Investigation of post-radiation grafting of acrylamide onto polypropylene films

El-Sayed A. Hegazy
National Center for Radiation Research and Technology, PO Box 29, Nasr City, Cairo, Egypt

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A study has been made on the post-radiation grafting of aqueous acrylamide (AAm) onto polypropylene films (PP). A good hydrogel supported on the polymer substrate was obtained by grafting of AAm onto preirradiated PP films. The effect of grafting conditions such as solvent and inhibitor concentration, preirradiation dose, monomer concentration and reaction temperature on the initial rate and grafting yield was determined. It was found that the addition of 0.05 wt% Mohr's salt into the reaction medium effectively reduced the homopolymerization of AAm and the grafting process was successfully achieved. The dependence of the initial rate of grafting on the preirradiation dose and AAm concentration was found to be of the order 1.3 and 1.7, respectively. Two overall activation energies for this grafting system were found: 31.1 and 13.5 kcal mol^{-1} below and above 35°C, respectively. Some selected properties of the prepared graft copolymer were investigated and the possibility of its practical use discussed.

(Keywords: radiation grafting; acrylamide; polypropylene; properties)

INTRODUCTION

Polymeric materials are unique because of the range of structural forms that can be synthesized and the way in which local or general changes can be made in the structure. Radiation initiated grafting is a very broad field which has attracted considerable interest over the last two decades. Graft copolymers are alloys of polymers which, at least in principle, may combine the desirable properties of two polymeric materials. Radiation methods are particularly suited for the production of a wide variety of graft copolymers with interesting properties.

Recently, much work has been devoted to the study of radiation grafting of vinyl and acrylic monomers onto different polymeric materials[1–8]. The graft copolymerization of acrylamide onto polyolefins brings about a marked improvement in hydrophilic properties and affinity to water and dyes. But radiation grafting by ordinary techniques is not efficient, since acrylamide itself is very susceptible to homopolymerization both in solution and in the crystalline state[9]. Moreover, when grafting was performed in a good solvent, a polymer gel was formed which hindered subsequent isolation of the grafted product[10].

Earlier studies[11–18] investigated the preparation and properties of different grafted copolymers, obtained by direct and preirradiation grafting of vinyl and acrylic monomers onto different polymeric substrates. These grafted copolymers showed great promise for practical uses.

In the present study, the preirradiation grafting of aqueous acrylamide (AAm) onto polypropylene (PP) films was studied. The influence of grafting conditions on the yield and initial rate of grafting was determined. Electrical and swelling properties of prepared graft copolymer were also investigated.

EXPERIMENTAL

Materials

Polypropylene films of thickness 60 μm (El-Nasr Co., Egypt) were washed with acetone and dried in a vacuum oven at 50°C. Acrylamide (Merck) of 99% purity, was used without further purification. The other chemicals were reagent grade and were used as received.

Graft polymerization

A glass ampoule containing strips of PP film was evacuated for 3 h under a pressure less than 0.133 Pa. Then it was kept at -78°C and subjected to gamma irradiation from ^{60}Co at a dose rate of 3–10 kGy h^{-1}. A monomer solution deaerated by bubbling nitrogen was then introduced into the preirradiated sample and the grafting was carried out in a nitrogen atmosphere at a given constant temperature. The grafted films were washed thoroughly with hot distilled water and soaked overnight in distilled water to extract the residual monomer and homopolymer. The film was then dried in a vacuum oven at 50°C and weighed. The degree of grafting was determined by the percentage increase in weight as follows:

$$\text{Degree of grafting} = (W_g - W_0)/W_0 \times 100$$

where W_0 and W_g represent the weights of initial and grafted films, respectively.

Swelling and electrical resistance measurements were carried out using the techniques described in the previous study[16].

