Grafting of acrylamide to nylon-6 by the electron beam preirradiation technique: 3. Degree of crystallinity at high grafting yields

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X-ray diffraction measurements of nylon-6 grafted with acrylamide indicate that the crystallites of the nylon-6 are only marginally affected by very extensive radiation grafting. Considerable stresses are built up in the samples during their grafting. Fusion endotherms of the grafted samples are masked to a large extent by the stress–release exotherms. Consequently, values of ΔH_f derived from d.s.c. measurements of the unannealed samples are not reliable. Stresses built up during grafting may be at least partially released by treating them with 65% formic acid at room temperature. This annealing procedure is preferable to thermal annealing because of the decomposition of polyacrylamide at elevated temperatures. Perfection and size of the nylon-6 crystallites also increases significantly as result of such treatment.

(Keywords: crystallinity; radiation grafting; nylon-6; acrylamide; X-rays; d.s.c.)

INTRODUCTION

The crystalline regions of semicrystalline polymers resist chemical attack, because penetration by the molecules of the attacking reagents is effectively prevented by the tightly packed ordered structure of the crystallites[1]. It is, therefore, not surprising that radiation grafting of such polymers leads to preferential grafting of the amorphous regions[2,3]. The distribution of the free radicals created by radiation is random, although at very low temperatures the actual concentrations of free radicals may be higher in the amorphous rather than in the crystalline regions. This is due to the higher probability of cage recombination in the crystallites.

Nylon 6-acrylamide (NYgAM) membranes containing up to 1300% of acrylamide (AM) have recently been prepared by the electron beam preirradiation technique[4]. In such highly grafted materials the host polymer (nylon-6) constitutes only a minor fraction of the product. To what extent do the crystallites of the nylon backbone remain immune to grafting under such extreme circumstances? Kinetic and spectroscopic evidence seems to indicate that at least part of the backbone crystallites is preserved even after very extensive grafting (cf. ref. 4). We decided, therefore, to undertake a quantitative study of the crystallinity of the nylon-6 backbone of the highly grafted materials, using X-ray diffraction and d.s.c. studies.

The crystalline structure of nylon-6 has been elucidated on the basis of X-ray studies. A detailed discussion of the subject was recently given by Parker and Lindenmeyer[5]. Several d.s.c. and d.t.a. investigations have dealt with the crystallinity of nylon-6 and of other radiation grafted semicrystalline polymers[2–6,7]. However, the possibility of distortion of the crystallites of the backbone polymer during the grafting process was not considered by these investigators. Recently, distortion of crystallines and crystalline transitions were noted in case of heterogeneous modification of polyethylene systems[8,9]. The effect of such changes on d.s.c. and X-ray diffraction results have been discussed in detail[9,10]. The possibility that analogous phenomena may occur during grafting of nylons must also be checked. Annealing procedures, aimed at the elimination of the eventual imperfections of the crystallites remaining in the grafted samples, were therefore applied during presently conducted experiments.

EXPERIMENTAL

13 μ thick, biaxially oriented nylon-6 films (SNIA Viscosa) were grafted as recently described elsewhere[4]. Nylon-6 films or their grafts were annealed at room temperature by immersion for 60 min in 65% (w/w) formic acid*. The treated films were then washed with distilled water and dried to constant weight in a vacuum oven at 50°C.

D.s.c. measurements

A DuPont 990 Thermal Analyser was used for d.s.c.

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* Acrylamide decomposes at elevated temperatures, which are required for the thermal annealing of nylon-6. A procedure which enables room temperature annealing of polyamides was, therefore, used in the present study.

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determinations. Measurements were performed in vacuum in the range of 160°–260°C. The heating rate in this range was 10°/min. The instrument was calibrated with tin (used as a reference). The heat of fusion ΔH_f of the samples was calculated from the area under the melting endotherms. The heat of fusion of nylon-6 backbone in the grafted samples was calculated from the relationship:

$$\Delta H_f^* = \Delta H_f(\text{sample})(100 + G)/100 \qquad (1)$$

where G is the graft yield in percent.

