed ~2%.

Both the polyAC grafting and the subsequent DR1 immobilization did not deteriorate appreciably the modified CR-39 transparency and mechanical durability, but the colourless plates of the starting polymer became red after DR1 immobilization, and the color intensity increased with the dye content.

The simplified Scheme 1 shows the AC radiation grafting followed by the DR1 immobilization. The proposed scheme of grafting is based on fundamental investigation of this process described in the appropriate monographs [15,26,29]. Irradiation of CR-39 results in abstraction of the hydrogen atoms from the polymer, preferably at the tertiary carbon atoms, and the formed CR-39 macroradicals initiate the AC graft polymerization (only one growing polyAC chain is shown in this scheme). Then, chloroanhydride groups of the grafted polyAC are involved in the acylation reaction with OH-groups of the DR1.

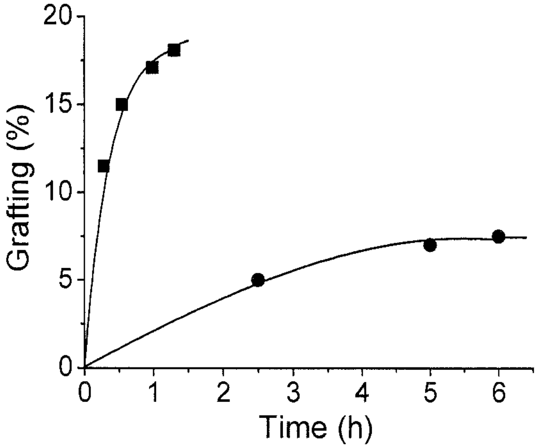


Fig. 1 Grafting of AC from 30% solution in toluene as a function of irradiation time. Dose rates: 4.4 (ν) and 0.4 (λ) kGy.

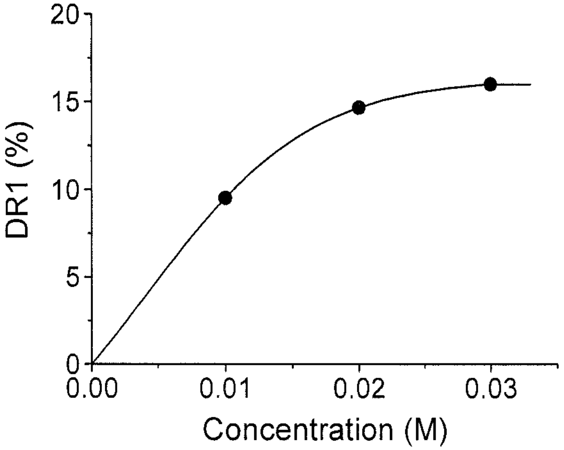


Fig. 2 Content of the immobilized DR1 in the modified CR-39 as a function of the DR1 concentration in dichloroethane. Content of the grafted poly AC – 15%.

