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Surface modification of polymers
VI. Thermal and radiochemical grafting of acrylamide on polyethylene and polystyrene

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Abstract

The surface of polyethylene and polystyrene samples has been made hydrophilic by extension and improvement of a two step method. The polymer surface is first hydroxylated by treatment with an aqueous sodium persulfate solution or by gamma irradiation in water. Afterwards grafting is initiated by the thermal decomposition of hydroxyl groups formed at the surface. In some conditions hydroperoxides can also initiate the grafting. Gamma irradiation of the polymers in the presence of a concentrated aqueous solution of acrylamide results in surface modification of polyethylene but not of polystyrene. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

For some applications the surface properties of polymeric materials are as important as their bulk properties, but it is often difficult to find a material that provides a suitable combination of both. To solve that problem different techniques for surface modification are commonly used such as flame, corona or plasma treatment, exposure to ozone or etching agents, etc. However, only surface grafting of selected monomers provides a good control of the nature of the new surface formed and this is especially important for biomedical applications [1]. In previous papers of this series we have shown that the grafting of acrylamide at the surface of hydrocarbon polymers can be conveniently initiated by near-UV irradiation of a photoinitiator previously adsorbed at the surface of the polymer [2] or by thermal decomposition of photogenerated hydroperoxides [3] in the presence of the monomer in aqueous solution. This results in a decrease of the contact angle of a water droplet with the surface of the polymer from about 90° to values as low as 20° and to a significant decrease of protein adsorption. Thermal [4,5] and radiochemical [6,7] methods of grafting acrylamide and other water soluble monomers are also described in the literature but most authors have followed the reaction by measuring the weight increase of the samples. An appreciable weight increase is not required and could even be detrimental if the aim is to make the surface of the material hydrophilic without changing its physical and mechanical properties. Also the surface could be already hydrophilic at an early stage of the grafting process when no weight increase can be detected yet. Therefore, in the present paper we have investigated thermal and radiochemical methods of grafting, as well as combinations of them, in order

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to compare their convenience and efficiency in decreasing the contact angle of a water droplet with the grafted polymer surfaces.

2. Experimental

2.1. Polymers

Low density polyethylene was supplied by DSM as Stamylan LD 2810 and polystyrene was obtained from Fina Chemicals as Crystal N 1280. Pellets of both polymers were compressed at 160°C to obtain films about 0.2 mm thick.

2.2. Reagents

Acrylamide 99% pure, sodium persulfate 98% pure, ceric ammonium nitrate 98.5% pure and ammonium iron (II) sulfate hexahydrate (Mohr's salt) 99% pure were obtained from Aldrich and used without further purification.

2.3. Hydroxylation

Polymer films (1 × 1 cm) were dipped in sodium persulfate solutions of various concentrations (in w/v %) contained in glass tubes. These, after nitrogen purging if required, were sealed and heated in a water thermostat at different temperatures. Alternatively, polymer films dipped in water and introduced into glass tubes were irradiated in a Gammacell 220 (Atomic Energy of Canada Ltd) at a dose rate of 0.23 kGy/h for various periods of time.

2.4. Grafting

After hydroxylation the films were recovered, washed copiously with water and introduced into glass tubes containing an aqueous solution of ceric ammonium nitrate, nitric acid and acrylamide all at the appropriate concentrations. After nitrogen purging, if required, the glass tubes were sealed and heated in a water thermostat at different temperatures. For some experiments the samples were introduced into test tubes containing an aqueous solution of acrylamide only. For the radiochemical grafting, samples were introduced into glass tubes containing an aqueous solution of acrylamide (different concentrations in w/v % were used) and Mohr's salt, 0.05 M. After nitrogen purging the glass tubes were sealed and irradiated with gamma rays in the Gammacell already mentioned.

2.5. Contact angle measurements

The grafted films were recovered, washed copiously with water to remove homopolymer and wiped dry with a soft piece of tissue. Static contact angles were measured with a specially assembled apparatus involving an optical projection technique to magnify a droplet of water placed on the film. The image of the droplet is projected on a screen and the contact angle measured directly.

3. Results and discussion

Four grafting methods have been investigated. Three of them involve two steps: first hydroxylation of the polymer surface, together sometimes with hydroperoxidation, followed by grafting initiated by the thermal decomposition of hydroxyl or hydroperoxide groups formed at the surface. In the last method the polymer is irradiated with gamma rays in the presence of an aqueous solution of monomer also containing Mohr's salt to inhibit homopolymerization.