RESULTS AND DISCUSSION

Solvent and inhibitor

Table 1 shows the effect of solvent and inhibitor on the preirradiation grafting of AAm onto PP films. In this

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Table 1 Effect of solvent and inhibitor concentration on the grafting of AAm onto preirradiated PP films

Solvent	AAm Concn (wt%)	Mohr's salt (wt%)	Grafting (%)	Remarks
H_2O	25	–	Unextractable	Homopolymer
H_2O	25	0.10	1.9	No homopolymer
H_2O	25	0.05	3.6	No homopolymer
H_2O	10	0.25	0.6	No homopolymer
H_2O/Isopropanol (8:1)	10	0.25	0.2	No homopolymer
H_2O/Isopropanol (8:1)	10	0.10	0.2	No homopolymer
H_2O/DMF	10	0.25	0.4	No homopolymer

Grafting conditions: preirradiation dose, 40 kGy; reaction temperature, 35°C; film thickness, 60 μm; reaction time, 1 h

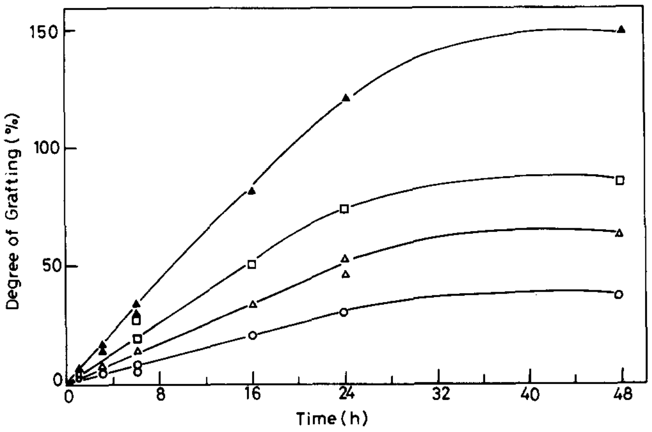

Figure 1 Degree of grafting *versus* reaction time at various preirradiation doses (kGy): ○, 30; △, 50; □, 70; ▲, 100. Grafting conditions: AAm concentration 25 wt%, Mohr's salt 0.05 wt%, reaction temperature 35°C

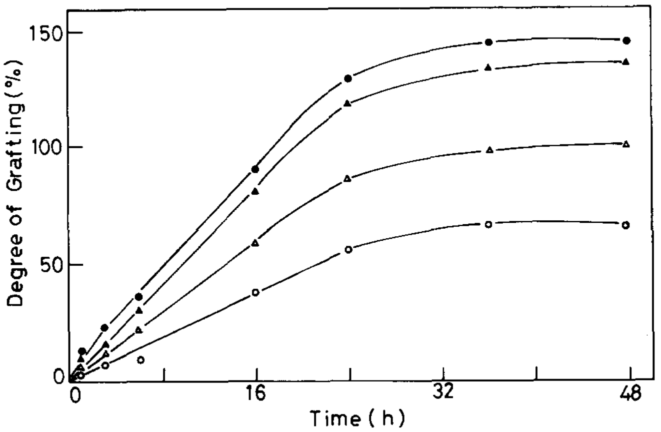

Figure 3 Degree of grafting *versus* reaction time at various aqueous AAm concentrations (wt%): ○, 10; △, 15; ▲, 25; ●, 35. Grafting conditions, except preirradiation dose: 100 kGy, other conditions as in *Figure 1*

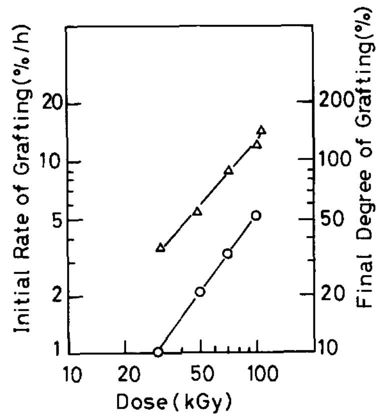

Figure 2 Logarithmic plots of initial rate and final degree of grafting as a function of preirradiation dose

grafting system the monomer was not exposed to irradiation, but homopolymerization of AAm took place and the grafted films were unextractable. By addition of 0.05 wt% of Mohr's salt (ammonium ferrous sulphate) to the reaction medium, homopolymerization was inhibited and the grafting process was significantly enhanced. The most suitable solvent for this grafting system is distilled water, as shown in *Table 1*.

Preirradiation dose

Figure 1 shows the degree of grafting *versus* time curves for the grafting of aqueous AAm onto preirradiated PP films at various doses. It can be seen that the grafting initially increases with reaction time, then tends to level off above 24 h. This behaviour is observed for grafting at the preirradiation doses investigated, ranging from 30 to 100 kGy. The grafting process levels off with a certain degree of grafting, which is termed the final degree of grafting. The higher the preirradiation dose the higher the rate and final degree of grafting.

