

Graft copolymerization of a series of alkyl acrylates and alkyl methacrylates onto polyethylene*

J. ŻURAKOWSKA-ORSZÁGH, K. SOERJOSOEHARTO, W. BUSZ,
and J. OŁDZIEJEWSKI

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

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Graft copolymerization of a series of alkyl acrylates and alkyl methacrylates onto polyethylene of Polish production was investigated, using benzoyl peroxide as initiator as well as the preirradiation technique, namely ionizing radiation from a ^{60}Co γ -source. The effect of α -carbon methyl substituent of methacrylates as well as the influence of the length of alkyl chains in the esters groups of both series of monomers onto the grafting process was observed. Both the ungrafted and some of the grafted polyethylene film obtained were studied by infrared spectrophotometry.

Исследовалась привитая сополимеризация ряда алкилакрилатов и алкилметакрилатов на полиэтилене польского производства. Образцы предварительно облучались в ^{60}Co источнике γ -излучения, в качестве инициатора применялась перекись бензоила. Изучалось влияние метильного заместителя в метакрилатах и длины алкильной цепи в эфирных группах на процесс прививки в обеих рядах мономеров. Как непривитые так и некоторые из привитых образцов полиэтиленовой пленки исследовались методом ИК-спектрофотометрии.

Graft copolymerization of some acrylic and methacrylic esters onto polyethylene has been investigated by many authors using different methods. Various experimental conditions had been applied and this makes it difficult to compare the results obtained [1—11].

The main aim of the present paper is a systematic study of the grafting process of two large homologous series of acrylic and methacrylic esters onto polyethylene of Polish production initiated by chemical method as well as preirradiation technique. In order to get comparable results all processes were performed under equal experimental conditions.

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Experimental

The long-chain alkyl acrylates were synthesized using the method proposed by *Rehberg* and *Fisher* [12], while long-chain methacrylates by *Crawford's* method [13], *i.e.* from the methyl esters which are available. The following monomers were used:

a) 8 acrylates, namely: the methyl (MA), ethyl (EtA), propyl (PrA), butyl (BuA), pentyl (PtA), heptyl (HpA), octyl (OctA), and decyl acrylate (DecA);

b) 8 methacrylates, namely: the methyl (MMA), ethyl (EtMA), propyl (PrMA), butyl (BuMA), pentyl (PtMA), heptyl (HpMA), octyl (OctMA), and decyl methacrylate (DecMA).

All liquid monomers were purified by extraction with dilute NaOH (to remove hydroquinone), thorough washing with distilled water, drying during 24 h over dry CaCl_2 , and used immediately after distillation.

Polyethylene film of thickness $60\ \mu\text{m}$ was selected for the experimental work. The properties of polyethylene were as follows: melting point 105°C ; density $0.919\ \text{g cm}^{-3}$; crystallinity 55%. Samples of dimension $6 \times 4\ \text{cm}$ were extracted in benzene and then in 1:1 benzene—methanol solution at $40\text{--}45^\circ\text{C}$ and dried to constant weight *in vacuo*.

The grafting by chemical method was performed in methanol solution of 1 M concentration of particular monomers in the presence of benzoyl peroxide as initiator. The reaction was performed at temperature of boiling methanol.

In the case of preirradiation grafting, polyethylene samples of the same dimension were subjected to irradiation in a γ -source "Gammacell-220" at dose rate $20.862\ \text{C kg}^{-1}\ \text{h}^{-1}$. The samples were placed in the γ -source chamber concentric to the γ -rays to get uniform irradiation conditions. Irradiation was performed in the air at temperature about 25°C for the time ranging from to 168 h. Immediately after irradiation the samples were placed into Erlenmeyer flask containing respective monomers for the grafting process. This operation was done simultaneously for both series of esters. The grafting procedure was the same as in chemical method, but benzoyl peroxide was not present.