3.1. Method 1: hydroxylation under nitrogen followed by grafting

This method is similar to that described by Bamford and Al-Lamee [4] but we have focused on the surface modification and not on the weight increase of the samples. In a first step, sodium persulfate is used as hydroxylating agent of the polymer P-H according to the following mechanism:

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\cdot} \tag{1}$$

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^- + HO^\cdot \tag{2}$$

$$HO^\cdot + \text{P-H} \rightarrow H_2O + P^\cdot \tag{3}$$

$$HO^\cdot + P^\cdot \rightarrow \text{P—OH} \tag{4}$$

$$2HO^\cdot \rightarrow H_2O_2 \tag{5}$$

Subsequently, after isolation of the hydroxylated polymer P—OH, decomposition of hydroxyl groups at the surface in the presence of ceric ammonium nitrate generates alkoxy radicals P—O$^\cdot$ that can initiate the grafting:

$$\text{P—OH} + Ce^{IV} \rightarrow \text{P-O}^\cdot + H^+ + Ce^{III} \tag{6}$$

Hydroxyl radicals also initiate some homopolymerization close to the surface. In the present work we have studied the influence of hydroxylation and grafting conditions of acrylamide on the decrease of the contact angle of a water droplet with the modified surface of low density polyethylene (LDPE) and polystyrene (PS).

After hydroxylation no change in the infrared spectrum and practically no change of the contact angle can be detected. Therefore the influence of hydroxylation conditions is revealed only after grafting in standardized conditions. Fig. 1 shows that after grafting the contact angle always drops to practically the same limiting value but a longer hydroxylation time is required if the concentration of sodium persulfate is lower. For instance, a contact angle of 30° is obtained after 25, 35, 50 or 70 min hydroxylation if sodium persulfate concentrations are 20, 10, 5 or 2.5%, respectively. Assuming that a given value of the contact angle after grafting corresponds to the same previous hydroxylation level, the inverse of the hydroxylation time required to reach that level is a measure of the rate of hydroxylation. The rate of hydroxylation estimated that way increases with the square root of the sodium persulfate concentration (Fig. 2) in agreement with the mechanism proposed where reaction (3) is rate determining. Fig. 3 (same grafting but different hydroxylation conditions) and Fig. 4 (same hydroxylation but different grafting conditions) show that LDPE and PS behave very similarly. The surface modification process is somewhat slower with PS but that small difference cannot be assigned specifically to one step or another or a combination of both. In the grafting step specifically, the time to reach a given contact angle after hydroxylation in standardized conditions increases as the acrylamide concentration decreases (Fig. 5). However, no quantitative correlation can be deduced because the rate of decrease of the contact angle is not a reliable measure of the rate of grafting if acrylamide concentration is not constant. Indeed, the length of the grafts depends on monomer concentration and probably also their effect on the contact angle. For the lowest concentration used (2.5%) the value of the contact angle seems to level off at about 45°. A similar effect has been observed when the grafting of acrylamide is initiated by the thermal decomposition of photogenerated hydroperoxides [3]. It has been assigned to the fact that in dilute acrylamide solutions the length of the grafts, proportional to the monomer concentration, is not large enough to allow full coverage of the surface as the macromolecular coils collapse. Of course, this also depends on the grafting density resulting from the previous hydroxylation level. The effect of grafting temperature is shown in Fig. 6: the rate of grafting measured from the initial rate of decrease of the contact angle increases with temperature. An activation energy of 40 kJ/mol is found from Fig. 7 in the range of values typical for propagation of most vinyl monomers [8]. No measurable weight increase can be detected after 1 h grafting, when the lowest value of the contact angle is reached, although Bamford [4]

