

Effect of Solvents on Gamma Radiation Induced Graft Copolymerization of Methyl Methacrylate onto Polypropylene

EMAN M. EL-NESR

National Center for Radiation Research and Technology, Madinat Nasr, Cairo, Egypt

SYNOPSIS

Methyl methacrylate was grafted onto polypropylene films using gamma radiation. Effects of different parameters, such as radiation dose, inhibitor concentration, monomer concentration, and type of solvents on the graft yield were investigated. It was established that the graft yield depends on the proper choice of solvent mixtures, and its maximum value can be obtained by using decalin/methanol mixture in the ratio 2 : 3 wt %. Thermal characteristics using differential scanning calorimetry shows that grafting has practically no effect on the crystallinity of PP. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Radiation grafting of vinyl monomers onto different substrates attracts the attention of many investigators.^{1,2} However, the acceleration effect of diluent on the rate of grafting was a matter of discussion of many authors. It was firstly reported by Dobo et al.,³ followed by Odian.^{4,5} It was stated in the literature that the observed maximum grafting is an optimum resulting from a high concentration of absorbed monomer and a low viscosity of the poorly swelled polymer matrix. However, high graft rates were observed for systems in which the diluent and not the monomer swells the substrate as in the case of grafting of styrene to nylon in presence of water or alcohol.⁶ A relation between Hildebrand solubility parameters of the monomer/solvent mixture and graft rate was established.⁷ For instance, for a mixture of the same solubility parameter, the graft rate increases on increasing the monomer concentration. Besides, the effect of diluent mixture over a range of monomer concentrations was reported. Thus, the correct choice of solvents is essential to the success of radiation-induced graft polymeriza-

tion.⁸⁻¹⁴ Accordingly, a trial was made in the present work to study, among other parameters, the role of solvents in the radiation copolymerization reaction of methyl methacrylate onto polypropylene (PP). Besides, a characterization of the grafted PP films was carried out.

MATERIALS AND TECHNIQUES

Materials

Polypropylene films of 20 μm thickness was provided by El-Nasr Co. for Medical Supplies, Egypt. Methyl methacrylate (MMA) purity 99% (Merck, Germany) was used as received. The other chemicals were reagent grade and were used as received.

Techniques

Graft Copolymerization

Strips of PP films were washed with acetone, dried at 50°C in a vacuum oven, weighed, and then immersed in the mixture of solvent (MeOH and decalin) and MMA monomer. Ferric chloride used as inhibitor was introduced in the reaction mixture to avoid the formation of homopolymers

usually formed during direct irradiation grafting. The reaction mixture was deaerated by bubbling nitrogen gas for 4–7 min, sealed, and then subjected to a Co-60 gamma source. The obtained grafted films were removed and washed thoroughly with hot toluene at 60°C to ensure the extraction of residual monomers and homopolymers that may be occluded in the films.

The degree of grafting was determined by the percentage increase in the weight, as follows:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100$$

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

Swelling Measurements

The clean and dried PP films of known weights were immersed in solvent or monomer for 48 h. The films were removed, blotted by absorbent solvent or monomer, and immediately weighed. The swelling percent was calculated as follows:

$$\text{Swelling (\%)} = \frac{W_s - W_o}{W_o} \times 100$$

where W_o and W_s represent the weights of initial and swelled films, respectively.

Infrared Spectroscopy

Infrared spectra were obtained in the region of 4000–400 cm^{-1} using a MATTSON 5000 FT IR spectrometer.

Thermal Analysis

Thermal analysis of the grafted film was carried out using a differential scanning calorimetry (DSC) Perkin-Elmer-7 and a polarizing microscope at 10°C/min under nitrogen atmosphere. These measurements were carried out at Applied Physics Department, Ulm University, Germany.

RESULT AND DISCUSSION

Effect of Solvent(s)

The effect of diluent mixtures on the grafting yield has received little attention. The work by some authors was devoted to aqueous systems in the

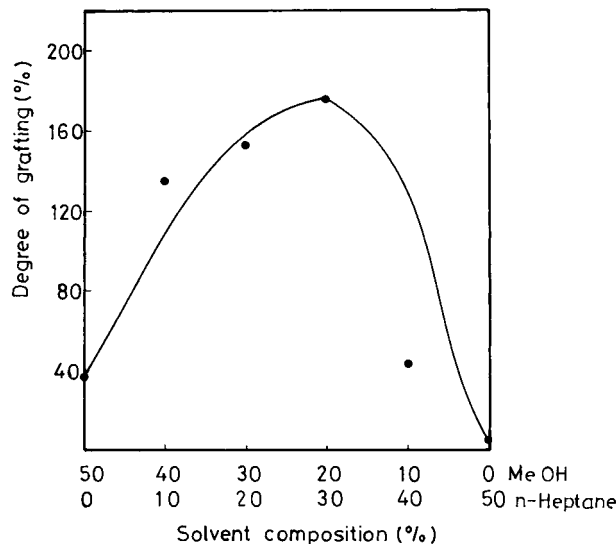


Figure 1 Effect of solvent composition (heptane/MeOH) on the graft yield of MMA (50 wt %) onto PP.

