Gamma Radiation-Induced Graft Copolymerization of Styrene onto Poly(ethyleneTerephthalate) Films

MOHAMED MAHMOUD NASEF

Membrane Research Unit, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia

ABSTRACT: Gamma radiation-induced graft copolymerization of styrene onto poly(ethylene terephthalate) (PET) films was studied using simultaneous irradiation technique. The effects of grafting conditions on the degree of grafting were investigated. The grafting conditions include monomer concentration, irradiation dose, dose rate, and the type of solvent. Moreover, the effect of the addition of crosslinking agents [i.e., divinylbenzene (DVB) and triallyl cyanurate (TAC)] having various concentrations were also investigated. The degree of grafting was found to be greatly dependent on the grafting conditions. Of the three diluents employed, methylene chloride was found to drastically enhance the degree of grafting. The order of dependence of the initial rate of grafting on the monomer concentration was found to be 2.2. The grafted PET films were identified by FTIR spectroscopy and characterized by X-ray diffraction (XRD). © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1003–1012, 2000

INTRODUCTION

Modification of polymers by graft copolymerization of functional monomers is a well-known method to impart favorable chemical and physical properties to given polymers. Several methods have been proposed for initiating graft copolymerization including ionizing radiation, ultraviolet light, decomposition of chemical initiators, plasma treatment, and oxidation of polymers. Among these methods, radiation-induced graft copolymerization is advantageous due to its extensive penetration in the polymer matrix and its rapid and uniform formation of radicals for initiating grafting in many kinds of polymers.

Poly(ethylene terephthalate) (PET) films are highly crystalline, thermally stable, markedly hydrophobic and do not contain chemically reactive groups in their structure.[1,2] To get desirable properties, PET can be grafted by monomers such as acrylic acid and styrene. The grafting of acrylic monomers directly confers weakly acidic charac-

ter to the polymer backbone, whereas grafting of styrene leads to the formation of neutral graft copolymers, which must be functionalized by a postgrafting reaction. Radiation-induced graft copolymerization of various vinyl monomers such as styrene, acrylic acid, methacrylic acid, 4-vinylpyridine, acrylonitrile, vinyl acetate, *N*-vinyl-3-morpholinone, and 2-methyl-5-vinylpyridine was carried out onto PET fibers on many occasions.[3–11] However, to the best of our knowledge, no detailed study has been reported on the radiation-induced graft copolymerization of styrene onto PET films. In the present study, the graft copolymerization of styrene onto PET films using simultaneous irradiation technique is reported. The effects of grafting conditions such as monomer concentration, irradiation dose, dose rate, solvent, and the addition of various concentrations of two crosslinking agents such as divinylbenzene (DVB) and triallyl cyanurate (TAC) are investigated in correlation with the degree of grafting. The structure of the PET graft copolymer films is investigated by means of FTIR and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

PET film of 60 μm thickness was obtained from commercial source. Styrene (Fluka, Switzerland) having a purity of more than 99% was used without any further purification. DVB (Fluka, Tech. Grade) and TAC (Fluka, > 97%) were used as crosslinking agents. Other chemicals were reagent grades and used as received.

Graft Copolymerization

PET film was cut into square pieces of known weight, washed with acetone, and then dried in a vacuum oven at 60°C for 1 h. The dried film was placed into a glass ampoule containing monomer solution of known concentration. The grafting solution was flashed with nitrogen for 8 min to remove the air and then the ampoule was sealed. The ampoule was subjected to γ-rays from a Co-60 source (Bhabha Atomic Research Center, Bombay, India) at dose rates ranging from 1.32 to 15.00 kGy/h. The grafted film was removed, washed with toluene, and soaked therein overnight to remove the residual monomer and homopolymer occluded in the film. The grafted film was then dried in a vacuum oven at 80°C until a constant weight was obtained. The degree of grafting was gravimetrically determined as the percentage of the weight increase of PET film using the following equation:

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

where W_g and W_0 are the weights of grafted and original PET films, respectively.

FTIR Measurements

FTIR measurements of original and grafted PFA films were carried out by means of a Mattson 6020-Galaxy Series FTIR spectrometer in transmittance mode at frequency in the range of $4000-400$ cm^{-1}. The spectra of the films were detected by attenuated total reflection (ATR) accessory equipped with a KRS5 crystal having crystal face angle of 45°.
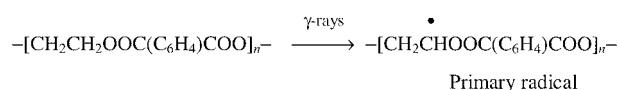
X-Ray Diffraction Measurements

XRD measurements were made on original and grafted films having various degrees of grafting using a Philips PW 1830 X-ray diffractometer. The diffractograms were measured at 2θ in the range of 5–60° using Cu-Kα radiation ($\lambda = 1.54$ Å) monochromated by means of a nickel filter.
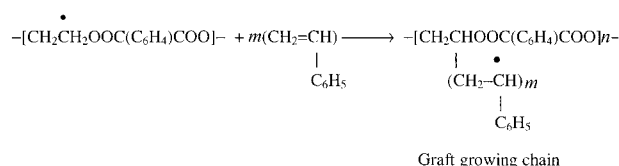
RESULTS AND DISCUSSION