Figure 2 shows the logarithmic relationship between the initial rate and final degree of grafting and preirradiation dose. The dependence of initial rate of grafting on preirradiation dose was calculated to be of the order 1.3. The final degree of grafting increases linearly with dose.

Generally, in the preirradiation method, the grafting process depends largely on the concentration of active trapped radicals in the preirradiated polymer. Results suggest that the concentration of such trapped radicals increases with dose in the range investigated here. Results also indicate that these radicals survived long enough for initiation of grafting sites and growth of chain radicals. Under such reaction conditions, graft copolymer with a high degree of grafting was obtained.

Monomer concentration

Figure 3 shows the effect of reaction time on the grafting of various AAm concentrations onto preirradiated PP films. It is obvious that the degree of grafting initially increases with grafting time, then tends to level off above 24 h. This behaviour can be seen for all AAm concentrations from 10 to 35 wt%. The higher the AAm

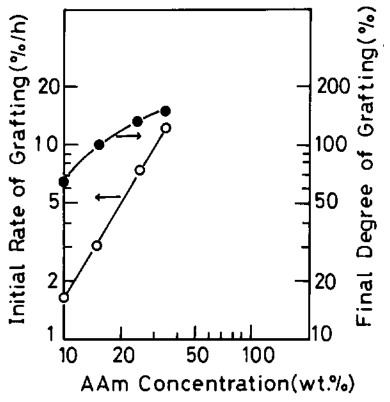

Figure 4 Logarithmic plots of initial rate of grafting and final degree of grafting *versus* AAm concentration

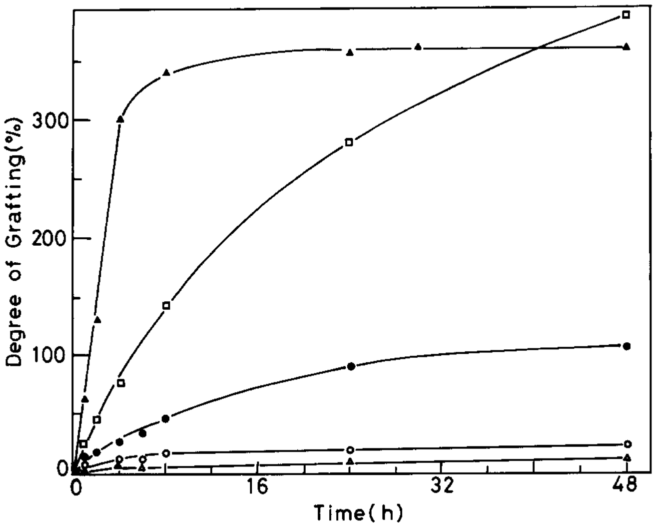

Figure 5 Degree of grafting *versus* reaction time at different temperatures (°C): △, 15; ○, 25; ●, 35; □, 45; ▲, 60. Grafting conditions: AAm concentration 35 wt%, preirradiation dose 100 kGy

concentration the higher the rate and final degree of grafting obtained, at a given grafting time.

Figure 4 shows the logarithmic relationship between the initial rate and final degree of grafting and AAm concentration. The dependence of the initial rate of grafting on AAm concentration was found to be of the order 1.7. Such relatively high dependence is due to the slow and difficult diffusion of this viscous monomer into the polymer matrices.

It can be assumed that this grafting process is greatly dependent on the diffusivity of such a viscous monomer into the bulk of polymer through the grafted layers initially formed near the surface of the film. Presumably the grafting proceeded through the whole bulk of polymer by the diffusion-controlled mechanism.

Grafting temperature

Figure 5 shows the degree of grafting *versus* time curves for grafting of aqueous AAm onto the preirradiated PP films at various reaction temperatures. It can be seen that at lower reaction temperature (15–25°C), the grafting is very low and the process levels off at a short reaction time. At higher temperatures (45–60°C) much higher degrees of grafting were obtained. Meanwhile, the degree of grafting increases with time at 35°C and 45°C. At 60°C a sharp increase in the grafting yield with time occurred initially, thereafter levelling off above 8 h. Raising the reaction temperature of this graft polymerization brought about a higher initial rate and final degree of grafting as well.

