

Structural Investigations of Poly(ethylene terephthalate)-graft-polystyrene Copolymer Films

MOHAMED MAHMOUD NASEF

Chemical Engineering Program, Universiti Teknologi Petronas, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

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ABSTRACT: Structural investigations of poly(ethylene terephthalate)-graft-polystyrene (PET-g-PS) films prepared by radiation-induced grafting of styrene onto commercial poly(ethylene terephthalate) (PET) films were carried out by FTIR, X-ray diffraction (XRD), and differential scanning calorimetry (DSC). The variation in the degree of crystallinity and the thermal characteristics of PET films was correlated with the amount of polystyrene grafted therein (i.e., the degree of grafting). The heat of melting was found to be a function of PET crystalline fraction in the grafted films. The grafting is found to take place by incorporation of amorphous polystyrene grafts in the entire noncrystalline (amorphous) region of the PET films and at the surface of the crystallites. This results in a decrease in the degree of crystallinity with the increase in the degree of grafting, attributed to the dilution of PET crystalline structure with the amorphous polystyrene, without almost any disruption in the inherent crystallinity. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1949–1955, 2002; DOI 10.1002/app.10515

Key words: structural investigations; PET-g-PS films; DSC; XRD

INTRODUCTION

Poly(ethylene terephthalate) (PET) has attracted interest in scientific and industrial sectors because of its good thermal stability, surface inertness, and excellent moisture resistance.^{1,2} To impart desirable properties, several vinyl monomers such as styrene, acrylic acid, methacrylic acid, 4-vinylpyridine, acrylonitrile, vinyl acetate, *N*-vinyl-3-morpholinone, and 2-methyl-5-vinylpyridine were grafted onto PET fibers in many occasions using graft copolymerization initiated by various techniques.^{3–11} This includes ionizing radiation, ultraviolet light, decomposition of chemical initiators, plasma treatment, and oxidation of polymers. Considering bulk modification, radiation-initiated

graft copolymerization is advantageous, particularly in terms of radiation-extensive penetration together with rapid and uniform radical initiation throughout the whole polymer matrix. However, radiation-induced graft copolymerization is well known to induce structural changes in the host polymer matrix.^{12,13} Such changes have a strong impact on the structural and other related (thermal and mechanical) properties of the grafted films. Therefore, monitoring of these structural changes is very significant to determine the applicability of the grafted films for certain uses.

In a previous study, grafting of styrene onto PET films was reported.¹⁴ The effect of the grafting parameters, that is, monomer concentration, irradiation dose, dose rate, and type of solvent, on the degree of grafting was investigated. The degree of grafting was found to be a function of grafting parameters. The dependency of the initial rate of grafting on the monomer concentration was found to be in the order of 2.2.

Correspondence to: M. M. Nasef (mahmoudeithar@mailcity.com).

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As for the present communication, poly(ethylene terephthalate)-*graft*-polystyrene (PET-*g*-PS) films were characterized using FTIR, XRD, and DSC. The aim is to establish correlations between the structural changes taking place in the membranes in terms of crystallinity and thermal behavior, represented by melting temperature as well as the heat of melting and the degree of grafting.

EXPERIMENTAL

Preparation of Grafted PET Films

PET-*g*-PS films were prepared by grafting of styrene (>99%; Fluka Chemie, Buchs, Switzerland) onto PET films (Dupont, Wilmington, DE) having a thickness of 60 μm and a size of 5×5 cm using a simultaneous irradiation technique. Styrene was diluted with methylene chloride in a glass ampoule and its concentration varied in the range of 2.11–5.77 mol/dm³. The grafting reaction was carried out by exposing the grafting mixture hosted in a nitrogen-flushed and tightly sealed ampoule to γ -rays from a ⁶⁰Co source at a dose rate of 1.32 kGy/h for 15 h. The grafted films were extracted, washed thoroughly with toluene, then dried under vacuum to a constant weight. The degree of grafting was gravimetrically determined as the percentage of weight gain in the grafted film using eq. (1):

$$\text{Degree of grafting} = [(W_g - W_0)/W_0] \times 100 \quad (1)$$

where W_g and W_0 are the weights of grafted and original PET films, respectively. The kinetics of the grafting reactions were discussed elsewhere.¹⁴

FTIR Measurements

FTIR measurements were performed with a Perkin Elmer spectrometer (Spectrum 2000 Explorer; Perkin Elmer Cetus Instruments, Norwalk, CT) at ambient conditions in transmittance mode at wavenumber in the range of 500–4000 cm⁻¹.