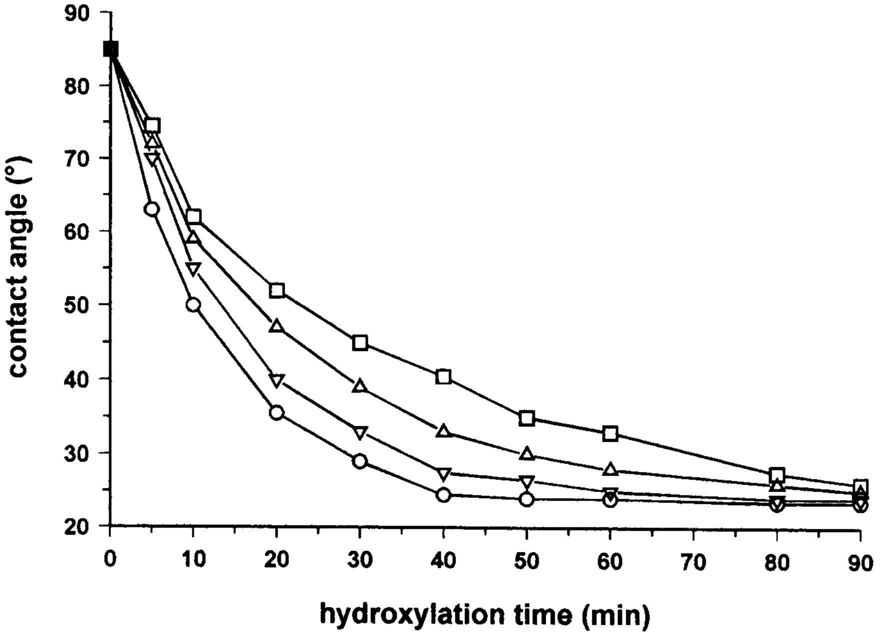

Fig. 1. Contact angle of LDPE after grafting acrylamide as a function of previous hydroxylation time. *Hydroxylation*: sodium persulfate 2.5% w/v (□), 5% w/v (△), 10% w/v (▽), and 20% w/v (○) at 80°C under nitrogen. *Grafting*: acrylamide 20% (w/v), ceric ammonium nitrate 0.002 M, and nitric acid 0.04 M at 50°C under nitrogen for 1 h.

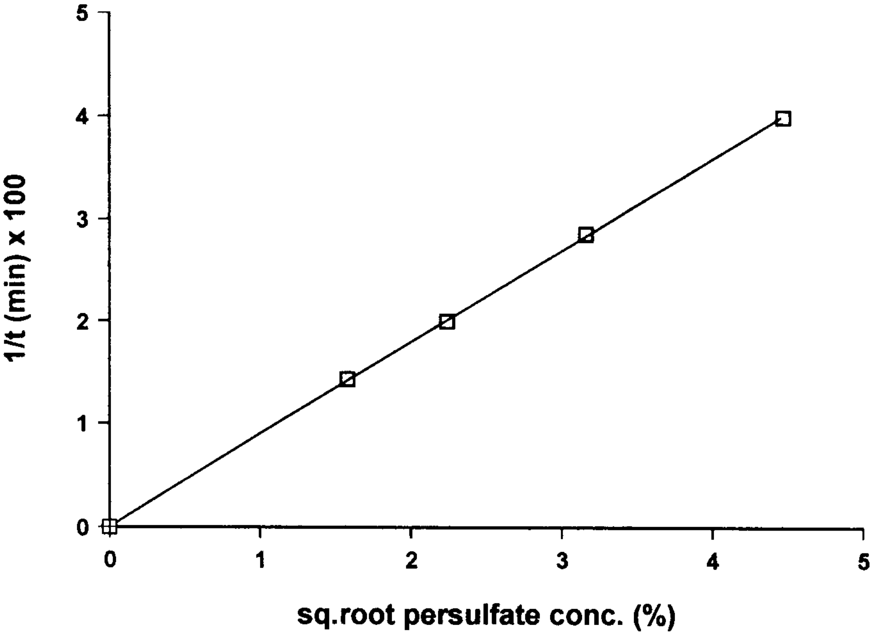

Fig. 2. Inverse of the hydroxylation time required to reach a contact angle of 30°C after grafting (acrylamide 20% w/v, ceric ammonium nitrate 0.002 M, and nitric acid 0.04 M at 50°C under nitrogen for 1 h) as a function of the square root of the sodium persulfate concentration used for hydroxylation (data from Fig. 1).