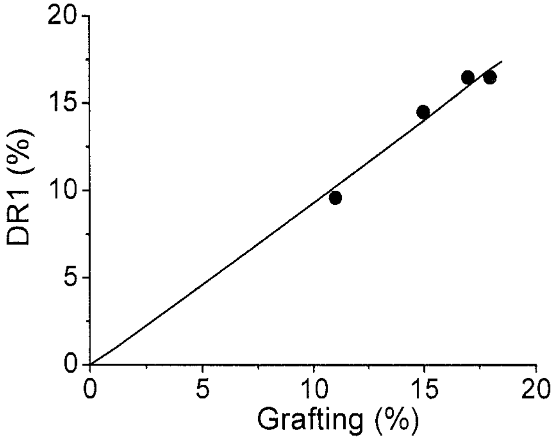
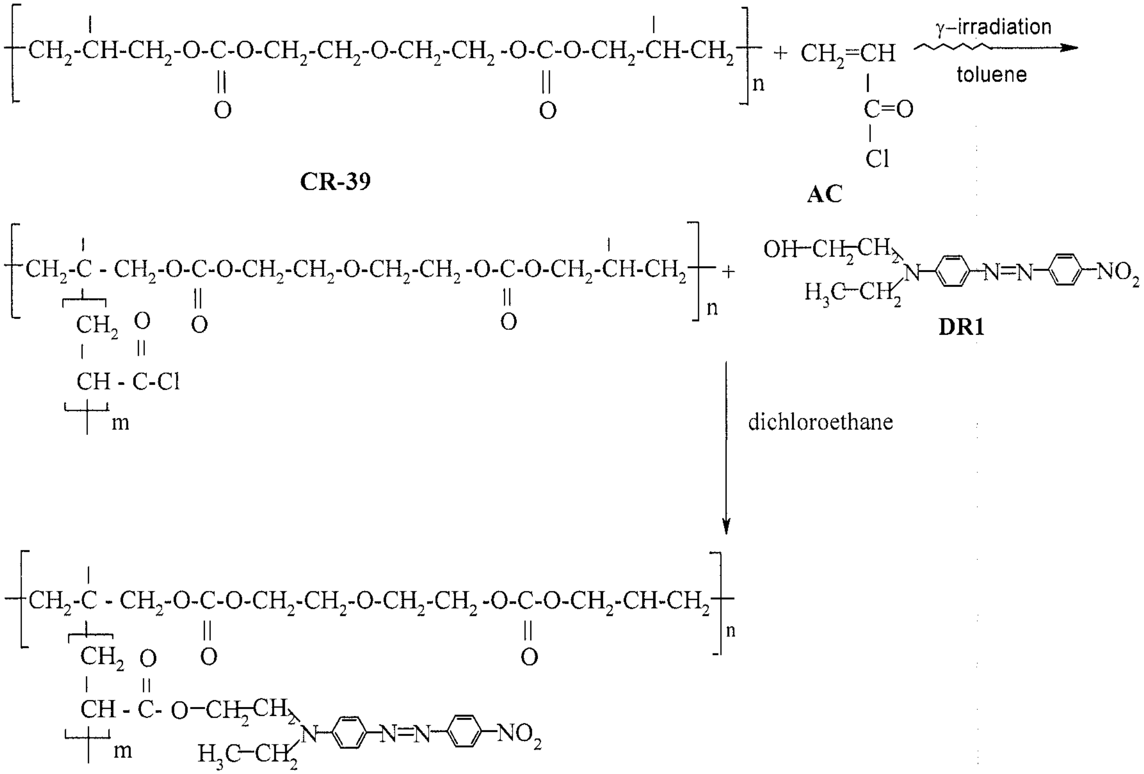


Fig. 3 Content of the immobilized DR1 in the modified CR-39 as a function of the poly AC grafting.



Scheme 1

The IR spectrum of the CR-39 with the grafted polyAC did not reveal new peaks as compared with the starting polymer. Apparently, the broad absoption bands of CR-39 (1732 and 950 cm^{-1}) overlap absorptions at 1750 cm^{-1} and 970-940 cm^{-1} attributed to the COCl groups [30] of the grafted polyAC. Besides, a broad band at 3300-2500 cm^{-1} responsable for the O-H stretching vibrations in carboxylic groups [31] was not found that indicated absence of the COCl groups hydrolysis. But spectrum of polymer composition with the immobilized DR1 (Fig.4) contained 3 new peaks at 1600, 1500 and 1328 cm^{-1} due to aromatic rings and NO_2 groups stretching vibrations, respectively [31], and some displacement of peak near 1400 cm^{-1} to a long-wave region can be explained by the poly(methyl acrylate) formation after treatment of the remaining chloride with methanol.

AFM revealed essential difference in topographies of the starting CR-39 and with the immobilized DR1 (Fig.5). The CR-39 surface (a) was relatively smooth with average roughness of 100 nm. An irregular covering of the polymer surface was observed at 10% of the immobilized dye (b), and the roughness increased significantly. But further increase in the DR1 content (c) resulted in its more uniform distribution on the polymer surface. These results can be explained by the different content of the grafted polyAC on the CR-39 surface (Fig.3). It has been shown earlier (32-34) that grafted chains formed separate microdrops on the starting polymers surfaces at an initial stage of grafting. These microdrops increased and merged as grafting values increased. Continuous grafted layers formation began at grafting contents of 10-15%, and the modified surfaces became more smooth. But in our case, it is possible to assume that higher DR1 content can contribute also in smoothing of the modified surface.

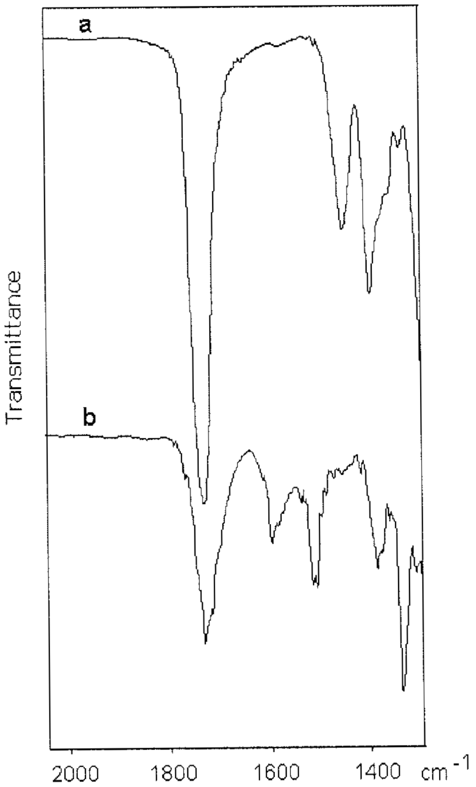


Fig. 4 FTIR spectra of the starting (a) and the modified (b) CR-39 surfaces. Content of the immobilized DR1-17%