The molten samples were recrystallized by cooling up to 150°C at a rate of 2°/min and the remelt endotherms of the recrystallized samples were again determined.

X-ray diffraction measurements

The X-ray diffraction measurements were performed on a Phillips PW 2053/65 horizontal goniometer (Cu target, $\lambda = 1.54431$ Å, 34 KV, 20 mA) at a rate of 1° (2θ)/min. All samples for X-ray measurements were 4 mm thick. Film samples were prepared by pressing several discs of the grafted films together. The analysis of the powdered samples was performed on tablets pressed at 50°C in vacuum. In order to obtain random distribution of crystallite orientations in such samples, fine powders were prepared by pulverizing nylon films by filing†.

The crystallinity of the nylon-6 samples was calculated from the X-ray diffractograms by the Hermans and Weidinger and by the Ruland procedures[10]. Hermans and Weidinger procedure was also used for the calculation of the crystallinity of the nylon backbone in the grafted samples. A correction for the contribution of the amorphous halo of polyacrylamide to the overall integral intensity of the grafted samples (I_{ov}) was introduced. It was derived from the measured amorphous scattering of pure polyacrylamide (I_{PAM}) by correcting it for the difference between the absorption of pure PAM and of its mixture with nylon-6.

$$I_{corr} = \rho_s\mu_s[I_{ov} - I_{PAM}\rho_{PAM}\mu_{PAM}G/\rho_s\mu_s(1 + G)] \qquad (2)$$

where ρ_s, ρ_{PAM}, μ_s and μ_{PAM} are the densities and molar absorption coefficients of the investigated samples and of the pure polyacrylamide, respectively, and G is the graft yield.

RESULTS AND DISCUSSION

Crystallinity of nylon-6 films

X-ray diffractograms of the commercial biaxially oriented nylon-6 films used in our experiments are shown in *Figure 1*. Only the reflection peak at 24.0° (characteristic of the 002 and 202 planes of the nylon-6 crystals in their α form) is noted when the film sample is mounted with the surface of the membranes perpendicular to the incident X-ray beam. On the other hand, the reflection peak at 20.2° (characteristic of the 200 plane of the crystallites) is predominant when the sample is mounted with the surface of the film discs parallel to the X-ray source. Obviously, the crystallites in the investigated films are oriented with their basal *ab* plane, corresponding to the plane of the CH_2 zig-zag chain (parallel to the film surface). Both grafting and annealing of such films, may induce changes in the crystal orientation[2,11], which could be confused with changes in the degree of crystallinity in case of experiments conducted with a horizontal goniometer. Consecutive experiments were conducted, therefore, on randomized samples prepared by compression of powder obtained by filing the nylon films. Their X-ray diffraction patterns before and after annealing by swelling with 65% formic acid are shown in *Figure 2*. It is evident that the perfection of the crystallites and/or their size increases as result of annealing, since the reflection peaks become much sharper. The overall degree of crystallinity also seems to increase significantly as result of such treatment. This is confirmed by d.s.c. measurements. Thus, the degree of crystallinity of the annealed material is calculated to be 49% and that of the initial product is found to be ≈30%.