Radiation-induced graft copolymerization of styrene onto PET films was carried out using simultaneous irradiation technique. The mechanism of the three kinetic steps involved in the graft copolymerization reaction in the present system can be proposed as follows:
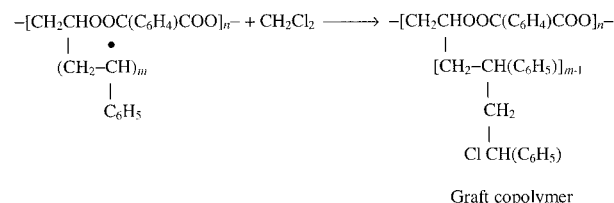
Initiation

$$-[CH_2CH_2OOC(C_6H_4)COO]_n- \xrightarrow{\gamma\text{-rays}} -[CH_2\overset{\bullet}{C}HOOC(C_6H_4)COO]_n-$$

Primary radical

Propagation

$$-[CH_2CH_2OOC(C_6H_4)COO]- + m(CH_2=CH) \longrightarrow -[CH_2\overset{\bullet}{C}HOOC(C_6H_4)COO]_n-$$

Graft growing chain

Termination

$$-[CH_2CHOOC(C_6H_4)COO]_n- + CH_2Cl_2 \longrightarrow -[CH_2CHOOC(C_6H_4)COO]_n-$$

Graft copolymer

Styrene concentration was varied by the dilution with methylene chloride during the grafting reaction so as to obtain grafted PET film having various degrees of grafting.

Effect of Monomer Concentration

The relationship between the degree of grafting and irradiation time at various styrene concentrations is shown in Figure 1. The degree of grafting increases linearly with the increase in the irradiation time for all styrene concentrations. Moreover, the degree of grafting increases as the styrene concentration increases until it reach its maximum value (168%) at a concentration of 5.77 mol/dm^3. Further increase in the styrene concentration leads to a sharp fall in the degree of grafting. This is most probably due to the increase in
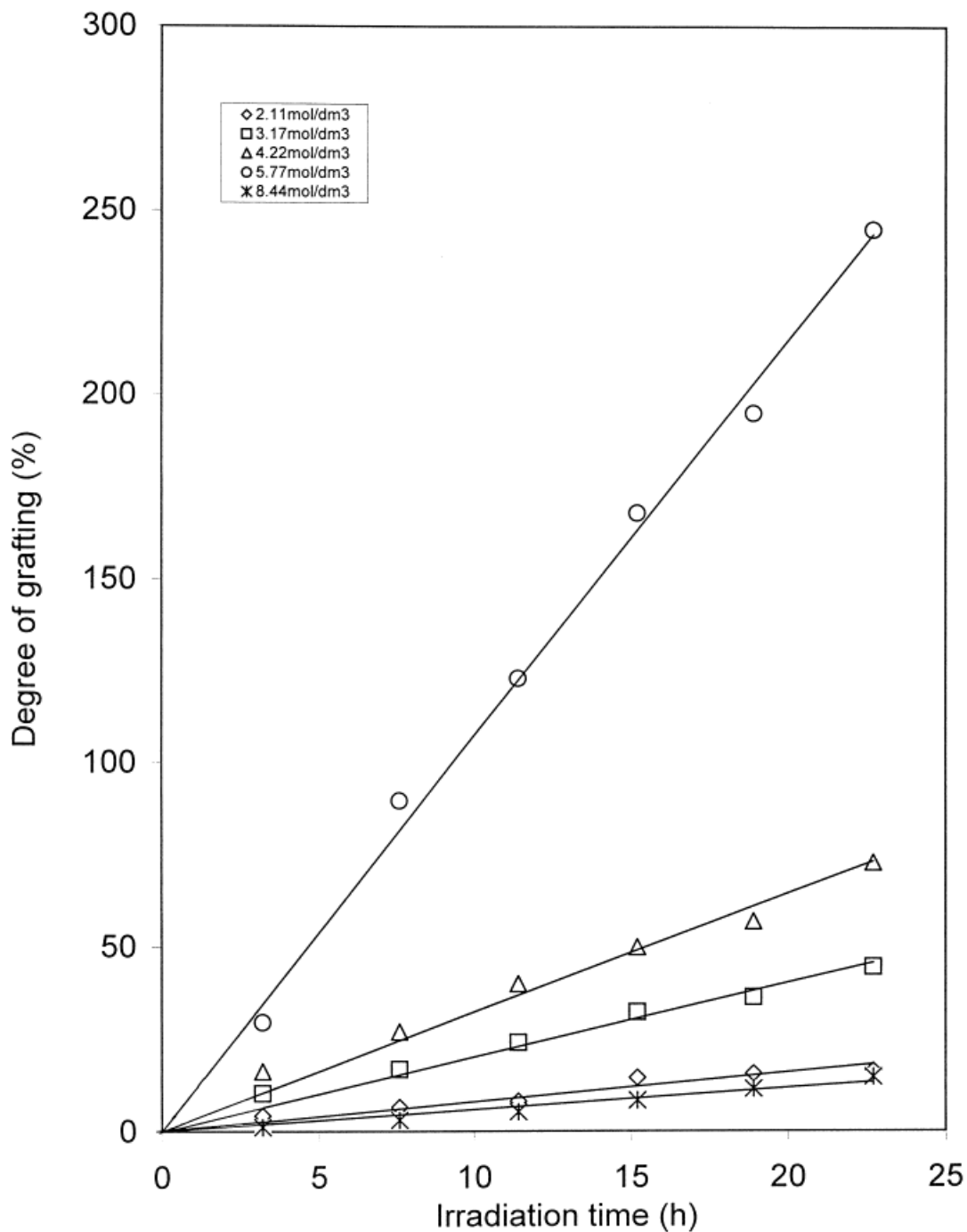
Figure 1 The relationship between the degree of grafting and the irradiation time at various styrene concentrations. Grafting conditions are dose rate, 1.32 kGy/h; diluent, methylene chloride; atmosphere, N_2; temperature, 30°C; film thickness, 60 μm.

the viscosity of the grafting solution under the influence of homopolymerization effect. This results in a reduction in the styrene diffusibility and a depletion in its concentration in the grafting layers and therefore the degree of grafting decreases.