As soon as the grafting process was finished, the samples were removed from the reaction mixture, extracted in benzene, further with 1:1 benzene—methanol solution and finally rinsed with methanol. The samples were then vacuum dried at 45°C and weighted. This operation was repeated several times until constant weight was obtained.

Results and discussion

Grafting by chemical method

The chemically induced graft copolymerization of alkyl methacrylates for different times of grafting, namely 1, 2, 3, 4, 6, and 8 h, is presented in Fig. 1. For all monomers of this series of homologues the general shape of curves representing the yield of grafting (in moles per 1 g film weight vs. time in h) is very similar. Fig. 1 also shows that the yields of grafting decrease with increasing lengths of the alkyl substituents.

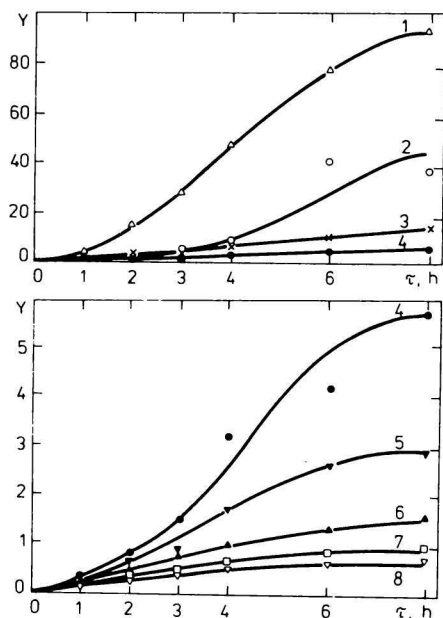


Fig. 1. Chemically induced graft copolymerization of *n*-alkyl methacrylates onto polyethylene film. τ — time of grafting; Y — grafting yield in mmoles per 1 g film weight.

1. MMA; 2. EtMA; 3. PrMA; 4. BuMA; 5. PtMA; 6. HpMA; 7. OctMA; 8. DecMA.

The comparison of data obtained for chemical grafting of acrylates and methacrylates presented in Table 1 and 2 shows that yields of grafting obtained for the acrylates are usually much smaller and not so regular as for the methacrylates. Relatively smaller differences are obtained for the esters of both series with long alkyl substituents.

As it is mentioned before, the competitive homopolymerization process occurs. The data obtained for these two processes in % to monomer are presented in Table 1 and 2 for methacrylic and acrylic esters. The comparison of these results shows that much larger number of monomer molecules were consumed by the homopolymerization than by the grafting reaction. The homopolymerization rate is always higher for the acrylic than for methacrylic esters, however the shapes of both curves are very similar.

The polyethylene samples (ungrafted and grafted) were studied by infrared spectrophotometry. New peaks characteristic of polyacrylic and polymethacrylic chain appeared in the spectra of grafted polyethylene. Especially the peak at 1730 cm^{-1} corresponding to the vibration of carbonyl group is very characteristic.

The experimental results show that the infrared spectrophotometric method is in a good agreement with the gravimetric method used in our experiments. The height of the characteristic peaks is proportional to the amount of grafting yields showing clearly the difference between the reactivity of acrylic and methacrylic monomers in the graft copolymerization process.

Table 1

Comparison of homopolymerization and graft copolymerization of the methacrylic series onto polyethylene