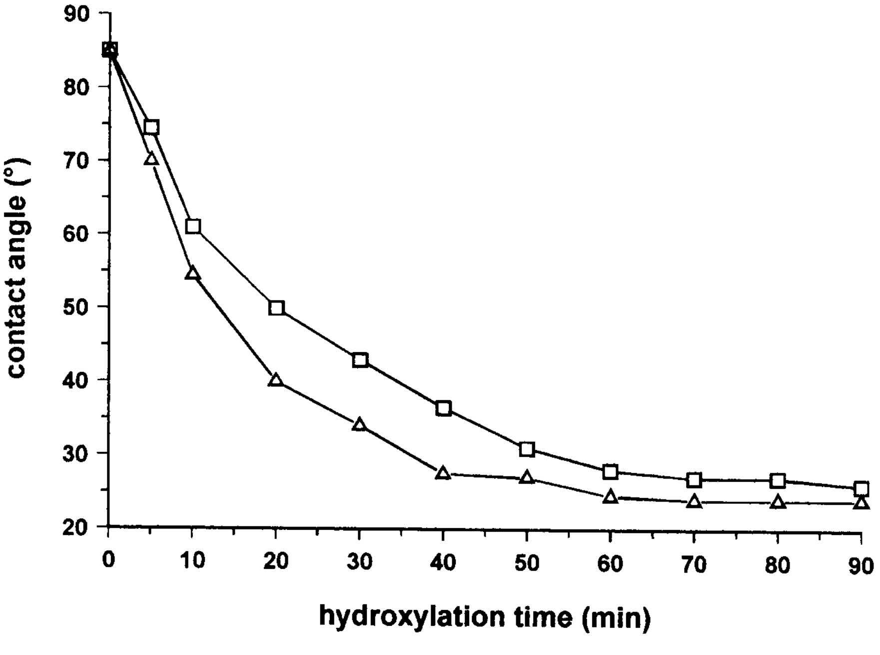

Fig. 3. Contact angle of LDPE (△) and PS (□) after grafting acrylamide as a function of previous hydroxylation time. *Hydroxylation*: sodium persulfate 10% w/v at 80°C under nitrogen. *Grafting*: acrylamide 20% w/v, ceric ammonium nitrate 0.002 M, and nitric acid 0.04 M at 50°C under nitrogen for 1 h.

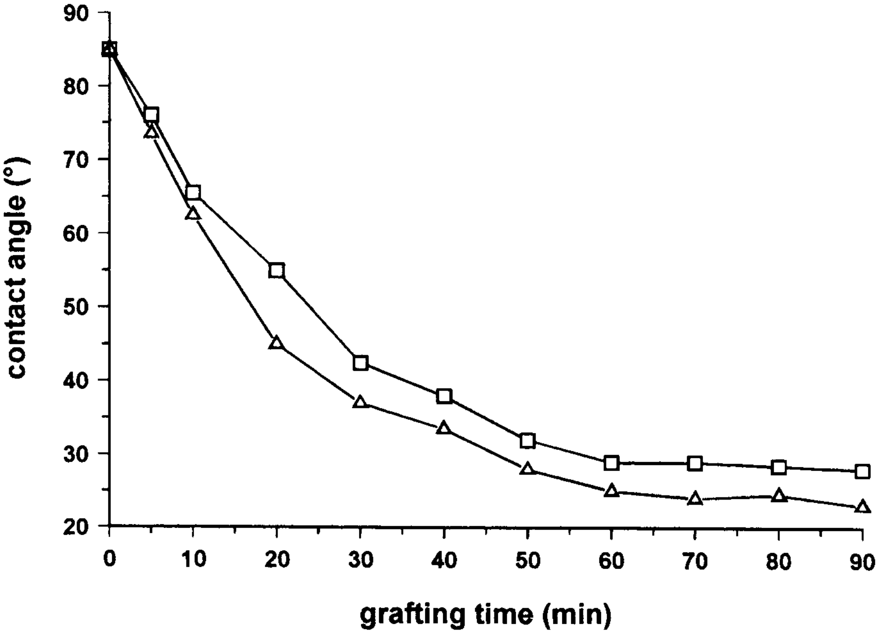

Fig. 4. Contact angle of LDPE (△) and PS (□) as a function of grafting time. *Hydroxylation*: sodium persulfate 10% w/v at 80°C under nitrogen for 1 h. *Grafting*: acrylamide 20% w/v, ceric ammonium nitrate 0.002 M, and nitric acid 0.04 M at 50°C under nitrogen.