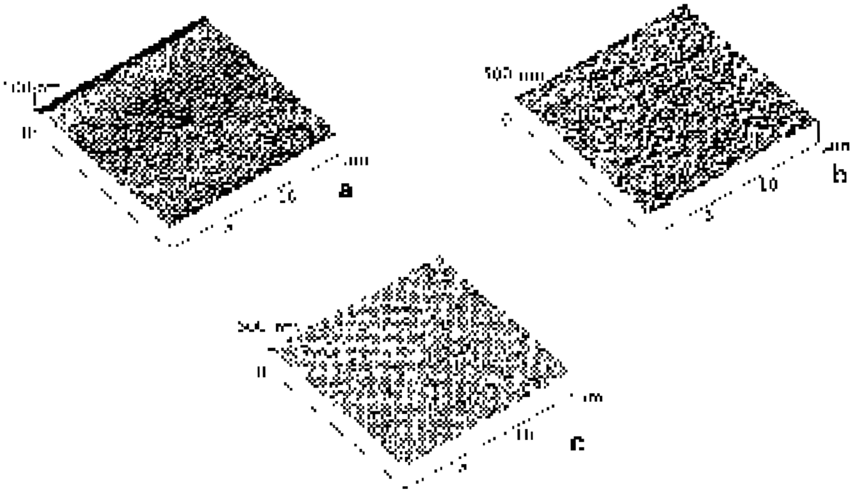


Fig. 5 AFM pictures of the starting CR-39 (a) and the modified compositions with different content of the immobilized DR1: 10% (b) and 17% (c).

Fig.6 shows essential changes in visible spectra of the immobilized DR1 caused by irradiation with the UV lamp. The peak at 515 nm decreased with irradiation time, and red color disappeared completely after ~2.5 h of irradiation (d) due to trans-cis transformation in this azo dye. But the colorless sample (d) regained partially its red color after storage for 24 h at room temperature (e).

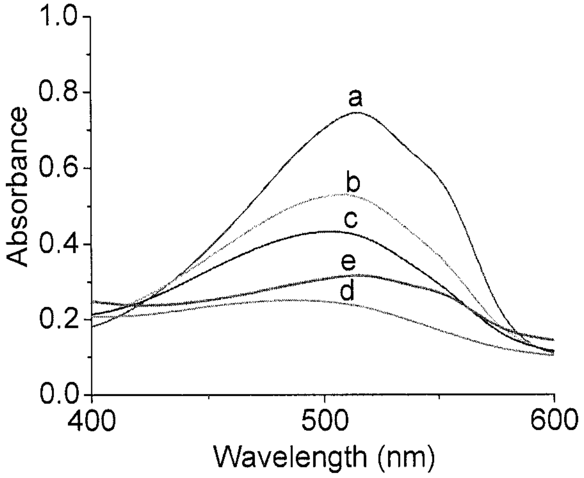


Fig. 6 Visible spectra of the immobilized DR1 (17%). UV irradiation time (min): 0(a), 20(b), 40(c) and 160(d). Irradiated sample (d) after storage for 24 h at 25^{0}C (e).

Conclusion

The efficient grafting of AC (15-18%) onto CR-39 from 30% solution of this monomer in toluene was achieved under mild irradiation conditions: dose rate of 4.4 kGy/h and absorbed doses of 2.2-5.5 kGy. But at lower dose rate (0.4 kGy/h), the grafting process was complicated with essential monomer homopolymerization that resulted in the grafting decrease. The immobilized DR1 yield increased with the grafted polyAC value. The DR1 immobilization resulted in the essential roughness of the polymer surface, and uniformity of the DR1 distribution on this surface increased with its content in the modified polymer. Colorless CR-39 became red due to DR1 immobilization, the color disappeared after ~2.5 h of the UV irradiation but it was regained partially after the sample storage for 24 h at room temperature.

Acknowledgements. This work was supported by the UNAM grant from DGAPA No 100400. The authors are grateful also to Francisco García, Martin Cruz and Salvador Ham (ICN-UNAM) for their technical assistance.

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