

# Graft copolymerization onto polycarbonate film\*

J. ŻURAKOWSKA-ORSZÁGH and M. GÓRA

*Department of Chemical Technology, University of Warsaw,  
02-093 Warsaw*

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Graft copolymerization of a series of acrylates and corresponding methacrylates onto polycarbonate film of Polish production has been investigated. The initiation was performed by chemical initiator as well as by simultaneous irradiation and preirradiation method. The regular decrease of the reactivity with the increase of alkyl substituent was observed and higher grafting yield was always obtained for the monomers of the methacrylic series. The influence of the thickness of the samples on the graft copolymerization has been discussed, too.

Была исследована привитая сополимеризация серии акрилатов и соответствующих метакрилатов на поликарбонатных пленках польского производства. Иницирование было вызвано химическим инициатором и также одновременным облучением или предварительным облучением. Было обнаружено регулярное уменьшение реактивности с увеличением алкильного заместителя и в случае мономеров серии метакрилатов был всегда обнаружен более высокий выход привитой сополимеризации. Обсуждается также влияние толщины образцов на привитую сополимеризацию.

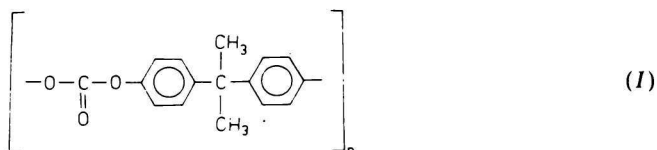
Little information is available in the literature on chemically induced graft copolymerization of polycarbonates [1, 2]. The purpose of this paper is to study the graft copolymerization of a series of methacrylic and acrylic esters onto polycarbonate films of various thickness using chemical initiators, simultaneous irradiation as well as the preirradiation method.

## Experimental

Polycarbonate *I* of Polish production of average molecular weight about 90 000 was the polymer selected for the investigation. Films of thickness 40, 60, and 80  $\mu\text{m}$  were prepared

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by casting from methylene chloride solution. Samples of area 50 cm<sup>2</sup> were cut from the films and submitted before use to extraction in boiling acetone to constant weight. Weight loss amounted to 1%.

The following monomers were used for grafting: methyl methacrylate (MMA), ethyl methacrylate (EtMA), butyl methacrylate (BuMA), and isooctyl methacrylate (OctMA) of the methacrylic series and methyl acrylate (MA), ethyl acrylate (EtA), and butyl acrylate (BuA) of the acrylic series. The monomers were purified before use by repeated vacuum distillation in order to remove traces of inhibitors.

The grafting process was performed in methanol solutions (200 ml) of respective monomers at 0.5 and 1 M concentration. In the case of chemical initiation benzoyl peroxide was added and the reaction was carried out at the boiling temperature of methanol. Radiation grafting was performed by simultaneous irradiation as well as by preirradiation method. All grafting reactions were carried out in pure, oxygen-free nitrogen. Irradiation was carried out in a  $\gamma$ -ray <sup>60</sup>Co source of activity about  $5.5 \times 10^{13} \text{ s}^{-1}$ . After the grafting reaction the polycarbonate films were removed from the solution and submitted to extraction in boiling acetone until constant weight was achieved. The grafting yield was determined gravimetrically. All results were calculated in mole % in relation to the monomer and in relation to the weight of the sample.

## Results and discussion

The effect of the structure of particular monomers on their ability to grafting onto polycarbonate shows certain regularity.

For instance the presence of the methyl substituent on the  $\alpha$ -carbon seems to increase the grafting efficiency. The comparison of graft copolymerization of pairs of monomers with similar esters groups shows that under identical experimental conditions grafting was always higher with monomers of the methacrylic series independently of the method of initiation. Results obtained for benzoyl peroxide initiated grafting of methyl methacrylate and methyl acrylate as well as butyl methacrylate and butyl acrylate are shown in Fig. 1.

To get comparable results from the point of view of the yield of grafting for particular monomers the data are expressed in mole % per 1 g film weight. It should be pointed out that similar differences even more pronounced in the grafting ability between acrylates and corresponding methacrylates have been reported in our previous paper dealing with the graft copolymerization of the same monomers onto polyethylene [3].

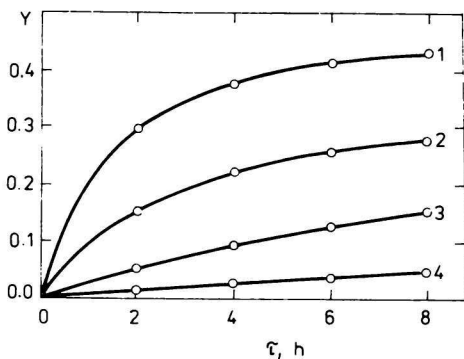


Fig. 1. Comparison of graft copolymerization of two pairs of acrylic and methacrylic series.  $\tau$  — time of grafting;  $Y$  — yield in mole % per 1 g film weight.

1. MMA; 2. MA; 3. BuMA; 4. BuA.

The study of grafting efficiency of particular series shows that under identical experimental conditions the same order in the monomer range was always obtained, namely:

for the methacrylic series

methyl methacrylate > ethyl methacrylate > butyl methacrylate,

for the acrylic series

methyl acrylate > ethyl acrylate > butyl acrylate.

The data obtained for chemically induced grafting of monomers of methacrylic series are presented in Fig. 2, those of acrylic series in Fig. 3.

For grafting copolymerization induced by simultaneous irradiation as well as preirradiation technique the same order in the monomer reactivity was observed, only the differences between the grafting yield of particular esters were smaller.