Figure 2 shows the log–log relationship between the initial rate of grafting as well as the final degree of grafting and styrene concentration. Both the initial rate of grafting and the degree of grafting were calculated from Figure 1 at a styrene concentration in the range of 2.11–5.77 mol/
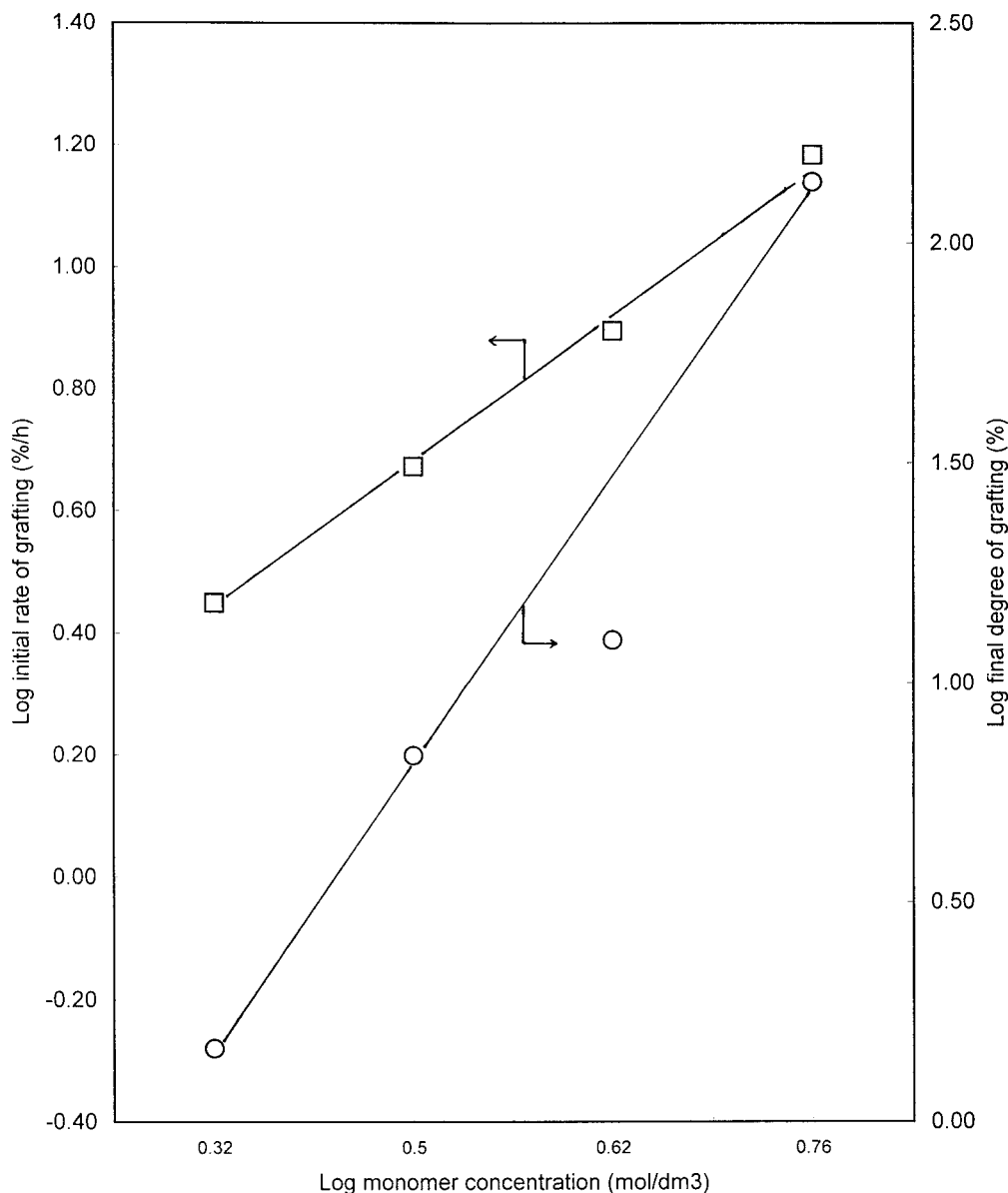
Figure 2 The log–log relationship between the initial rate of grafting as well as the final degree of grafting and styrene concentration. The initial rate of grafting and the degree of grafting are calculated at a total dose of 5 and 20 kGy, respectively. The rest of grafting conditions is similar to those in Figure 1.

dm^3. Both the initial rate of grafting and the degree of grafting were found to increase linearly with the styrene concentration. The dependence of the initial rate of grafting on the styrene concentration was obtained from the slope and was found to be on the order of 2.2.