Monomer	<i>t</i> h	Homopoly- merization %	Graft %	Monomer	<i>t</i> h	Homopoly- merization %	Graft %
MMA	1	18.77	0.084	PtMA	1	10.50	0.005
	2	28.60	0.300		2	16.95	0.012
	3	49.95	0.553		3	32.50	0.016
	4	61.50	0.955		4	40.65	0.034
	6	65.85	1.538		6	55.35	0.049
	8	75.12	1.884		8	59.20	0.057
EtMA	1	13.80	0.019	HpMA	1	7.10	0.004
	2	29.40	0.032		2	15.20	0.009
	3	47.10	0.116		3	19.25	0.016
	4	58.90	0.167		4	35.65	0.013
	6	75.10	0.322		6	41.20	0.024
	8	81.50	0.745		8	63.25	0.031
PrMA	1	11.65	0.032	OctMA	1	30.10	0.006
	2	22.50	0.051		2	49.25	0.007
	3	39.10	0.073		3	55.10	0.009
	4	55.75	0.134		4	65.75	0.015
	6	62.30	0.184		6	71.20	0.017
	8	70.65	0.271		8	72.50	0.019
BuMA	1	24.50	0.006	DecMA	1	35.65	0.002
	2	39.35	0.016		2	54.80	0.005
	3	50.80	0.029		3	58.50	0.007
	4	51.50	0.064		4	72.70	0.009
	6	60.90	0.083		6	79.50	0.012
	8	62.75	0.114		8	85.15	0.014

Grafting by preirradiation technique

To establish the most appropriate time of preirradiation, some experiments were done in grafting of methyl methacrylate (MMA) for systematically increasing preirradiation time ranging from 8 to 168 h and for time of grafting 2 h. The results are presented in Fig. 2. The yield of grafting expressed in mmoles per 1 g film weight as well as in % to monomer increases with time of irradiation of polyethylene film, reaching maximum value at 48 h. For longer times of preirradia-

Table 2

Comparison of homopolymerization and graft copolymerization of the acrylic series onto polyethylene

Monomer	<i>t</i> h	Homopoly- merization %	Graft %	Monomer	<i>t</i> h	Homopoly- merization %	Graft %
MA	1	26.50	0.005	PtA	1	51.90	0.014
	2	47.90	0.013		2	69.70	0.017
	3	58.10	0.020		3	78.15	0.021
	4	72.00	0.034		4	82.90	0.025
	6	80.60	0.063		6	87.65	0.038
	8	85.10	0.088		8	91.25	0.041
EtA	1	34.00	0.007	HpA	1	52.60	0.014
	2	55.10	0.018		2	61.40	0.019
	3	66.50	0.024		3	69.30	0.022
	4	72.80	0.057		4	78.25	0.029
	6	83.50	0.074		6	80.10	0.033
	8	85.20	0.189		8	85.20	0.035
PrA	1	20.25	0.011	OctA	1	64.20	0.016
	2	32.50	0.023		2	67.95	0.018
	3	43.00	0.038		3	72.30	0.020
	4	50.75	0.052		4	76.25	0.023
	6	61.10	0.072		6	85.30	0.028
	8	76.50	0.095		8	88.10	0.041
BuA	1	25.25	0.014	DecA	1	65.50	0.023
	2	35.00	0.033		2	70.20	0.024
	3	49.50	0.055		3	71.35	0.026
	4	53.50	0.073		4	79.60	0.029
	6	57.85	0.087		6	82.45	0.033
	8	61.25	0.092		8	88.90	0.047

tion the yield of grafting decreases slowly. This effect can be explained by the following factors:

- a) increasing concentration of macroradicals,
- b) decreasing crystallinity,
- c) increasing formation of crosslinks with time of irradiation.

These phenomena influence the grafting yield simultaneously, but in the opposite way directions, so that the resulting effect is obtained. Oxidation occurs during irradiation in air and the appearance of C=O bands is observed in the infrared spectra. The intensity of these peaks increases regularly with time of irradiation. However, for lower doses corresponding to time of exposition up to 16 h selected for these investigations the effect of oxidation can be neglected.