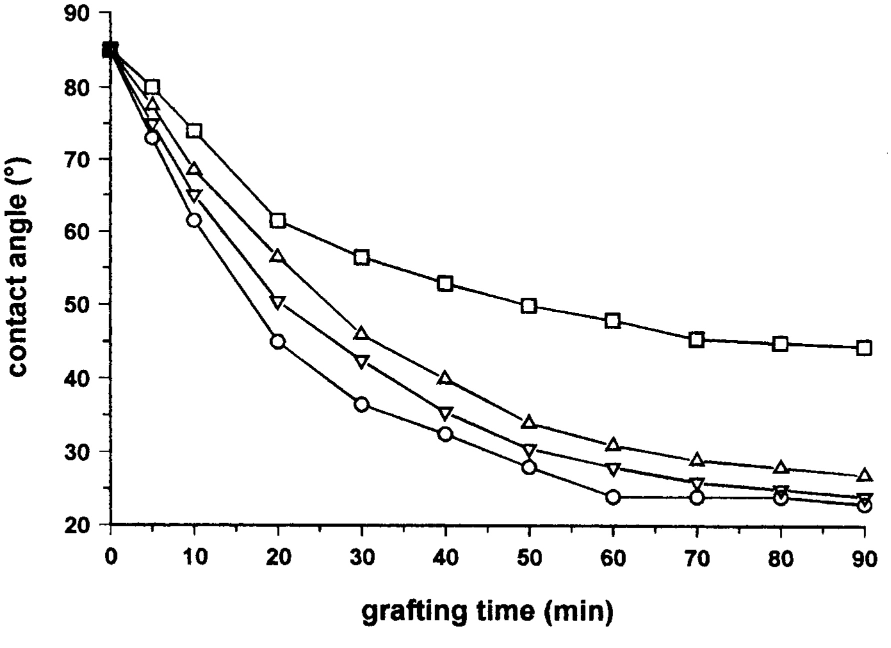

Fig. 5. Contact angle of LDPE as a function of grafting time. *Hydroxylation*: sodium persulfate 10% w/v at 80°C under nitrogen for 1 h. *Grafting*: acrylamide 2.5% w/v (□), 5% w/v (△), 10% w/v (△), 20% w/v (○), ceric ammonium nitrate 0.002 M, and nitric acid 0.04 M at 50°C under nitrogen.

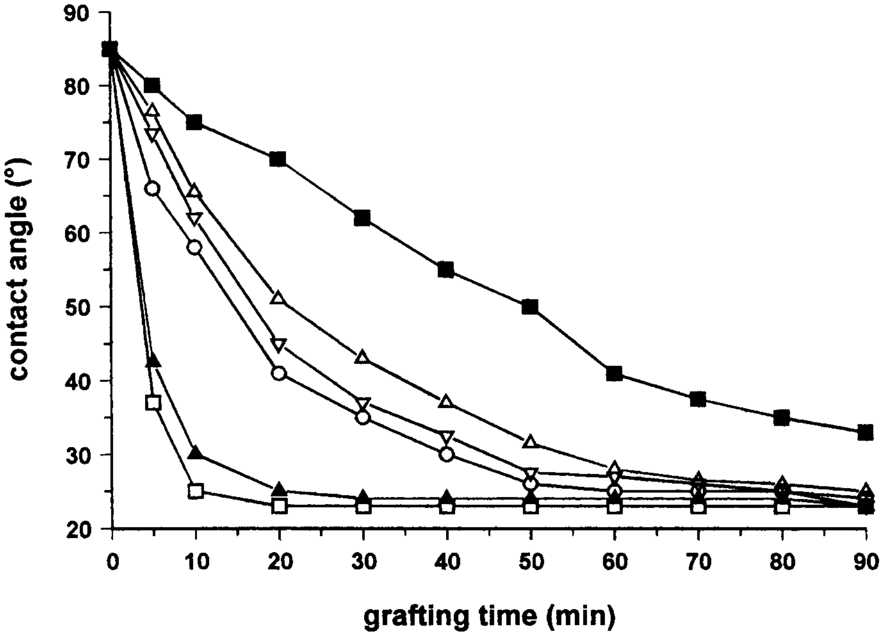

Fig. 6. Contact angle of LDPE as a function of grafting time. *Hydroxylation*: sodium persulfate 10% w/v at 80°C under nitrogen for 1 h. *Grafting*: acrylamide 20% w/v, ceric ammonium nitrate 0.002 M, and nitric acid 0.04 M under nitrogen at 30°C (■), 40°C (△), 50°C (▽), 60°C (○), 70°C (▲) and 80°C (□).

mentions a weight increase of 16% after 2 h grafting and larger than 76.5% after 4 h. Since a thin layer of homopolymer is always formed close to the surface it is likely that, after long grafting periods, the homopolymer layer binds to the grafted surface as a consequence of chain transfer and macroradical recombination. As a conclusion, our results show that the best experimental conditions to make the surface