This result suggests that the degree of grafting of styrene onto PET films not only depends on the amount of free radicals formed but also on the diffusivity of styrene through the poly-

mer matrix and its concentration in the grafting layers. It means that grafting in this system is critically controlled by the diffusion of the styrene through the already grafted layers that were initially formed near the film surface. Moreover, the grafting process starts at the surface of the film and proceeds internally by successive diffusion of the styrene until equilibrium swelling is reached at 5.77 mol/dm^3 monomer concentration.
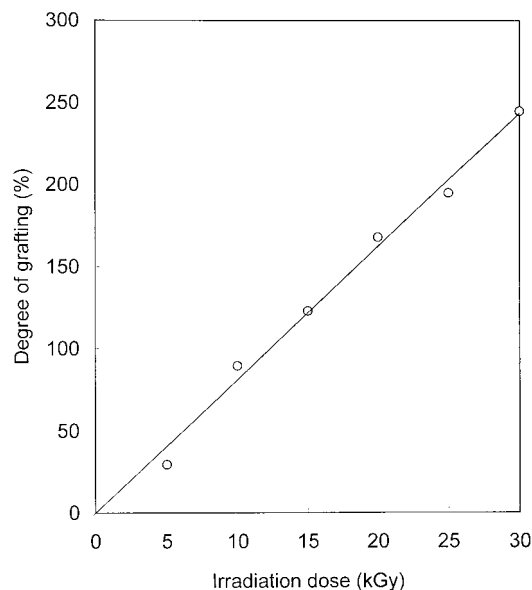
Figure 3 The relationship between the degree of grafting and the irradiation dose for grafting of styrene having a concentration of 5.77 mol/dm^3 onto PET films. Grafting conditions are similar to those in Figure 1.

Figure 4 The relationship between the degree of grafting and the dose rate for grafting of styrene having a concentration of 5.77 mol/dm^3 onto PET films. The rest of grafting conditions is similar to those in Figure 1.

Effect of Irradiation Dose

Figure 3 shows the relationship between the degree of grafting and irradiation dose for grafting of styrene having a concentration of 5.77 mol/dm^3 onto PET films. It is found that the degree of grafting increases linearly with the increase in the irradiation dose. This is due to the increase in the number of radical sites formed in the grafting system, which consequently leads to an increase in the number of radicals taking part in the grafting reaction.

Effect of Dose Rate

Figure 4 shows the relationship between the degree of grafting and the dose rate for grafting of styrene having a concentration of 5.77 mol/dm^3
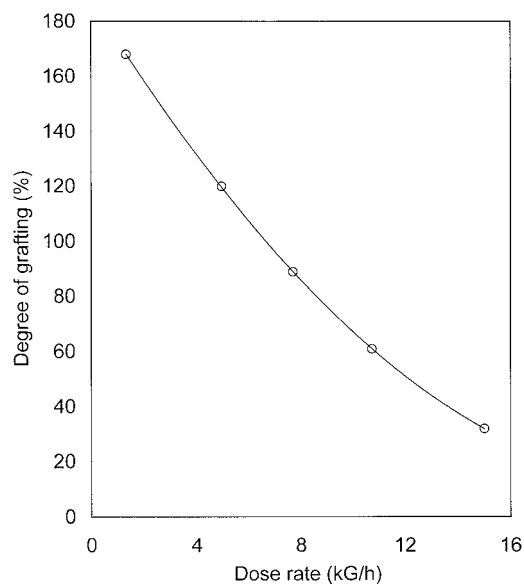
onto PET films. The dose rate was varied in the range of 1.32–15.00 kGy/h. As can be seen, the degree of grafting decreases with the increase in the dose rate and vice versa. This means that higher degrees of grafting were obtained on irradiation at low dose rates, whereas lower degrees of grafting were obtained at high dose rates. It well known that in simultaneous methods of graft copolymerization, the length of the side-chain grafts depends ultimately on the dose rate. Irradiation at high dose rate caused a formation of short grafted chains as a result of radicals' tendency to decay by recombination and fast termination as well as degradation of polystyrene-growing chains. In contrast, irradiation at low dose rate results in longer polystyrene-grafted chains and eventually higher degrees of grafting

Table I Effect of the Type of Diluent on the Degree of Grafting of Styrene onto PET Film

Diluent	Chain Transfer Constant (60°C)[a]	Degree of Grafting (%)	Remarks
Methanol	0.296	3.6	Much homopolymer formed
Benzene	0.200	5.3	Much homopolymer formed
Methylene chloride	0.150	168.0	No homopolymer formed

Note. Grafting conditions are monomer concentration, 5.77 mol/dm^3; irradiation dose, 20 kGy. The rest of grafting conditions is similar to Figure 1.
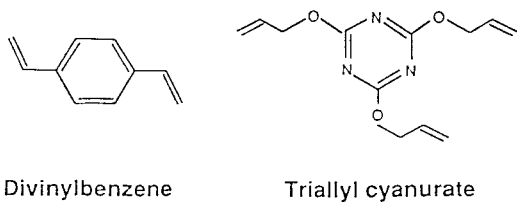[a]Obtained from Ref. 12.

Figure 5   The chemical structures of DVB and TAC.

due to the survival of radicals formed for longer time and the slow down in the termination of the polystyrene growing chains.

Effect of Diluent Type

The role of diluent in graft copolymerization of styrene onto PET films was investigated. Three different diluents (i.e., methanol, benzene, and methylene chloride) were used to dilute styrene during its copolymerization. Table I shows the effect of the type of diluent on the degree of grafting of styrene having a concentration of 5.77 mol/dm³ onto PET films. It was found that the degree of grafting drastically increased on the dilution of the styrene with methylene chloride compared to the dilution with methanol and benzene. Moreover, no homopolymer was noticed in the grafting residue with methylene chloride, unlike dilution with methanol and benzene, which leaves much homopolymer.