These results assumed that both the diffusivity of monomer and the decay of trapped radicals were enhanced at elevated temperatures. As a consequence, a higher rate of grafting was achieved, and the grafting process levelled off faster. At lower temperature, however, the diffusivity of this viscous monomer was restricted and the grafting localized on the film surface.

Figure 6 shows the Arrhenius plot for this graft polymerization. The plot shows a break around 35°C and two overall activation energies were found: 31.1 and 13.5 kcal mol^{-1} below and above 35°C, respectively. At high temperatures, the diffusion of monomer is enhanced and consequently a lower activation energy is obtained. The break in the Arrhenius plot corresponds to a sudden change in the shape of grafting curves between 25 and 35°C (*Figure 6*).

Gupta and Chapiro[19] reported a similar break at 40°C when grafting acrylic acid onto preirradiated polyethylene films and this behaviour was related to a kinetic effect. Such breaks in Arrhenius diagrams have also been found for several other grafting systems[13,16,20–22]; they are usually related to transition points in the polymer film.

Swelling and electrical properties

Swelling and electrical resistance of the prepared graft copolymer were investigated by the preirradiation method at different grafting conditions. Such a non-ionic membrane possesses hydrophilic properties: its water uptake initially increases as the degree of grafting increases then it tends to level off at higher grafting yield (*Figure 7*).

The specific electrical resistance of the graft copolymer at first decreases monotonically as the degree of grafting

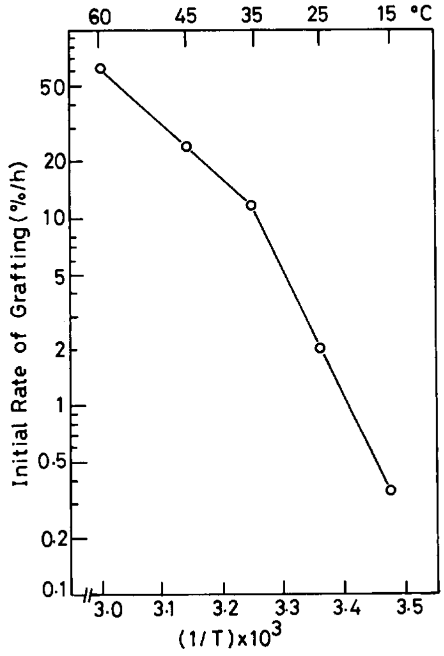

Figure 6 Arrhenius plot for post-radiation grafting of AAm onto PP films

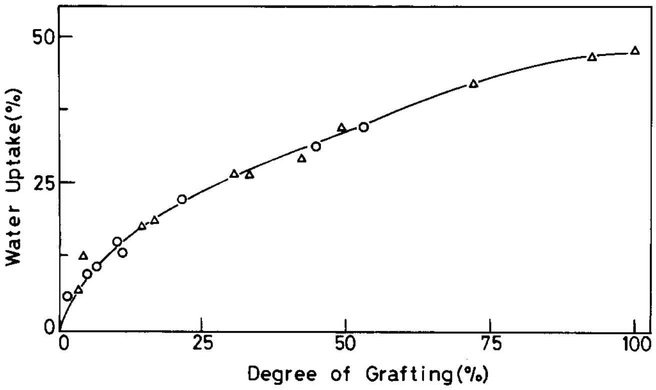

Figure 7 Water uptake *versus* degree of grafting for the graft copolymer prepared at different preirradiation doses (kGy): ○, 30; △, 100

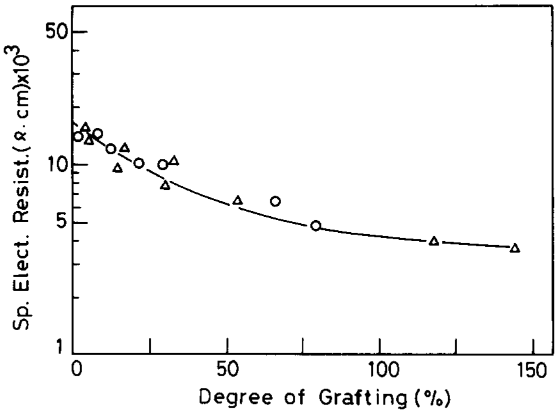

Figure 8 Specific electrical resistance *versus* degree of grafting at 25°C for the graft copolymer obtained at various AAm concentrations (wt%): ○, 25; △, 35

increases, and no significant decrement is observed at degrees of grafting higher than 100% (*Figure 8*).