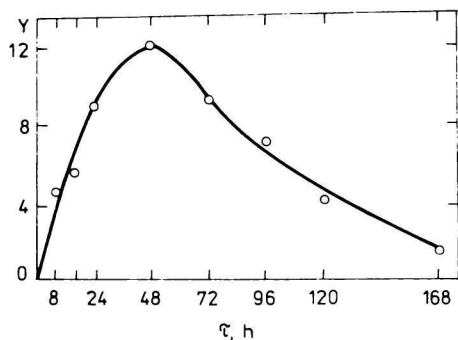
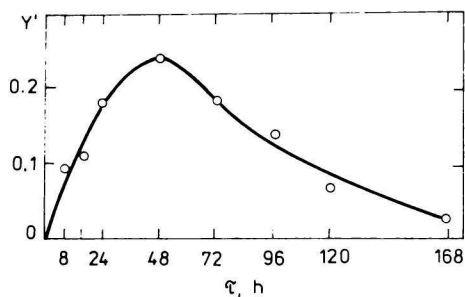


Fig. 2. Effect of the preirradiation time on the graft copolymerization of methyl methacrylate onto polyethylene. τ — preirradiation time; Y' — grafting yield in % to monomer; Y — grafting yield in mmoles per 1 g film weight.

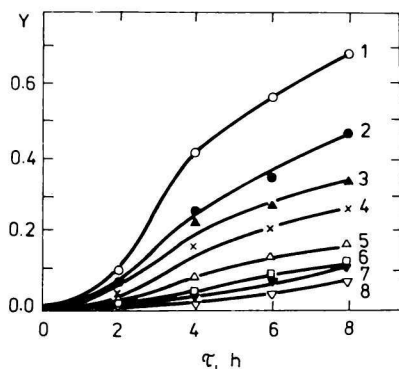


Fig. 3. Graft copolymerization of alkyl methacrylates series onto preirradiated polyethylene. Time of preirradiation 8 h. τ — time of grafting; Y — grafting yield in % to monomer.

1. MMA; 2. EtMA; 3. PrMA; 4. BuMA; 5. PtMA; 6. HpMA; 7. OctMA; 8. DecMA.

The reactivity of both series of monomers in the grafting process for different times of reaction, namely 2, 4, 6, and 8 h, is presented in Figs. 3—5. As seen from these figures at longer time of grafting, *i.e.* at 8 h, the yield values for both homologous series decrease with the increasing length of the alkyl substituents. This is similar to results obtained for chemically induced grafting. However, for lower times of grafting reaction, *i.e.* up to 6 h, some deviations occurred for acrylic esters, especially for monomers with longer alkyl substituents.

For methacrylic esters the decrease of yield of grafting with the length of alkyl substituents is very regular, moreover, the yield of grafting is always lower for the lower time of preirradiation (Fig. 6). For the acrylic series some deviations appear (Fig. 7). However, as the grafting yield is very small for acrylates some of the results are within the limits of experimental error.

The experimental data show that methacrylic esters always give higher yield of grafting than the corresponding acrylates.

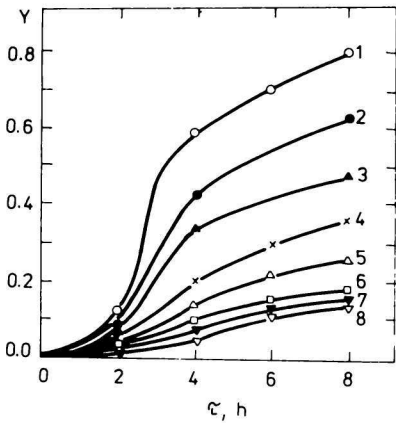


Fig. 4. Graft copolymerization of alkyl methacrylates series onto preirradiated polyethylene. Time of preirradiation 16 h. τ — time of grafting; Y — grafting yield in % to monomer. 1. MMA; 2. EtMA; 3. PrMA; 4. BuMA; 5. PtMA; 6. HpMA; 7. OctMA; 8. DecMA.