The high degree of grafting obtained on dilution with methylene chloride, which has low chain-transfer constant $(0.15)^{12}$ can be explained
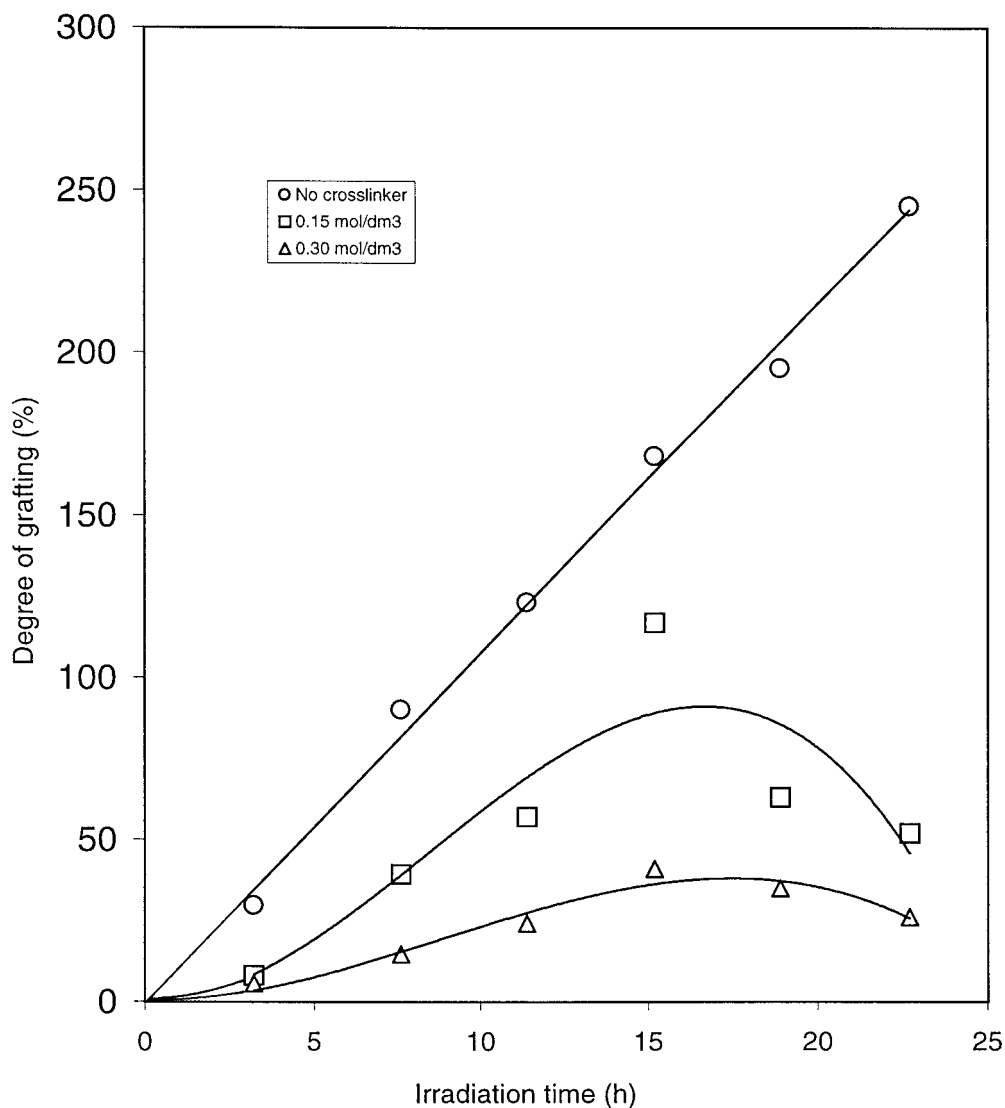