X-ray Diffraction Measurements

X-ray diffraction (XRD) measurements were performed using a Philips PW 1830, X-ray diffractometer (Philips, Almelo, The Netherlands). The diffractograms were measured at 2θ in the range

of 5–60° using Cu-K α radiation ($\lambda = 1.54$) monochromated by means of a nickel filter.

DSC Measurements

The thermal characteristics of PET-*g*-PS samples having various degrees of grafting were measured by differential scanning calorimetry (DSC, Pyris-1; Perkin Elmer). Typical samples having weights of 3–5 mg were used. The thermograms were obtained from the first-heating run in a temperature range of 50–300°C at a constant heating rate of 20°C/min and under nitrogen atmosphere. The degree of crystallinity (X_c) or crystallinity (%) of the original PET film was calculated using eq. (2):

$$X_c = (\Delta H_m / \Delta H_{m100}) \times 100 \quad (2)$$

where ΔH_m is the heat of melting of PET film and ΔH_{m100} is the heat of melting of 100% crystalline PET polymer, which is 115 J/g.¹⁵

The weight fraction of PET in grafted films (W_{PET}) is calculated using eq. (3):

$$W_{\text{PET}} = m_{\text{PET}} / (m_{\text{PET}} + m_{\text{PS}}) \quad (3)$$

where m_{PET} is the weight of PET film and m_{PS} is the weight of the grafted polystyrene, which is obtained from eq. (1) without multiplying by 100. Using eq. (2), the degree of crystallinity of the grafted PET film (X_c)_{grafted} is calculated as follows:

$$(X_c)_{\text{grafted}} = (\Delta H_{m \text{ grafted}} / \Delta H_{m100}) \times 100 \quad (4)$$

where $\Delta H_{m \text{ grafted}}$ is the heat of melting of PET fraction in the grafted film.

RESULTS AND DISCUSSION

Several PET-*g*-PS films having degrees of grafting in the range of 12–168% were prepared for this study. During the grafting reactions, only the monomer concentration was allowed to vary from 2.11 to 5.77 mol/dm³, whereas other grafting parameters such as irradiation dose, dose rate, type of solvent, temperature, and atmosphere were kept constant. The reason behind this step was to unify the sources causing the structural changes in all grafted films. A general molecular structure of the resulting PET-*g*-PS films is shown in Fig-

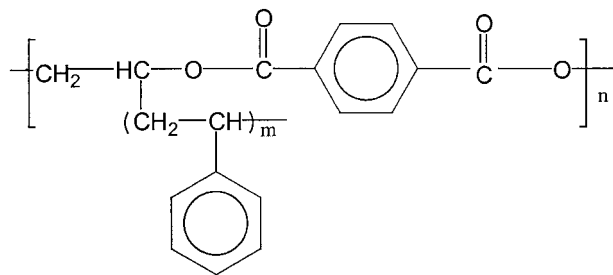


Figure 1 General molecular structure of PET-*g*-PS films.

ure 1. The grafted films were found to be rigid and translucent compared to the original (pregrafted) PET film, which was perfectly transparent. The grafted films were identified using FTIR spectral analysis. Figure 2 shows typical FTIR spectra of original and grafted PET films with a degree of grafting of 168%. The original PET film is characterized by strong bands at 1740 and 730 cm^{-1} , representing the stretching vibration of the $\text{C}=\text{O}-\text{O}^-$ (ester group), and the absorption bands at 2872 and 2951 cm^{-1} , representing the symmetric and the asymmetric stretching vibration of the 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 $=\text{C}-\text{H}$ stretching vibration at 3049 cm^{-1} and the skeletal $\text{C}=\text{C}$ in-plane stretching vibrations at 1503 and 1598 cm^{-1} , respectively. The para-disubstitution of the benzene ring is represented by the band at 859 cm^{-1} . Grafting of styrene onto PET films is confirmed by the monosubstitution of the benzene ring of the polystyrene side chains, which is represented by the aromatic out-of-plane $\text{C}-\text{H}$ deformation strong bands at 760 and 690 cm^{-1} , respectively. The absorption band at 2977 cm^{-1} is assigned for the symmetric stretching of $-\text{CH}-$ of the polystyrene. Figure 3 shows typical spectra of PET-*g*-PS films having various degrees of grafting. As can be seen, the size of the characteristic bands is proportional to the degree of grafting, that is, the increase in the degree of grafting is accompanied by an increase in the size of the characteristic bands.