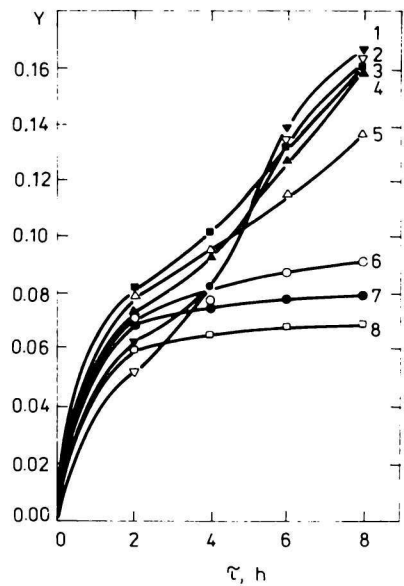


Fig. 5. Graft copolymerization of alkyl acrylates series onto preirradiated polyethylene. Time of preirradiation 16 h. τ — time of grafting; Y — grafting yield in % to monomer. 1. EtA; 2. MA; 3. BuA; 4. PrA; 5. PtA; 6. HpA; 7. OctA; 8. DecA.

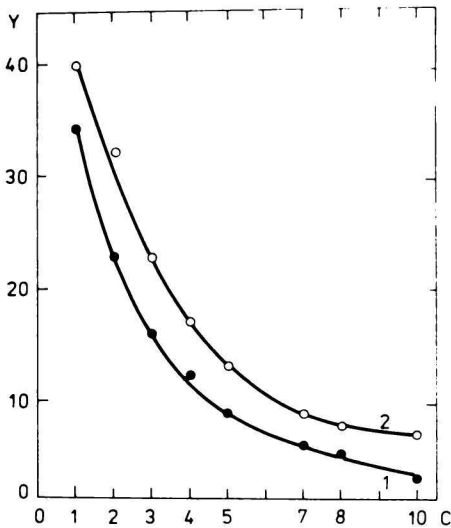


Fig. 6. Effect of the length of alkyl substituents of methacrylic esters onto grafting yield. C — number of carbon atoms in the alkyl group; Y — grafting yield in mmoles per 1 g film weight. Time of preirradiation: 1. 8 h; 2. 16 h.

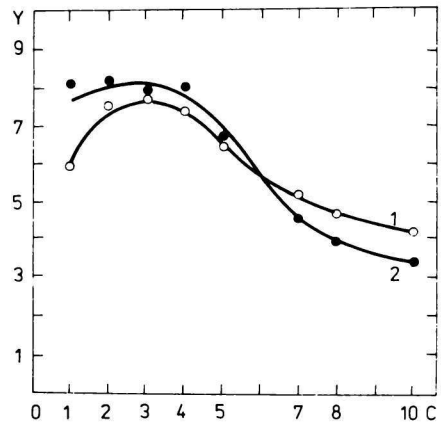


Fig. 7. Effect of the length of alkyl substituents of acrylic esters onto grafting yield. C — number of carbon atoms in the alkyl group; Y — grafting yield in mmoles per 1 g film weight. Time of preirradiation: 1. 8 h; 2. 16 h.

Conclusion

Although the grafting yields obtained with preirradiation technique are in general much higher than for chemical initiation similar regularity in the reactivity of particular monomers is observed. In both cases a regular decrease of the grafting yield appears with the increase of chain length of alkyl substituent. This effect is especially regular for methacrylic esters. It can be explained by the increase of steric hindrances causing the difficulty in penetration of monomers molecules with the solvent into the interchain spaces of the polymer. Presumably, the grafting process for monomers with longer alkyl substituents proceeds only on the surface layer of the polyethylene film. The higher yields of grafting for methacrylic esters compared to those of the corresponding acrylates could be attributed in the case of chemical initiation to the higher ability of acrylic monomers to homopolymerization than to graft copolymerization. However, as a similar effect of the presence of the CH_3 substituent in the α -carbon is observed also in the case of the preirradiation method where no competitive homopolymerization occurs and the radicals are formed only on the polyethylene film, the only explanation is the higher reactivity of methacrylic esters with polyethylene radicals than that of acrylic monomers.

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