The influence of the so-called "thickness effect" on graft copolymerization was studied in the relation to the monomer introduced into the system and in the

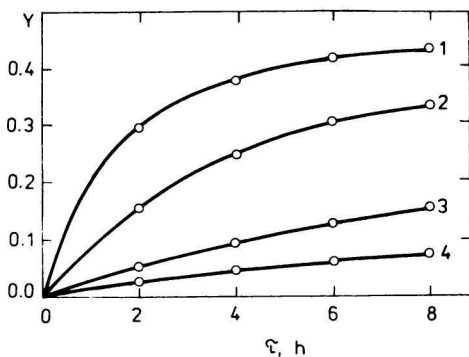


Fig. 2. Grafting of the series of methacrylic esters onto polycarbonate film.  $\tau$  — time of grafting;  $Y$  — yield in mole % per 1 g film weight.

1. MMA; 2. EtMA; 3. BuMA; 4. OctMA.

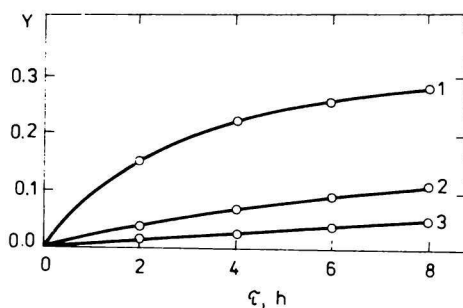


Fig. 3. Grafting of the series of acrylic esters onto polycarbonate film.  $\tau$  — time of grafting;  $Y$  — yield in mole % per 1 g film weight.

1. MA; 2. EtA; 3. BuA.

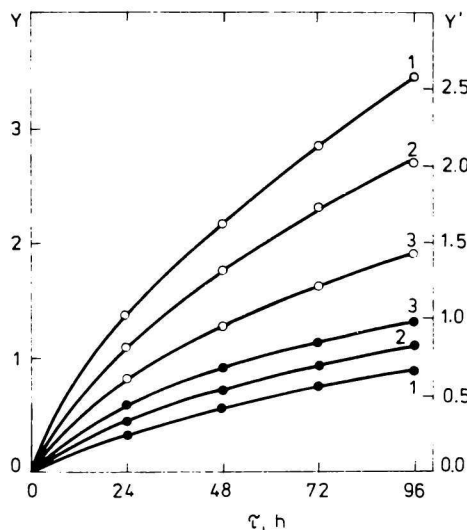


Fig. 4. Effect of film thickness on graft copolymerization of butyl methacrylate on preirradiated polycarbonate.  $\tau$  — time of preirradiation;  $Y$  — yield in mole % in relation to the monomer;  $Y'$  — yield in mole % per 1 g film weight.

1. 80  $\mu$ ; 2. 60  $\mu$ ; 3. 40  $\mu$ .

○ mole % per 1 g film weight; ● mole % in relation to the monomer.

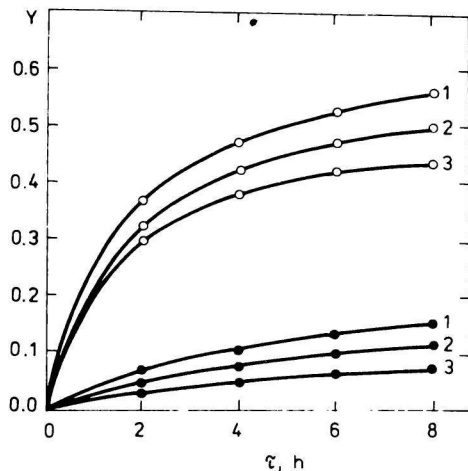


Fig. 5. Grafting yield calculated in relation to the film weight of methacrylic esters on polycarbonate film of various thickness.  $\tau$  — time of grafting;  $Y$  — yield in mole % per 1 g film weight.

1. 40  $\mu$ ; 2. 60  $\mu$ ; 3. 80  $\mu$ .

○ MMA; ● OctMA.

relation to the weight of the polymer film. When grafting yield was calculated in relation to the monomer higher values were obtained always with thicker film independently of the method of grafting applied. This is quite understandable as in this case the random possibility of graft copolymerization of the given amount of monomer increases in relation to the competitive homopolymerization due to higher amount of polymer present in the system, which may cause the formation of a larger amount of active centres on the macromolecules. The accelerating influence of film thickness is especially pronounced in the case of radiation initiation due to the degradative effect of the ionizing radiation on the polycarbonate chains enabling diffusion of the monomer among the polymer chains. On the other hand, when grafting yield is given in weight % or in mole % but in relation to the weight of the polymer film sample then, according to our experiments, the grafting yield usually decreases with the increase in film thickness. The results obtained for graft copolymerization of butyl methacrylate on preirradiated polycarbonate film are shown in Fig. 4, the data being expressed in relation to the monomer and to the weight of the sample.

The comparison of the influence of the film thickness on chemically initiated

graft copolymerization of methyl methacrylate and iso-octyl methacrylate calculated in relation to the film weight is presented in Fig. 5. Some deviations of this order have been observed only for iso-octyl methacrylate in the case of simultaneous irradiation due probably to the effect of the branched substituent.

The experimental results show that the chemically initiated grafting process proceeds mainly on the surface layer of the polycarbonate film.

Some deviations of the results were obtained for the source irradiation method, where the so-called "thickness effect" is so pronounced that even when results were given in relation to the weight of the sample similar or even higher data were obtained for film of higher thickness. This may be due to the constant formation of new macroradicals during simultaneous irradiation enabling the formation of new branches and thus increasing the branching yield.

### References

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