To monitor the variation in the degree of crystallinity induced by the structural changes taking place during radiation-initiated grafting, the various PET-*g*-PS samples were primarily investigated using XRD. Figure 4 shows typical diffractograms of PET-*g*-PS having various degrees of grafting compared to that of the original PET film. As can be seen, the degree of crystallinity of

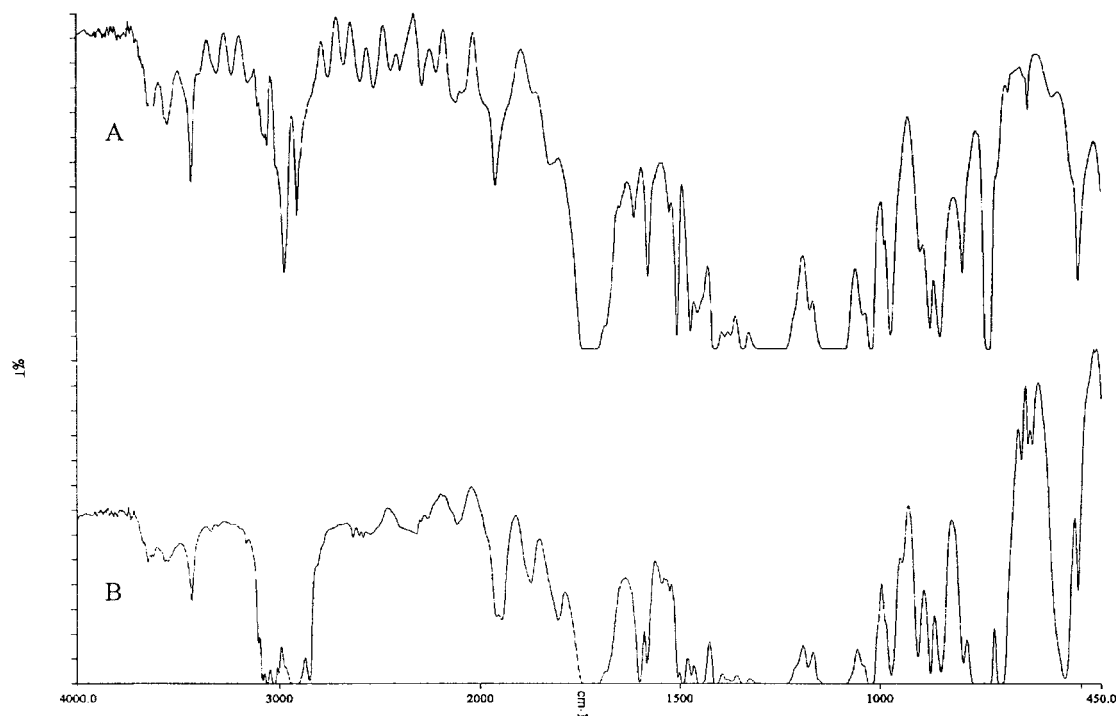


Figure 2 Typical FTIR spectra of (A) original PET film and (B) 176% grafted PET-*g*-PS film.