grafting monomers to polyvinyl alcohol;¹⁵ other authors showed that an accelerative effect of diluent can be obtained over a range of monomer concentration by the use of diluent mixtures.¹⁶ For this purpose, MMA was grafted to PP using MeOH or heptane and their mixtures. The results obtained are shown Figure 1. From this figure, it can be seen that although MMA is soluble in MeOH and in heptane, the graft yield is lower than in their mixture. The maximum value of grafting was obtained in a MeOH/heptane mixture in the ratio of 2 : 3 wt %. In the case of using a MeOH/decalin mixture, Figure 2 shows that the same finding holds true, and the maximum graft yield was obtained at the same ratio. This indicates that MeOH in this percentage is necessary for obtaining the maximum graft yield in both cases. However, as shown from these two figures, the maximum graft yield in case of decalin/MeOH is higher than that in case of heptane/MeOH.

For an explanation of this behavior, PP films were swelled in both diluent mixtures. The results show that the maximum swelling is obtained at the same ratio needed for obtaining the maximum graft yield. This indicates that swelling of PP films in the reaction mixtures enhances the graft copolymerization reaction and, consequently, increases the graft yield. A comparison between the swelling ability of PP films in diluent mixtures are shown in Figure 3. From this figure, it is shown that the swelling ability in the decalin/MeOH mixture is higher than in heptane/MeOH mixture at all ratios. Besides, the swellability of

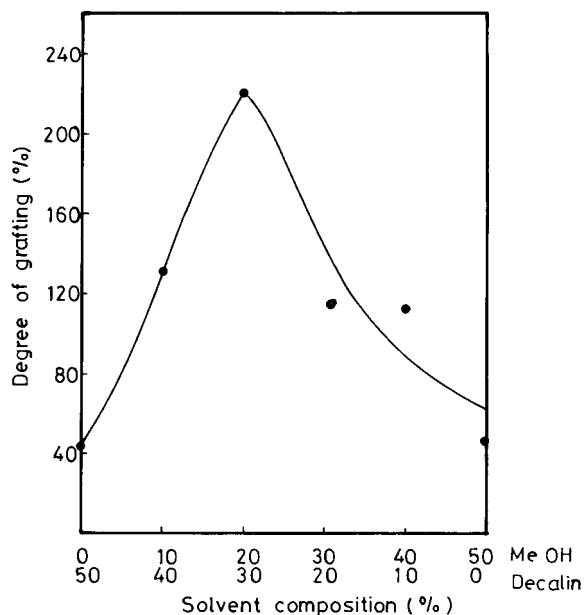


Figure 2 Effect of solvent composition (decalin/MeOH) on the graft yield of MMA (50 wt %) onto PP.

this mixtures practically attains its maximum value at the same composition of maximum grafting. The presence of MeOH accelerates the graft copolymerization process due to the Thromsdorff effect, as MeOH is not a suitable solvent for PMMA.

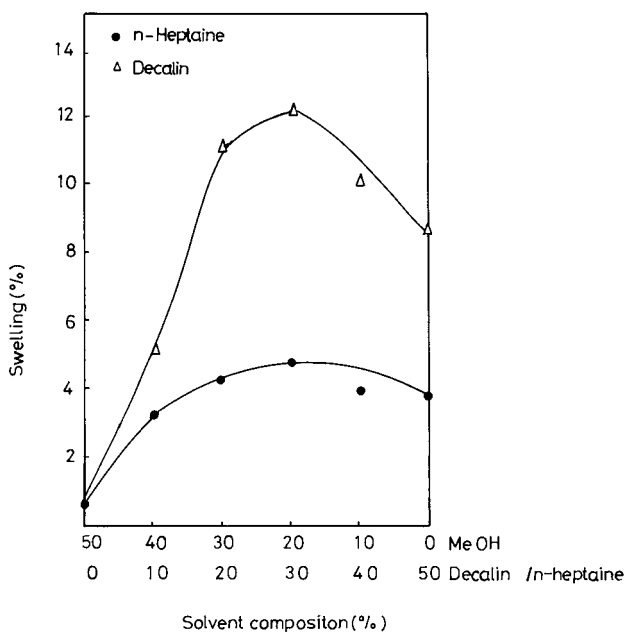


Figure 3 Effect of solvent composition: (Δ) decalin/MeOH, and (\circ) heptane/MeOH on the equilibrium swelling of PP.