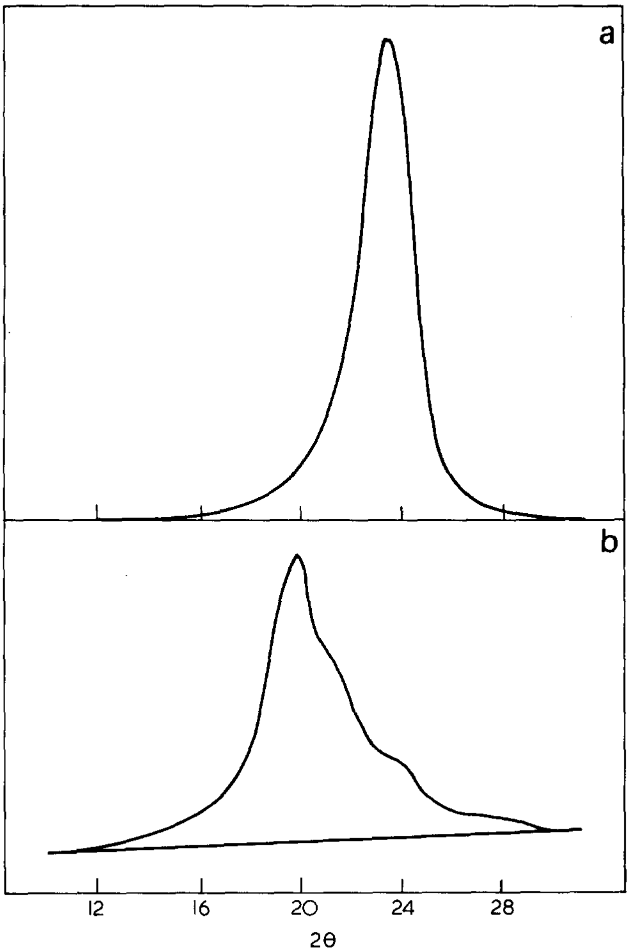

Figure 1 Diffractometer scans of the investigated, biaxially oriented nylon-6 films. (a) Film surface mounted in a plane perpendicular to X-ray. (b) Film surface mounted in a plane parallel to X-ray source

An analogous increase in the perfection of crystallites and in the degree of crystallinity of semicrystalline polymers due to swelling by suitable solvents has been previously observed also for other systems[11], and was attributed to increased mobility of the polymer chains within the solvent swollen armosphous regions, which enables rearrangement and enlargement of the adjacent crystalline phase. When crystallites become larger as a result of such changes, the entanglement of the polymeric chains in the amorphous regions diminishes and the amorphous phase becomes more accessible to penetration by alien molecules. It may be seen indeed from

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† Grinding of the nylon films yielded thin flakes which tended to align themselves during compression in a more or less regular fashion.

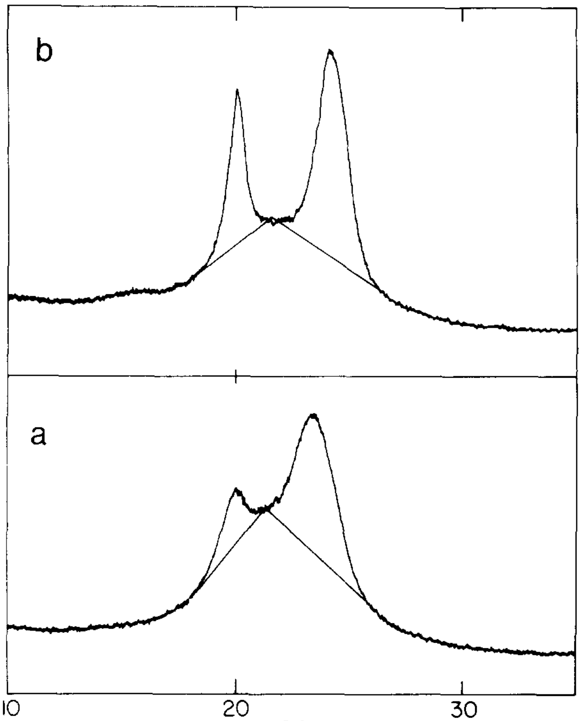

Figure 2 Diffractometer scans of the randomized samples of nylon-6 before (a) and after (b) annealing with 65% formic acid