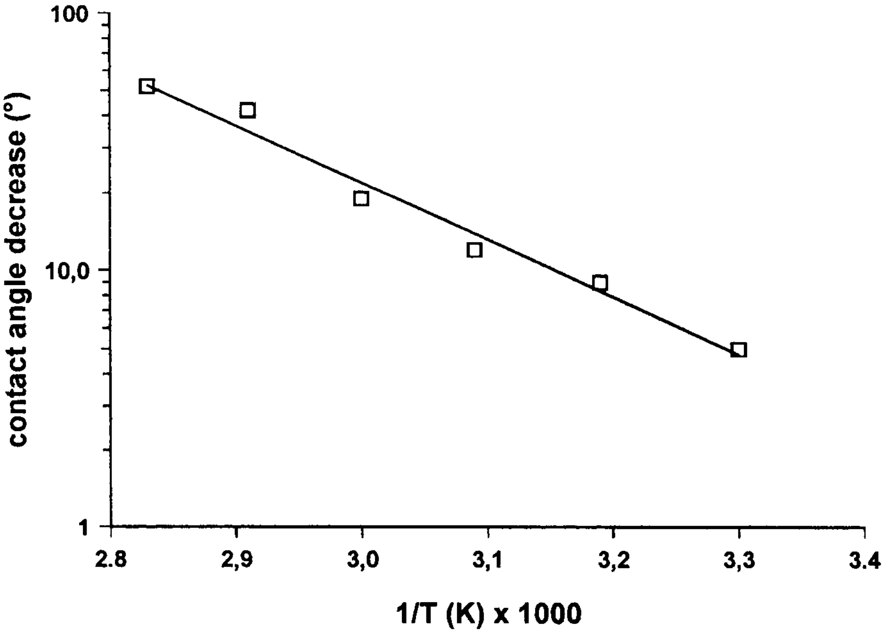

Fig. 7. Contact angle decrease after 5 min grafting (data from Fig. 6) as a function of reciprocal temperature of grafting (in K).

of LDPE and PS hydrophilic according to Bamford's method but without measurable weight increase or distortion of the sample are the following:

First step: heating of the samples at 80°C for 1 h in a 10% sodium persulfate solution.

Second step: heating of the previously hydroxylated samples at 50°C for 1 h in a 20% acrylamide solution also containing ceric ammonium nitrate 0.002 M and nitric acid 0.04 M.

Although our preliminary experiments were all performed under nitrogen as in Bamford's paper, we have checked that the same low values of the contact angle are obtained if both hydroxylation and grafting are carried out in the presence of air. Neither of those steps is thus inhibited by the low concentration of oxygen present in aqueous solutions at 50 or 80°C.

3.2. Method 2: hydroxylation (and hydroperoxidation) in air followed by grafting

If the hydroxylation step is performed in the presence of air, oxygen can compete with hydroxyl radicals to produce hydroperoxides instead of hydroxyl groups, as in reaction (4):

$$P^{\cdot} + O_2 \rightarrow P—OO^{\cdot} \qquad (7)$$

$$P—OO^{\cdot} + PH \rightarrow POOH + P^{\cdot} \qquad (8)$$

Although few hydroperoxide groups are probably formed at the surface of the samples because of the low oxygen concentration in water at 80°C, their thermal decomposition according to:

$$POOH \rightarrow PO^{\cdot} + HO^{\cdot} \qquad (9)$$

could initiate the grafting of acrylamide. Indeed, after persulfate treatment in the presence of air low values of the contact angle are obtained without the use of ceric ammonium nitrate but a higher temperature (90°C) and nitrogen atmosphere are now required (Table 1). In this case, traces of oxygen are sufficient to inhibit the grafting and contact angles do not decrease below 65–70° in the presence of air. However, with addition of ceric ammonium nitrate, grafting proceeds as usual at 50°C even in the presence of air. Clearly now, initiation is again due to the decomposition of hydroxyl groups and the results, equivalent to those obtained by method 1, are summarized in Table 1. It is interesting to note that the use of ceric ammonium nitrate, a fairly expensive product, can be avoided provided some hydroperoxidation occurs and a higher grafting temperature is used in the absence of oxygen. From a practical viewpoint, it is also important that both hydroxylation and grafting steps are possible in the presence of air, but ceric ammonium nitrate is then required for the grafting.

3.3. Method 3: gamma irradiation in water followed by grafting

Instead of using sodium persulfate to generate hydroxyl radicals we have tried gamma rays since the radiochemical decomposition of water generates hydroxyl radicals [9]. The samples, dipped in water, have been irradiated with a dose of 100 kGy in the presence of air. One can expect that hydroxyl groups and also some hydroperoxides are formed as in method 2. Indeed, the results summarized in Table 2 are almost identical to those of Table 1, both in the presence and absence of ceric ammonium nitrate. From the comparison of Tables 1 and 2 it appears that treatment of the samples for 1 h at 80°C in a 10% sodium persulfate solution or irradiation in water with a dose of 100 kGy are practically equivalent with respect to the efficiency of subsequent grafting of acrylamide. It should be pointed out that if the samples are irradiated with the same dose of 100 kGy in air instead of water they become brittle and unable to initiate grafting in any conditions. This is the consequence of extensive oxidation resulting in chain scission and in the formation of clusters of hydroperoxides that are progressively transformed into ketones, alcohols and carboxylic acids [10] unable to initiate the grafting.