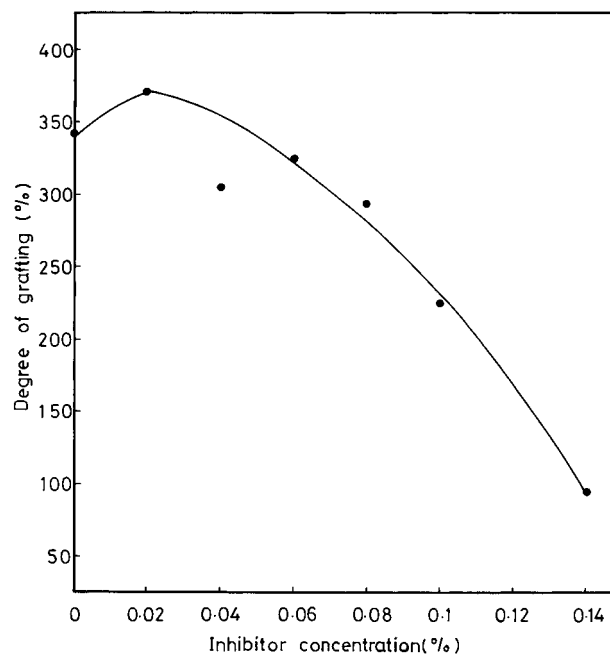
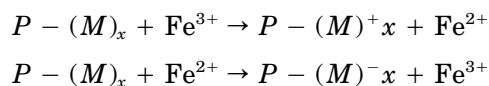


Figure 4 Effect of inhibitor (FeCl_3) concentration on the graft yield of MMA onto PP: radiation dose, 20 kGy; decalin/MeOH, 50 wt %.

Effect of Inhibitor Concentration

Inhibitors are usually added to the reaction mixture to minimize the homopolymer formation. For this reason, FeCl_3 , used as inhibitor, was added in different concentrations ranging from 0 to 0.14 wt % to the diluent mixture (decalin/MeOH). The results obtained are shown in Figure 4. From this figure, it can be seen that the graft yield slightly increases with increasing FeCl_3 concentration up to 0.02 wt %, after which it starts to decrease. This indicates that this optimum concentration is sufficient to inhibit the possible homopolymerization. Above this value, iron ions move to the surface of PP and inhibit the growing macroradicals of grafted part.

The mechanism of inhibition of grafted macroradical can be explained as follows:¹⁷



where P is the polymer chain, M is methyl methacrylate monomer, and x is the degree of polymerization.

The same mechanism is valid for inhibition of homopolymerization process of MMA.

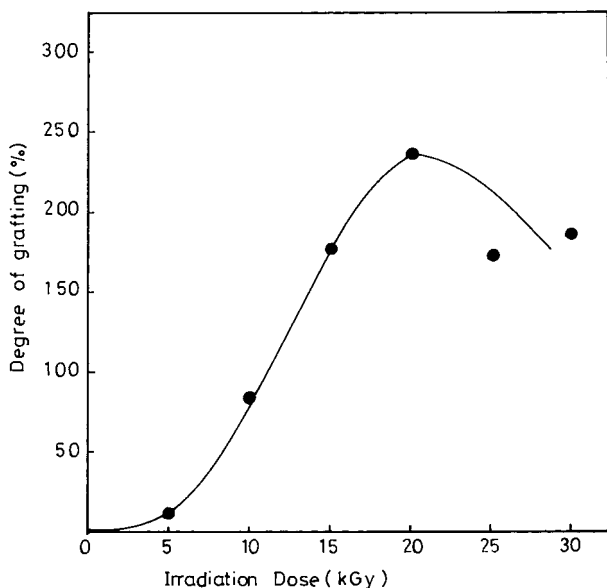


Figure 5 Effect of irradiation dose on the graft yield of MMA onto PP: MMA, 50 wt %; FeCl_3 concentration, 0.05 wt %; decalin/MeOH, 50 wt %.

Effect of Radiation Dose

Effect of radiation dose on the graft yield was studied, and the results obtained are shown in Figure 5. From this figure, it can be seen that the graft yield increases by increasing the radiation dose up to 20 kGy, after which a slight decrease was observed. It is expected that such a decrease in the graft yield should be more pronounced at higher doses due to degradation of polymethylmethacrylate grafted on to PP. Thus, it is desirable to use a low irradiation dose not exceeding 20 kGy to avoid such degradation.