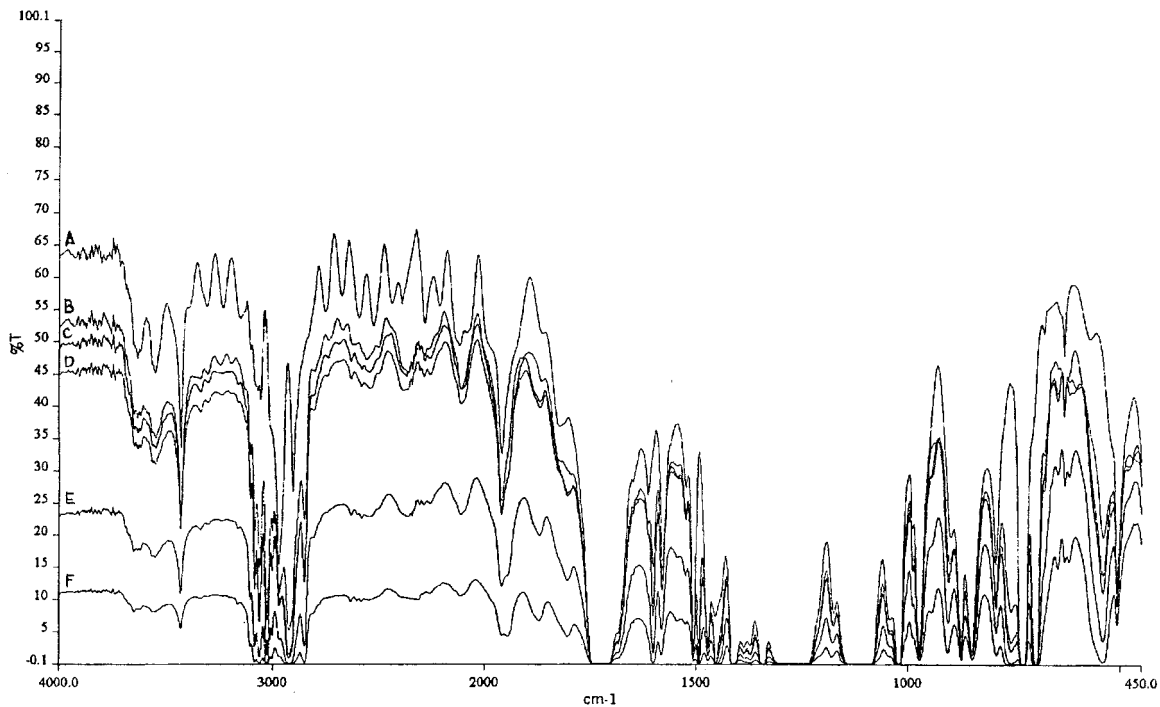


Figure 3 Typical FTIR of original PET film (A) and PET-g-PS films having various degrees of grafting: (B) 12%; (C) 30%; (D) 55%; (E) 66%; and (F) 168%.