Figure 6   The relationship between the degree of grafting and the irradiation time at two different concentrations of DVB. Styrene concentration is 5.77 mol/dm³. The rest of grafting conditions is similar to Figure 1.
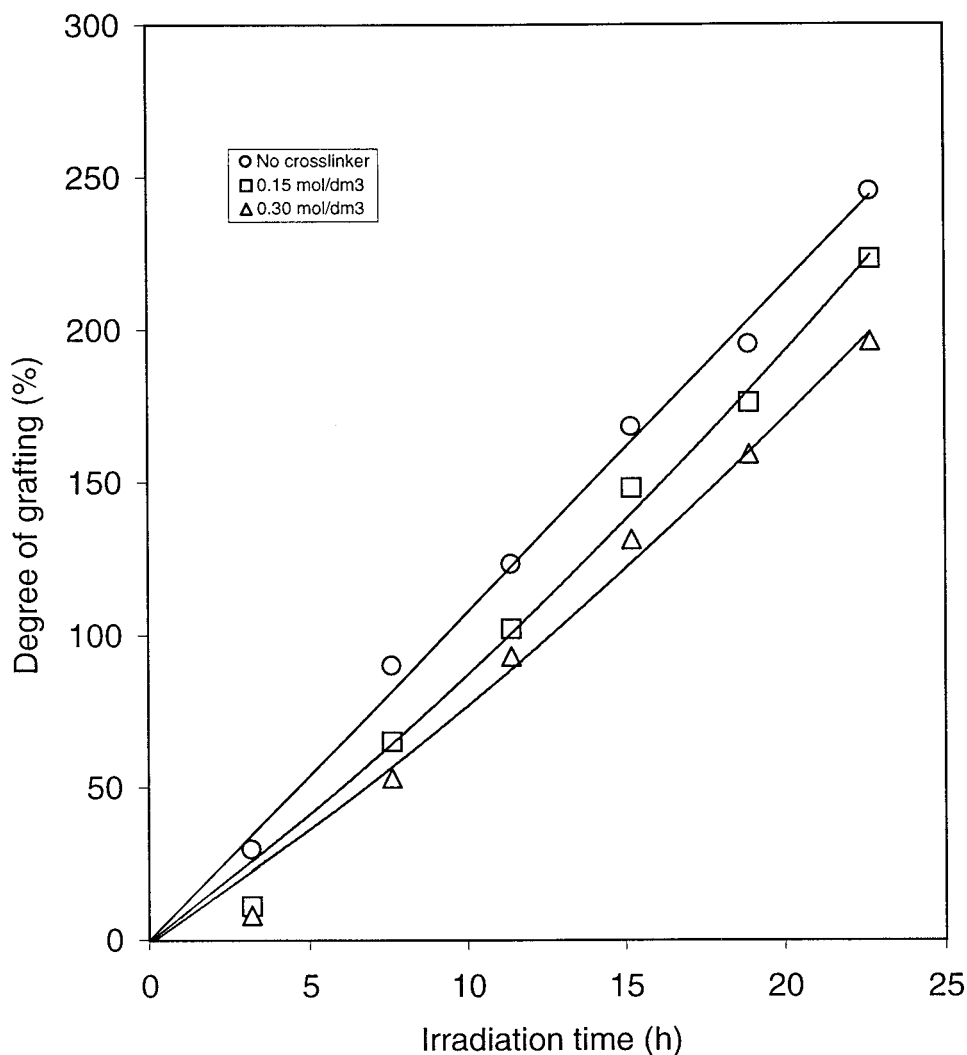
Figure 7 The relationship between the degree of grafting and the irradiation time at two different concentrations of TAC. Styrene concentration is 5.77 mol/dm^3. The rest of grafting conditions is similar to Figure 1.

on the basis of a simple series of polymerization reactions starting with an initial reaction of styrene with the free radical formed on the surface of PET film. This is followed by an increase in the length of polystyrene side chain as a result of the branching initiated by abstraction of the hydrogen at α-carbon of the polystyrene. On the other hand, the dilution of styrene with methanol which has high chain-transfer constant (0.296),[12] causes quick termination in the graft growing chains and as a result low degree of grafting is obtained and the grafting locates only at the surface of the PET film. The very low degree of grafting reported on dilution of styrene with benzene despite the fact that it is a strong solvent of polystyrene as methylene chloride could be attributed to the reactivity of the radicals formed on each diluent. The pres-

ence of resonance stabilization effect of benzene ring acts as an energy transfer agent and reduces the reactivity of the benzene radicals. The behavior the three diluents investigated in this study is similar to that observed on grafting of styrene with the same diluents onto fluorinated polymers such as polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA) films.[13-15]

Addition of Crosslinking Agents

Crosslinking agents are polyfunctional monomers having at least two double bonds in their chemical structure and are normally added to the grafting mixture to enhance desirable properties such
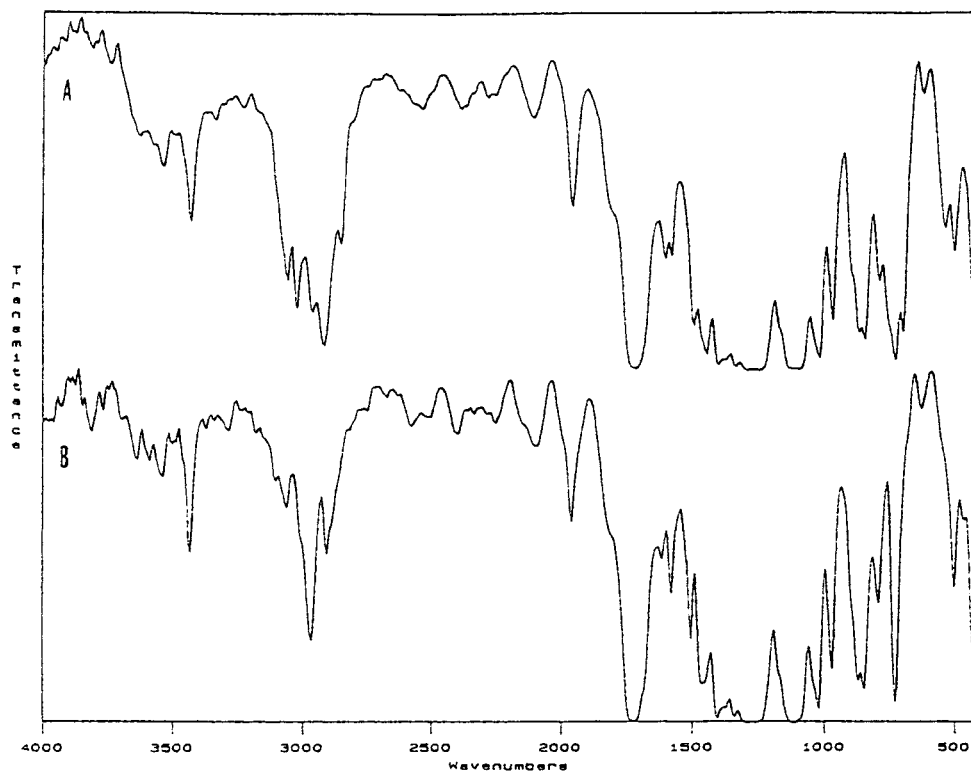
Figure 8 Typical FTIR spectra of (A) original and (B) grafted PET film having a degree of grafting of 55%.

chemical and mechanical stability in the grafted films. The effect of the addition of the crosslinking agents (i.e., DVB and TAC) on the degree of grafting was investigated at two different concentrations. The chemical structures of DVB and TAC is given in Figure 5.