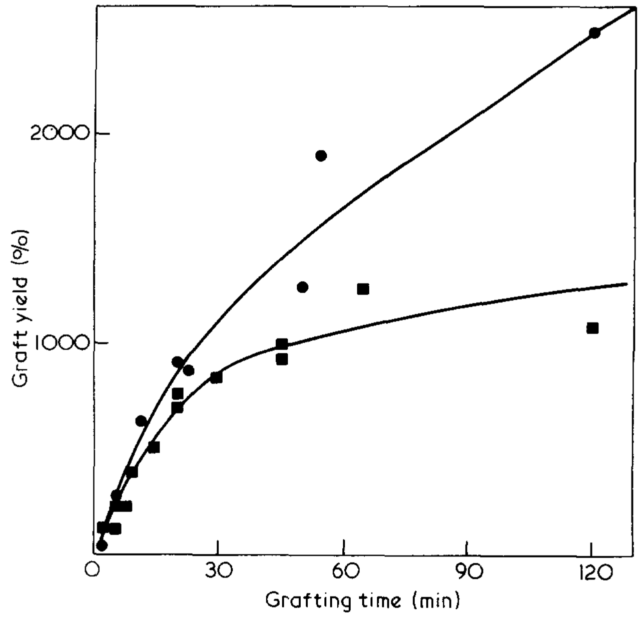

Figure 3 Rate of grafting by acrylamide of the preirradiated samples. 10% AM; temp. 50°C, 12 Megarad. ■, untreated Nylon-6; ●, film annealed with 65% formic acid

Figure 3 that, at high grafting yields, the rate of grafting is much faster for the annealed material than for the untreated one. The effect of annealing of nylon on the rate of grafting was previously reported[12] and was also observed for other semicrystalline systems[12,13].

Crystallinity of the nylon-6 radiation grafted by acrylamide

Grafting experiments were conducted on the untreated nylon-6 films and on samples annealed by immersion for 60 min in 65% formic acid at room temperature. Typical X-ray diffraction patterns of the powdered samples of the untreated Nylon-6 grafted with AM are shown in *Figure 4*. Fusion endotherms of such materials before and after annealing as well as after recrystallization from a melt are shown in *Figure 5*. X-ray diffractograms and d.s.c. endotherms of similar grafts crosslinked with 5% of bis-acrylamide are shown in *Figure 6* (see also *Figure 8*).

It is evident that the reflections at 20.2° and 24.0°, assigned to the 200 and 002; 202 planes in the α form of nylon-6 crystallites[6], became much sharper, upon annealing. Moreover, a reflection at 22° is also noted in samples crosslinked with bis-AM. This reflection has been assigned to the 002 plane of the γ form of nylon-6 crystallites, which is characterized by a twisted amide group. Apparently the α to γ transition may provide a route for release of stresses built up during grafting.

Inspection of X-ray data in *Table 1*, reveals that even very extensive grafting affects only marginally the crystalline phase of the nylon-6. Moreover, up to 100–200% grafting yields, the effect of annealing is nearly identical for the original unmodified nylon-6 and for the

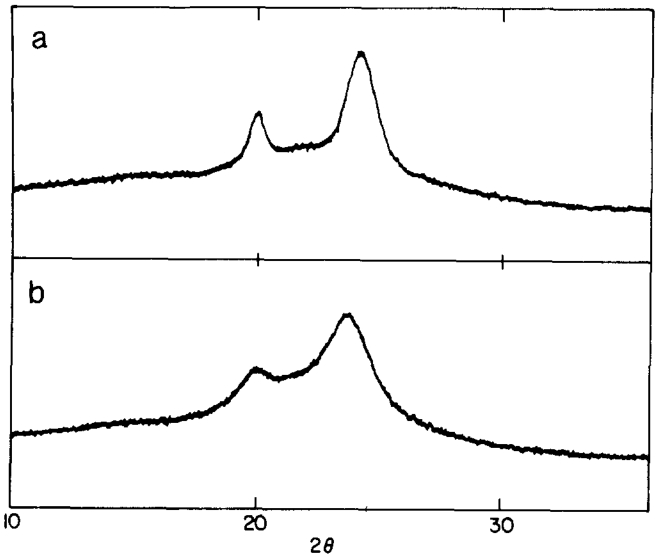

Figure 4 Diffractometer scans of a grafted sample after randomization. Graft yield: 147% AM. (a) After annealing with 65% formic acid. (b) Before annealing