Effect of Monomer Concentration

Figure 6 shows the effect of monomer concentration on the graft yield. From this figure, it can be seen that the graft yield increases significantly as the monomer concentration increases.

The increase in the graft yield could be associated with the gel effect brought about by the solubility of PMMA in its own monomer. It is known that the extent of entanglement is dependent on the molecular weight. Once the propagating chain length exceeds the critical value at which the entanglement occurs, the termination rate constant is greatly reduced, while the propagation constant is hardly affected, given rise to a large increase in the polymerization rate. Entanglement would also be expected in poor solvent of PMMA, such

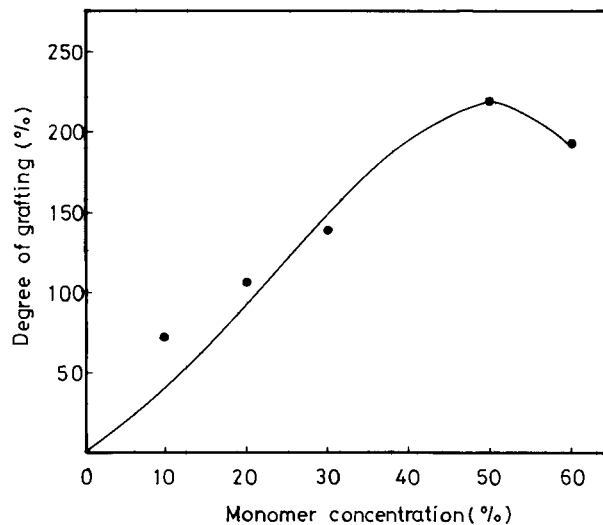


Figure 6 Effect of monomer concentration on the graft yield of MMA onto PP: radiation dose, 20 kGy; FeCl_3 concentration, 0.05 wt %; decalin/MeOH, 50 wt %.

as MeOH. These two factors lead to an increase in the graft yield.

Effect of Grafting on the Crystallinity of PP

Effect of grafting on the crystallinity was investigated by many authors.¹⁸ Some authors stated that a slight decrease in the crystallinity occurs, and this was taken as indication that the graft copolymerization proceeds not only on the surface of the films but also in the amorphous part. Measuring the ΔH values of grafted films shows that this value of grafted films decreases with increasing the graft yield, as shown in the Table I. From this table, it is shown that the crystalline melting temperature slightly changes while ΔH markedly decreases. This gives a false indication about the degree of crystallinity. However, if one considers the weight percent of PP in the grafted film, it should be clear that the calculated ΔH is practi-

Table I Effect of Graft Yield on Thermal Characteristics of PP Using DSC

Graft Yield (%)	ΔH (J/g)	Peak Temperature (°C)
—	99.995	161.112
60	66.933	185.198
365	27.011	160.371

cally the same, and this means that no change occurs in the crystallinity of PP due to grafting.

Measuring the crystalline melting temperature of grafted PP and plotting it against the degree of grafting was carried out using polarizing microscope. The results obtained are shown in Figure 7. From this figure, it can be seen that the melting temperature markedly changes by changing the degree of grafting. Such a decrease cannot be explained in terms of change in crystallinity rather than by considering the changes in the size of crystalline domains, which can not be easily detected by polarizing microscope. Accordingly, this change in the melting temperature can also be explained in terms of the weight fraction of PP in the grafted samples.

Spectroscopic Analysis

Infrared spectrum of isotactic PP (itPP) differs from atactic PP (atPP) in the appearance of characteristic bands reflecting its crystallinity, such as the CH_3 -rocking band appears at 973 cm^{-1} and strong band of assymmetric deformation vibration of the methyl group at 1455 cm^{-1} . It was found that these bands also appear after grafting up to the 90% graft yield. This indicates that practically no change in the crystallinity of PP occurs as a result of grafting, which occurs mainly onto film surface. Besides, new bands appear after grafting at 1732 and 1268 cm^{-1} , corresponding to $\text{C}=\text{O}$