Figure 6 shows the relationship between the degree of grafting and the irradiation time at two different concentrations of DVB. It can be obviously seen that the addition of DVB led to a considerable decrease in the degree of grafting and the amount of such decrease was found to increase as the DVB concentration increased from 0.15 to 0.30 mol/dm^3, respectively. Moreover, the degree of grafting tends to level off after 15 h with both DVB concentrations.

The behavior of the grafting system on addition of DVB presented here could be attributed to the deactivation of the initiated polystyrene growing chains in the PET matrix by crosslinking and/or termination by recombination due to the high concentration of formed organo-radicals. The former leads to a considerable hindrance in the mobility of the macromolecular chains. This resulted in a reduction in the swelling of the PET matrix and consequently the diffusibility of the

styrene and its concentration in the internal layers were lowered. The latter leads to the formation of short side-chain grafts. Therefore, low levels of grafting were obtained and the degree of grafting was eventually decreased. The increase in irradiation time apparently led to the enhancement of the hompolymerization effect and subsequent gelation of the monomer. As a result the degree of grafting tended to level off at high-irradiation time (beyond 15 h).

Figure 7 shows the relationship between the degree of grafting and the irradiation time at two different concentrations of TAC. The addition of TAC was found to lead to a decrease in the degree of grafting and such decrease was enhanced as TAC concentration in the grafting mixture was increased. However, the degrees of grafting obtained on the addition of TAC were found to be higher than those obtained on the addition of the same concentrations of DVB to the grafting mixture.

The effect of the addition of TAC can be explained on the same basis, which was suggested for the addition of DVB. However, the flexibility resulted from the presence three ether linkages in the allyl side chains of the TAC molecules leads to
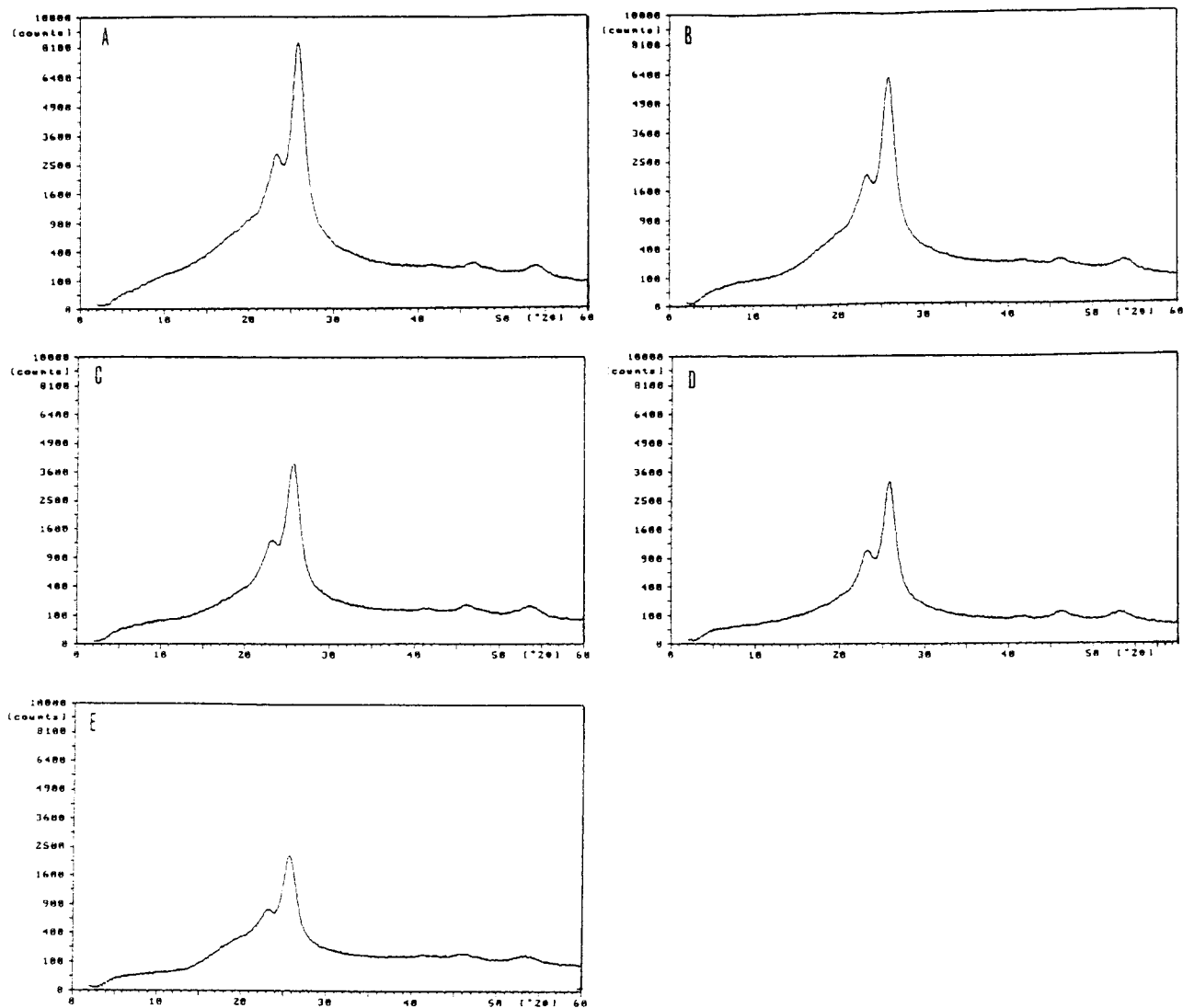
Figure 9 Diffractograms of the (A) original and grafted PET films having various degrees of grafting: (B) 13%, (C) 30%, (D) 55%, and (E) 168%.