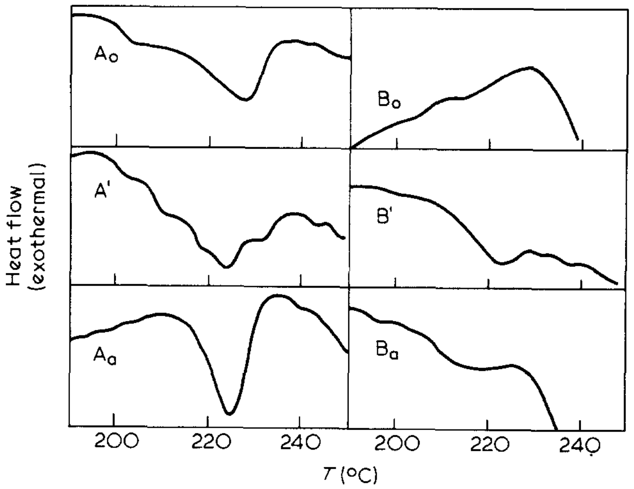

Figure 5 D.s.c. curves of grafted samples before and after annealing and after recrystallization from a melt. A, 323% graft; B, 856% graft. Subscripts o and a denote the original and the annealed samples, respectively. A' and B' denote samples A and B recrystallized from a melt

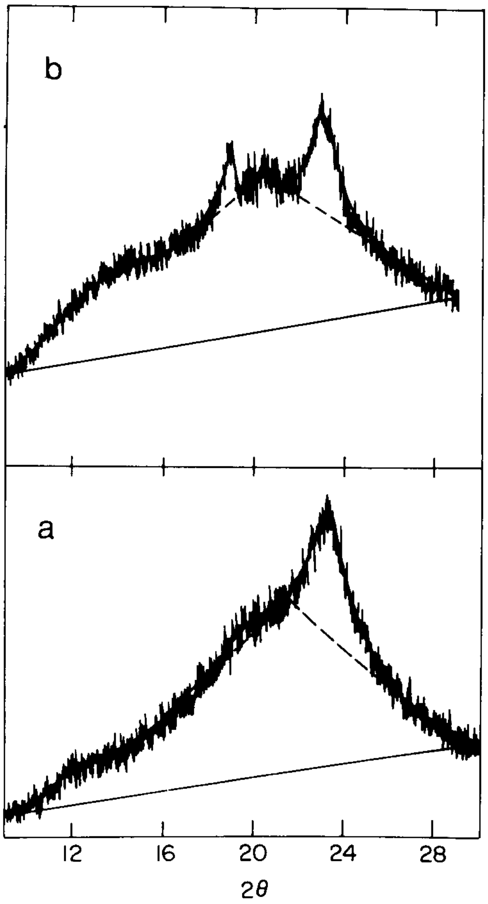

Figure 6 Diffractogram of grafted nylon-6 crosslinked with bis-acrylamide. Grafting yield 867% (bis-AM-44%). (a) Before, and (b) after annealing with 65% formic acid

Table 1 Crystallinity of the nylon-6 backbone in the radiation grafted samples

Sample	Graft yield (%)	Annealing after grafting[a]	Degree of crystallinity of nylon-6 (%) Calculated from X-ray[b]	Degree of crystallinity of nylon-6 (%) Calculated from d.s.c.[c]
No	none	–	35.2 (30)	25.5
N[a]	none	–	48.6 (41)	49.4
776	147	none	34.9	25.5
776a	147	yes	47.0	38.5
381a	323	yes	–	30.3
673[d]	506	none	–	10.0
673[d]	506	yes	38.0	21.5
775	650	none	35.2	7.5
775a	650	yes	35.2	25.0
777	914	none	31.6	–
777a	914	yes	34.4	22.5

[a] Annealed by treatment for 60 min in 65%formic acid at 25°C
[b] Numbers in brackets were calculated by the Ruland procedure. All other values were calculated using the Herman–Wadinger procedure corrected for the presence of PAM (see Experimental)
[c] Using ΔH = 45.5 cal/g as the heat of fusion of the nylon-6 crystallites
[d] Graft crosslinked with bis-acrylamide

grafted samples, especially for these crosslinked with bis-AM (compare *Figures 7* and *8*). Apparently many crystalline regions are still surrounded by unmodified amorphous regions in such samples and the perfection and size of the crystallites may still increase significantly as result of annealing.