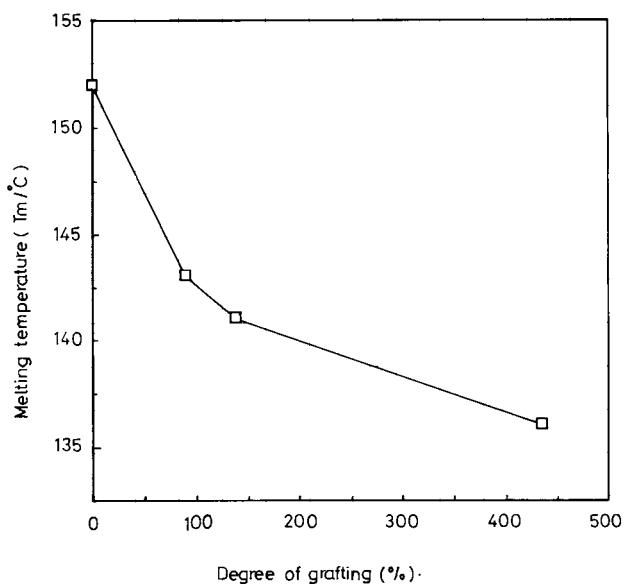


Figure 7 Effect of graft yield on the crystalline melting temperature using a polarizing microscope (heating rate: $10^\circ\text{C}/\text{min}$).

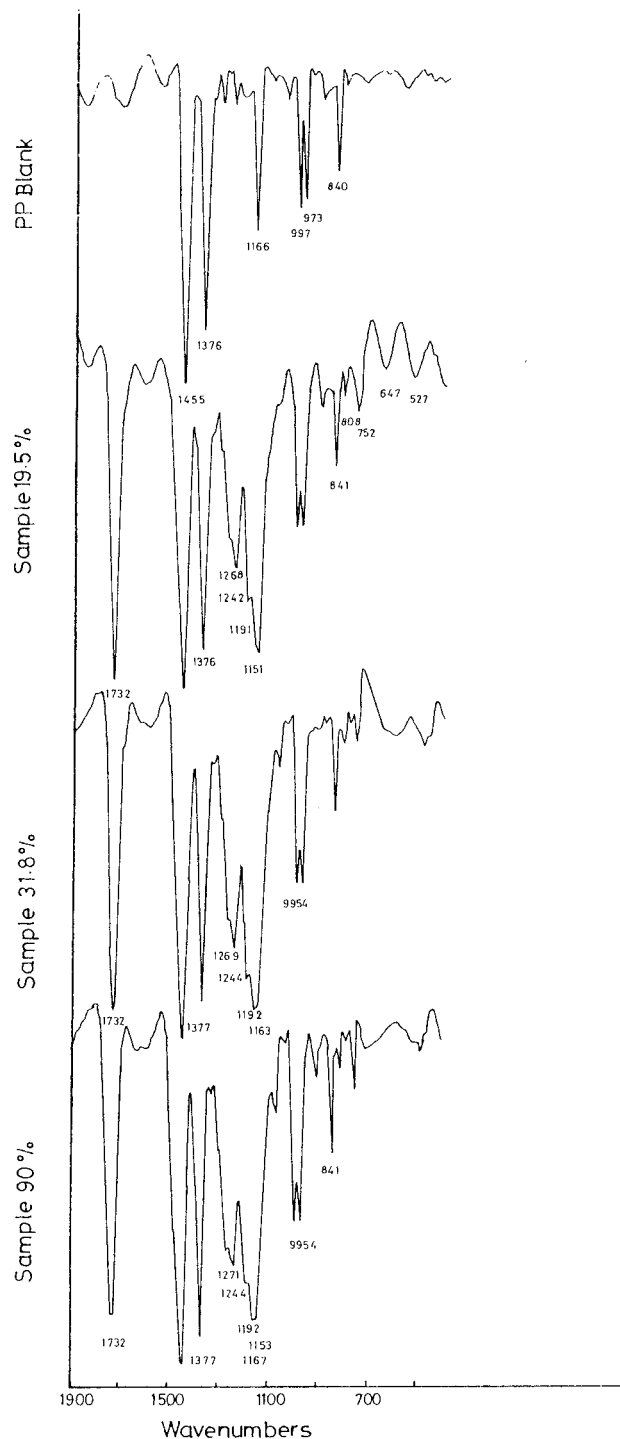


Figure 8 Infrared spectra of grafted and ungrafted PP films.

and $\text{C}-\text{O}-\text{C}$ stretching vibrations of the acrylate group, respectively. The intensity of these absorption bands increases with increasing graft yield, as shown in Figure 8.

CONCLUSION

From the results obtained, one can conclude that the diluent mixture markedly affects the graft yield. The graft yield depends on the proper choice of solvent mixtures, and its maximum value can be obtained by using decalin/methanol mixture in the ratio of 2 : 3 wt %. Thermal characteristics using differential scanning calorimetry shows that grafting has practically no effect on the crystallinity of PP.

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