higher flexibility in the side-chain polystyrene grafts. Therefore, higher swelling in the PET film was achieved compared to that with DVB and more styrene molecules were available in the grafting layers. Moreover, the presence of an inhibitor in technical DVB also causes an inhibition of polystyrene growing chains. The behavior of DVB and TAC in the present grafting system is found to be quite similar to that reported for the addition of the same crosslinking agents to styrene/FEP grafting system using preirradiation technique.[16]

Verification of Graft Copolymerization

The grafting of styrene onto PET film was verified from the IR spectra and the physical changes took place in the grafted films. Figure 8 shows typical FTIR spectra of original and grafted PET films having a degree of grafting of 55%. The original PET film is characterized by a strong band at 730 cm^{-1} representing the stretching vibration of the $C=O-O^-$ (ester group) and the absorption bands at 2870 and 2950 cm^{-1} representing the symmetric and the asymmetric stretching vibration of CH_2 group of ethylene, respectively, as depicted from spectrum A. The presence of the benzene ring in the PET films is established by the $=C-H$ stretching vibration at 3050 cm^{-1} and the skeletal $C=C$ in-plane stretching vibrations at 1500 and 1600 cm^{-1}, respectively. The *para*-substitution of benzene ring is represented by the band at 860 cm^{-1}. The grafting of styrene is confirmed by the mono-substitution of the benzene

ring of the polystyrene, which is represented by the aromatic out-of-plane C—H deformation band at 730 cm^{-1}. The absorption bands at 2975 cm^{-1} is assigned for the symmetric stretching of CH of the polystyrene.

In addition, the grafted films were found to be translucent compared to the original PET film, which was transparent. Moreover, their dimensions were found to be increased compared to that of the original films. All these features together confirm the successful grafting of styrene onto PET films.

X-Ray Diffraction Measurements

Figure 9 shows diffractograms of the original and grafted PET films having various degrees of grafting. The degree of crystallinity of the grafted films was found to decrease with the increase in the degree of grafting and vice versa as illustrated from the inverse proportional relationship between the peak intensity and the degree of grafting. Moreover, there is no shift in the Bragg's angle (2θ) of the grafted films compared to that of the original PET film. These results suggest that no changes and no new phases were induced in the chemical structure of the bulk of PET film by grafting of styrene. The reduction in the degree of crystallinity is most likely to be due to the dilution of the crystalline structure of PET matrix with the amorphous polystyrene grafts, which were found to increase gradually with the degree of grafting.

REFERENCES

1. Kale, P. D.; Lokhande, H. T. J Appl Polym Sci 1979, 19, 461.
2. Yeo, Z. P.; Rånby, B. J Appl Polym Sci 1990, 41, 1549.
3. Kurilenko, A. I.; Smetanina, L. V.; Alkesandrova, L. B.; Karpova, V. L. Vysokomol Soedin 1965, 7, 1935.
4. Korshak, V. V.; Mozgova, K. K.; Krukovskii, S. P. Vysokomol Soedin 1962, 4, 1625.
5. Shalaby, S. E.; Bayzeed, A. M.; Hebeish, A. J Appl Polym Sci 1978, 22, 1359.
6. Rao, K. N.; Rao, M. H.; Moorthy, P. N.; Charlesby, A. J Polym Sci, Polym Lett Ed 1972, 10, 893.
7. Sakurada, I.; Okada, T. Chem Abstr 1970, 73, 131883 V.
8. Harry, W.; Coover, J. Ger. Pat. 1,204,209, 1965.
9. Maga, E. E.; Tanner, D. U.S. Pat. 3,412,176, 1968.
10. George, W. S.; Teobly, G. T. U.S. Pat. 3,090,766, 1963.
11. Hebeish, A.; Shalaby, S. E.; Bayzeed, A. M. J Appl Polym Sci 1978, 22, 3335.
12. Brandrup, J.; Immergut, E. H., Eds.; Polymer Handbook; Wiley: New York, 1989; Chapter 2, p 81.
13. Nasef, M. M.; Saidi, H.; Dessouki, A. M.; El-Nesr, E. M. Polym Int 2000, 49, 399.
14. Nasef, M. M.; Saidi, H.; Nor, H. M. J Appl Polym Sci 2000, 76, 220.
15. Nasef, M. M.; Saidi, H.; Nor, H. M.; Dahlan, K. M.; Hashim, K. J Appl Polym Sci 1999, 73, 2095.
16. Gupta, B.; Büchi, F.; Scherer, G. G. J Polym Sci, Part A: Polym Chem 1994, 32, 1931.