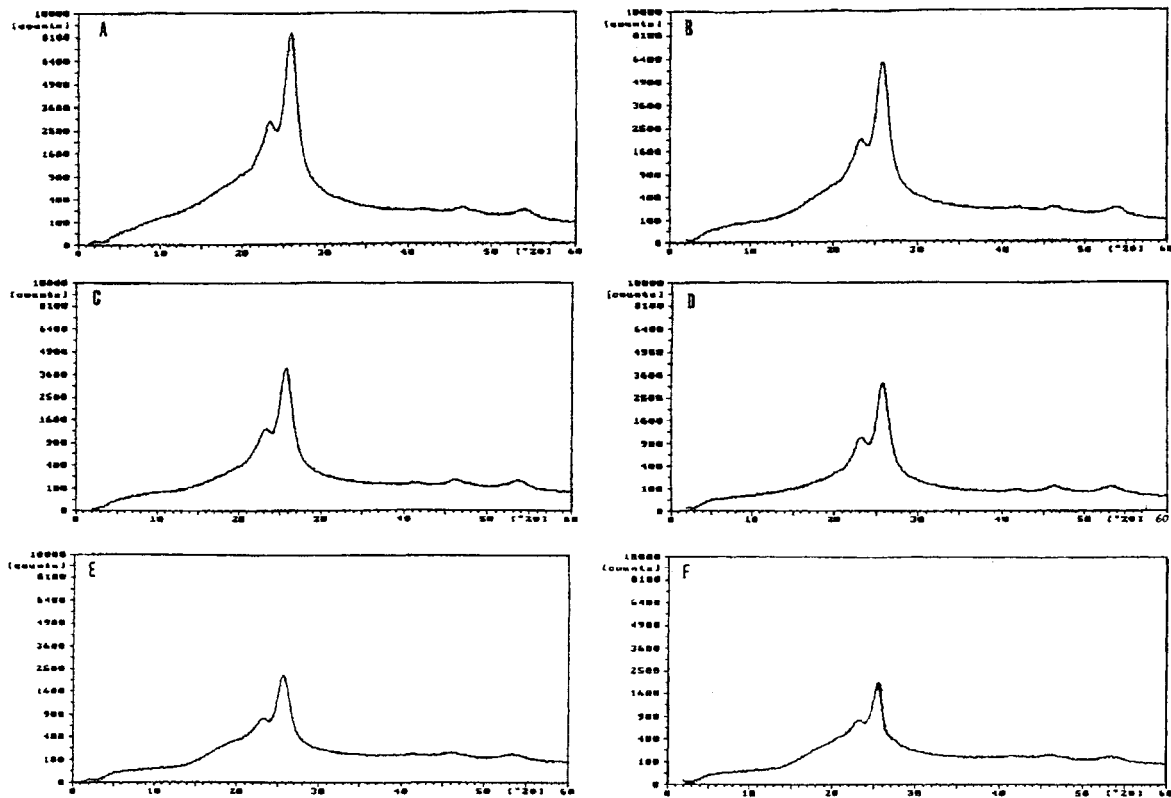


Figure 4 Typical diffractograms of original PET film (A) and PET-g-PS films having various degrees of grafting: (B) 12%; (C) 30%; (D) 55%; (E) 66%; and (F) 168%.

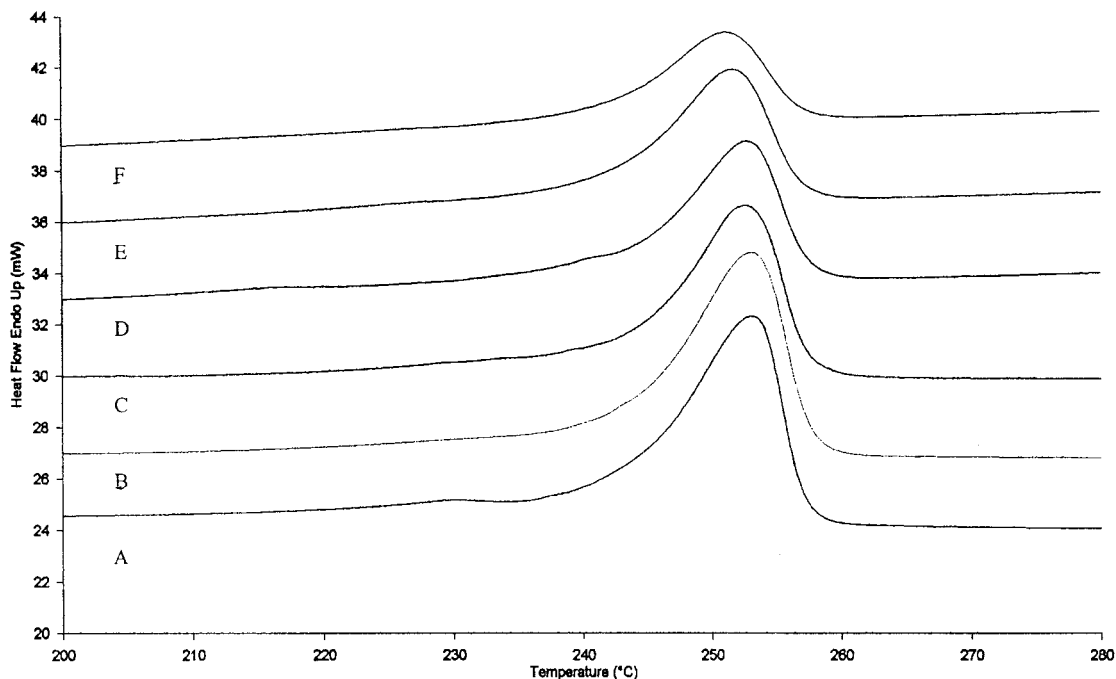


Figure 5 Typical DSC thermograms of original PET film (A) and PET-g-PS films having various degrees of grafting: (B) 12%; (C) 30%; (D) 55%; (E) 66%; and (F) 168%.

the grafted films decreases with the increase in the degree of grafting and vice versa, as illustrated from the inverse proportional relationship between the intensity of the reflection peak and the degree of grafting. Moreover, there is no shift in the Bragg's angle ($2\theta = 26 \pm 1$) of the grafted films compared to that of the original PET film. These results suggest that no changes took place in the crystalline structure during the grafting reactions and the reduction in the degree of crystallinity is mostly attributable to the dilution of the crystalline structure of the PET matrix with the amorphous polystyrene grafts.