Table 1
Contact angle after 1 h grafting of acrylamide (20% solution) (hydroxylation: 1 h at 80°C in a 10% sodium persulfate solution)

Polymer	*T* (°C)	Ce^{IV} (M)	Atmosphere	Contact angle (°)
LDPE	90	0	Nitrogen	20
LDPE	90	0	Air	65
LDPE	50	0.002	Air	23
PS	90	0	Nitrogen	28
PS	90	0	Air	70
PS	50	0.002	Air	25

Table 2
Contact angle after 1 h grafting of acrylamide (20% solution) (hydroxylation: gamma irradiation in water, 100 kGy)

Polymer	*T* (°C)	Ce^{IV} (M)	Atmosphere	Contact angle (°)
LDPE	90	0	Nitrogen	23
LDPE	90	0	Air	70
LDPE	50	0.002	Air	25
PS	90	0	Nitrogen	22
PS	90	0	Air	70
PS	50	0.002	Air	23

3.4. Method 4: Gamma irradiation in an aqueous monomer solution

Radiochemical grafting of acrylamide was carried out by the simultaneous or mutual method in conditions similar to those used by Haddadi-Asl and Burford [7] but we have focused on the surface modification rather than on the weight increase of the samples. LDPE and PS samples dipped in a 70% acrylamide solution (also containing 0.05 M Mohr's salt to inhibit homopolymerization) were irradiated at a dose rate of 0.23 kGy/h. Fig. 8 shows that the contact angle decreases regularly with irradiation time in the case of LDPE to reach the usual low value after 5 h. This corresponds to a dose of 1.15 kGy lower than that used by Burford in order to get a measurable weight increase of his samples (7.5 kGy). With PS, however, the grafting is much less efficient and a contact angle lower than 70° could not be obtained even for higher doses. The difference between LDPE and PS can be assigned to the lower radiochemical yield of radical production in this last polymer (0.08 as compared to 2.8 for LDPE [11]). Fig. 9 shows that, in the case of LDPE, at a constant dose (1.15 kGy) the decrease of the contact angle is almost proportional to the acrylamide concentration. From this it can be concluded that surface modification by radiochemical grafting of acrylamide using the simultaneous or mutual method is quite efficient and requires only low doses in the case of LDPE but is unsuccessful in the same conditions for PS. Again it is clear that, if the aim of the surface grafting is to make hydrophilic the surface of hydrocarbon polymers, measuring the contact angle is a more suitable method than measuring

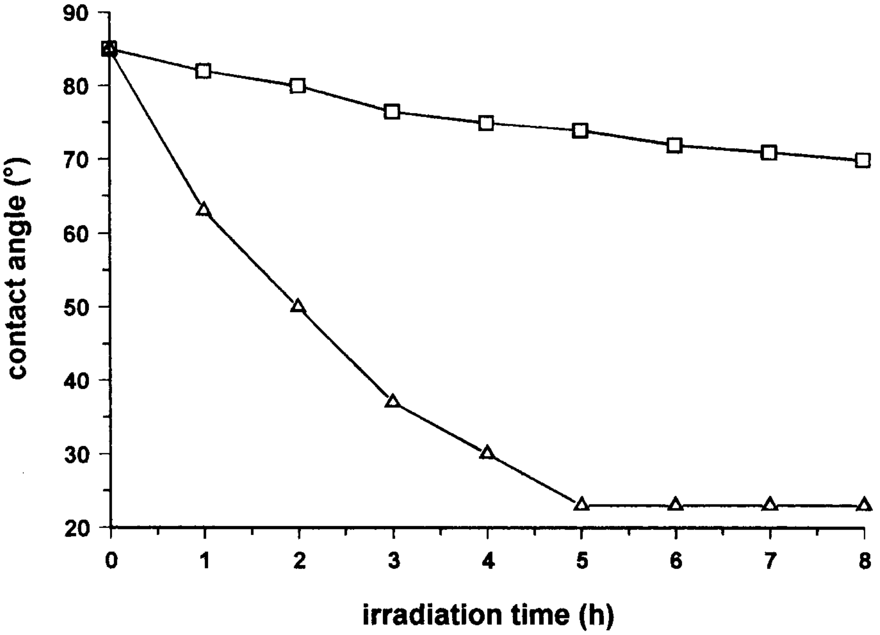

Fig. 8. Contact angle of LDPE and PS after grafting acrylamide as a function of irradiation time (dose rate 0.23 kGy/h, acrylamide 70%, Mohr's salt 0.05 M); PS (□), LDPE (△).