This study investigated the influence of grafting conditions, such as monomer concentration, preirradiation dose and reaction temperature, on the swelling and electrical resistance of the prepared graft copolymer. No very significant effect of these grafting conditions on the property of graft copolymer was observed. The swelling and specific electrical resistance depend mainly on the amount of hydrophilic groups introduced into the trunk polymer by the grafting process.

It can be assumed that, at lower degrees of grafting, the crosslinking content is not high and is randomly distributed in the polymer substrate. Therefore, water uptake increased and specific electric resistance decreased for films with degrees of grafting lower than 100%. At higher degrees of grafting, the content of crosslinking may be increased and consequently the mobility of the grafted chains was restricted. Such restriction results in limitation of electrical conductivity and swelling was also hindered.

Generally, it can be concluded that the prepared graft copolymer possesses good hydrophilic properties, suitable specific electrical resistance and acceptable mechanical properties for practical use. Such properties may make this graft copolymer of interest for applications in which high electrical conductivity is not required, such as in biomaterials.

REFERENCES

1 Vigo, F., Capannelli, G., Uliand, C. and Munari, S. *Desalination* 1981, **36**, 63

2 Omichi, H. and Okamoto, J. *J. Polym. Sci.* 1982, **20**, 521

3 Aly, M., Hegazy, E. A. and Rabie, A. *Polym. J.* 1979, **11**(8), 601

4 Gouloubandt, R. and Chapiro, A. *Eur. Polym. J.* 1980, **16**, 957

5 Bittencourt, E., Stannett, V., Williams, J. L. and Hopfenberg, H. B. *J. Appl. Polym. Sci.* 1981, **26**, 879

6 Fuehrer, J. and Ellinghorst, G. *Macromol. Chem.* 1981, **93**, 175

7 Charlesby, A. *Radiat. Phys. Chem.* 1977, **9**, 17

8 Charlesby, A. and Fydelor, P. J. *Int. J. Radiat. Phys. Chem.* 1972, **4**, 107

9 Hegazy, E. A., Dessouki, A. and El-Boohy, H. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 1983

10 Hayakawa, K., Kawase, K. and Yamakita, H. *Radioisotopes* 1970, **19**(2), 21

11 Hegazy, E. A., El-Assy, N., Taher, N. and Dessouki, A. *Radiat. Phys. Chem.* 1989, **33**(6), 539

12 Hegazy, E. A., Taher, N., Ebaid, A., Rabie, A. and Kamal. H. *J. Appl. Polym. Sci.* 1990, **39**, 1029

13 Hegazy, E. A. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 493

14 Hegazy, E. A., Mokhtar, S., Osman, S. and Mostafa, A. *Radiat. Phys. Chem.* 1989, **36**(3), 365

15 Hegazy, E. A. and Dessouki, A. *Radiat. Phys. Chem.* 1986, **28**(3), 273

16 Hegazy, E. A., El-Dessouky, M. and El-Sharabasy, S. *Radiat. Phys. Chem.* 1986, **27**(5), 323

17 Hegazy, E. A., Taher, N. and Kamal, H. *J. Appl. Polym. Sci.* 1989, **38**, 1229

18 Hegazy, E. A., Ishigaki, I., Rabie, A., Dessouki, A. and Okamoto, J. *J. Appl. Polym. Sci.* 1983, **28**, 1465

19 Gupta, B. D. and Chapiro, A. *Eur. Polym. J.* 1989, **25**(11), 1137

20 Hegazy, E. A., Ishigaki, I. and Okamoto, J. *J. Appl. Polym. Sci.* 1981, **26**, 3117

21 Chapiro, A. *J. Polym. Sci.* 1958, **29**, 321

22 Chapiro, A., Bex, G., Bonamour, A. M. J. and O'Neill, T. *Adv. Chem. Ser.* 1969, **91**, 560