To further quantify the decrease in the degree of crystallinity and determine the extent of variation in the thermal characteristics, DSC analysis was performed on samples having the same degrees of grafting. Figure 5 shows typical DSC thermograms of original PET film and PET-g-PS films having various degrees of grafting. The melting temperature of the various grafted PET films shows a very tiny shift toward a lower value compared to that of the original PET film. The shape of thermograms under the melting peak remains almost similar in all grafted samples. However, the melting peaks broaden and the front part of the thermograms of the grafted films shows different shapes with the variation of the

degree of grafting, which is most likely the result of variation in the specific heat associated with the polystyrene grafts at various grafting levels. The area under the peaks was found to decrease with the increase in the degree of grafting. Accordingly, the heat of melting that was calculated from these areas shows a considerable decreasing trend with the increase in the degree of grafting, as depicted in Table I, which shows a summary of the thermal characteristics of PET-g-PS films as

Table I Summary of Thermal Characteristics of Various PET-g-PS Films as Revealed by DSC Measurements

Degree of Grafting (%)	Peak Area	Thermal Characteristics	
		T_m (°C)	ΔH_m (J/g)
0	241.2	253.1	40.2
12	235.1	253.0	36.9
30	194.4	252.7	32.2
55	145.6	252.8	27.1
66	142.2	251.7	22.3
168	96.2	251.0	16.3

Original PET (0% grafting) is used as a reference.

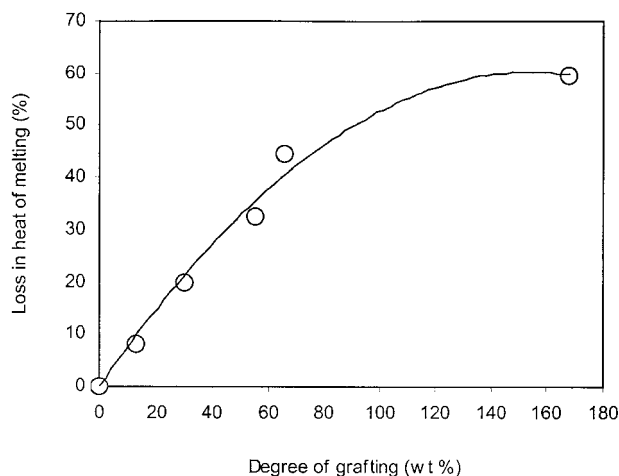


Figure 6 Relationship between the loss in the heat of melting and the degree of grafting.

revealed by DSC measurements. The original PET film was found to have a melting temperature and a heat of melting at 253.1°C and 40.2 J/g, respectively. The melting temperature was found to be reduced marginally with the increase in the degree of grafting up to 55%. As the degree of grafting further increased, the reduction in melting temperature slightly increased. Because the changes in the melting temperature were very small, it can be assumed that no disruption took place in the crystalline structure of the original PET films as a result of styrene grafting, and the melting temperature is independent of the degree of grafting (below 66% degree of grafting). At a degree of grafting as high as 168%, very minor crystal disruption took place, causing a reduction in melting temperature of the original PET film by 2°C. This can be understood based on the fact that radiation-initiated radicals are normally produced in both amorphous and crystalline regions. Below 66% degree of grafting, the polystyrene chains are entirely formed in the amorphous region of the PET film and possibly near the surface of the crystallites. As the degree of grafting increases, a small part of the formed polystyrene chains tends to attach to the lamellar surfaces of crystallites, causing very minor reduction in the melting temperature. Consequently, it can be concluded that grafting was initiated and took place in the entire amorphous region of PET film and mostly in areas very close to the surface of the crystallites, depending on the level of grafting. This is also supported by the fact that the crystal melting temperature of PET film (253.1°C) is much higher than the temperature at which the