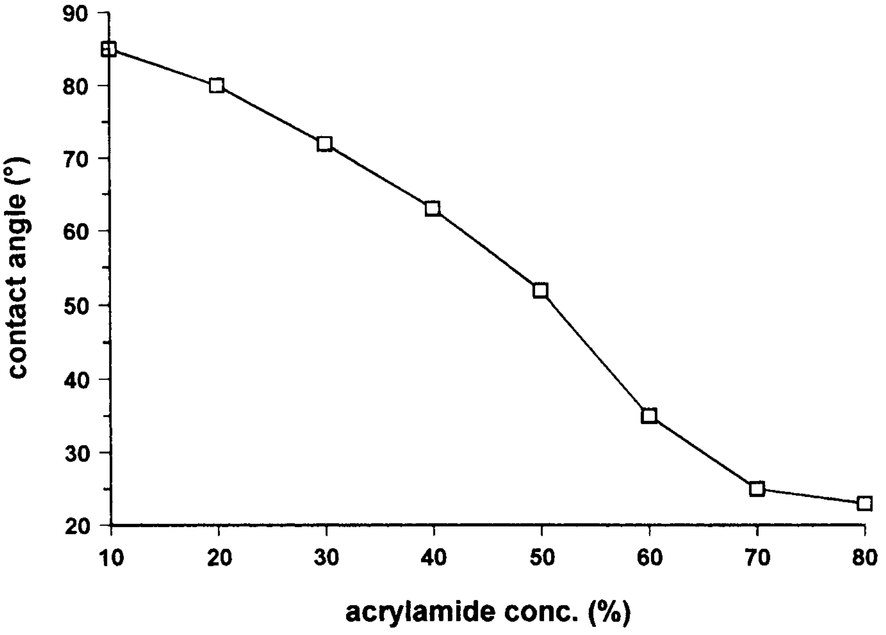

Fig. 9. Contact angle of LDPE after grafting as a function of acrylamide concentration (dose rate 0.23 kGy/h, irradiation time 5 h, Mohr's salt 0.05 M).

the weight increase of the samples to follow the progress of the reaction and to select the best experimental conditions.

4. Conclusion

Our results show that the two steps grafting method developed by Bamford and Al-Lamee [4] is quite suitable for making hydrophilic the surface of LDPE and PS and that the original experimental procedure can even be simplified. A contact angle of about 20° is reached at an early stage of the process when no weight increase can be measured yet. This ensures that no distortion of the samples occurs. Moreover, both the hydroxylation and the grafting steps can be carried out in air, which makes their extrapolation to a large scale production much easier. For the hydroxylation step, gamma irradiation of the samples dipped in water is an interesting alternative to the sodium persulfate treatment. Whatever the hydroxylation method, if it is carried out in air some hydroperoxides are also formed, the thermal decomposition of which can initiate the grafting provided a slightly higher temperature and a nitrogen atmosphere are used. The surface of LDPE can also be made hydrophilic by gamma irradiation of the sample with a fairly low dose in the presence of a concentrated aqueous solution of the monomer, but such treatment is not successful for PS.

Acknowledgements

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References

[1] Hubbel JA. Trends Polym Sci 1994;2:20.
[2] Ruckert D, Geuskens G. Eur Polym J 1996;32:201.
[3] Geuskens G, Thiriaux Ph. Polym Degrad Stab 1995;48:371.
[4] Bamford CH, Al-Lamee KG. Polymer 1994;35:2844.
[5] Karlsson JO, Gatenholm P. Polymer 1996;37:4251.
[6] Haddadi-Asl V, Burford RP, Garnett JL. Radiat Phys Chem 1994;44:385.
[7] Haddadi-Asl V, Burford RP. Radiat Phys Chem 1996;47:907.
[8] Brandrup J, Immergut EH, editors. Polymer handbook 2nd ed. New York: Wiley-Interscience, 1975.
[9] Farhataziz I, Rodgers MAJ, editors. Radiation chemistry: principles and applications. Weinheim: VCH, 1987.
[10] Geuskens G, Nedelkos G. Makromol Chem 1993;194:3349.
[11] Dole M, editor. The radiation chemistry of macromolecules. New York: Academic Press, 1972.