grafting reaction was conducted (30°C). Accordingly, it can be suggested that styrene does not cause any swelling to the crystallites during grafting reactions and the formed polystyrene grafts did not penetrate the crystallites of PET films. These results are also in good agreement with the previous results that showed grafting of styrene onto PET films proceeds by a front mechanism, that is, grafting was found to start at layers close to the film surface and moves internally toward the middle of the film by progressive diffusion through successive swollen grafted layers.¹⁴ It can be finally concluded that the incorporation of the amorphous polystyrene grafts is the main reason behind the changes taking place in the thermal characteristics in general and heat of melting in particular.

To further investigate the effect of the incorporation of amorphous polystyrene on the heat of melting, the loss in the heat of melting is plotted against the amount of grafted polystyrene (i.e., degree of grafting), as shown in Figure 6. The loss in the heat of melting is found to increase drastically with the increase in the degree of grafting. This indicates that the decreasing trend in the heat of melting (observed in Table I) increases with the increase in the amount of incorporated amorphous polystyrene grafts. This leads to a considerable decrease in PET crystalline fraction in the grafted films with the increase in the degree of grafting, as shown in Figure 7, which shows the relationship between the degree of crystallinity and the degree of grafting. The degree of crystallinity of the original film was cal-

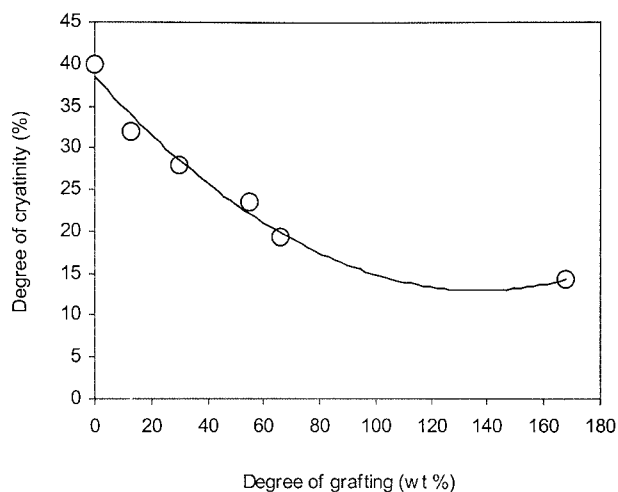


Figure 7 Relationship between the degree of crystallinity and the degree of grafting.

culated using eq. (2) and that of the various grafted PET films using eq. (4), after taking the weight fraction of PET in the grafted film into consideration. The degree of crystallinity was found to have a decreasing trend, which is a function of the amount of polystyrene grafted therein (i.e., the degree of grafting). These observations are in a complete agreement with the XRD results, which showed the intensity of the crystalline reflection peaks of PET decreasing with the degree of grafting. These results suggest that the reduction in the crystallinity of the grafted films is mainly attributed to the dilution of the crystalline structure with the amorphous polystyrene grafts, which increase gradually with the degree of grafting. The extent of the dilution effect in the present system is well recognized from the fact that the degree of crystallinity of 168% grafted PET film was reduced to approximately one-third of its original value.

CONCLUSIONS

The structural investigations of PET-*g*-PS films prepared by radiation-induced grafting of styrene onto commercial PET films was carried out. Grafting of styrene was confirmed by FTIR spectral analysis, which showed a strong band at 730 cm^{-1} coupled with an increase in the intensity of aliphatic —CH— band at 2977 cm^{-1} , representing monosubstitution of the benzene ring of the polystyrene. The XRD results showed that the degree of crystallinity decreased with the increase in the degree of grafting, according to the inverse relationship between the peak intensity and the degree of grafting, together with the absence of any remarkable shift in the Bragg's angle (2θ). DSC analysis showed that the melting tem-

perature is independent of the degree of grafting (below 66%), whereas the heat of melting and the degree of crystallinity are functions of the degree of grafting. The decrease in the degree of crystallinity is attributed to the dilution of the crystalline structure with amorphous polystyrene without any crystalline disruption, except above 55% degree of grafting.

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