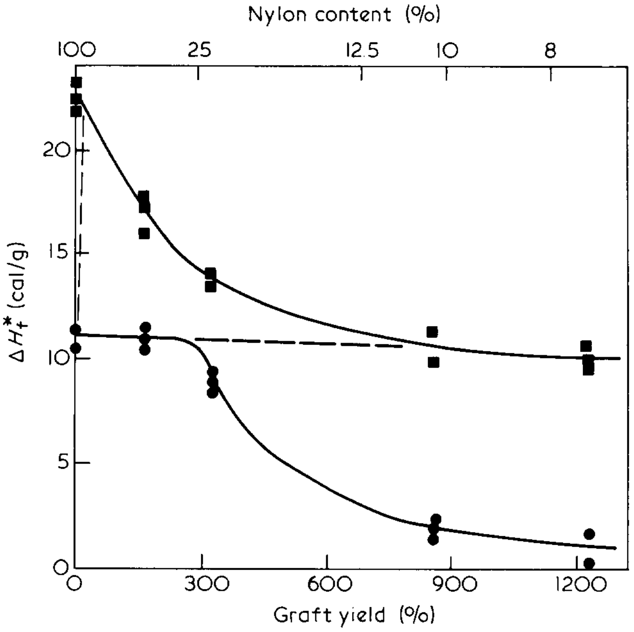

Figure 7 Values of ΔH_f normalized for the weight of nylon in samples obtained by grafting with AM the untreated nylon-6 films; ● and ■ denote results obtained before and after annealing, respectively

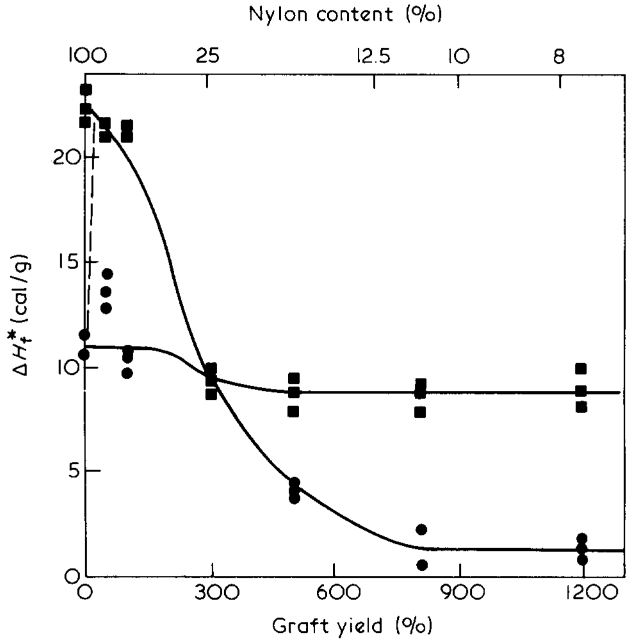

Figure 8 Values of ΔH_f normalized for the weight of nylon in samples grafted with AM containing 5% of bis-AM; ● and ■ denote results obtained before and after annealing, respectively

X-ray diffractograms of both annealed and non-annealed samples were used for the calculations of their crystallinity.

Inspection of *Figure 5* reveals that d.s.c. measurements of the non-annealed grafts cannot yield reliable values of the heat of fusion of such samples, because their fusion endotherms overlap with the huge exotherms due to the release of stresses build up during grafting. Such stresses are apparently at least partially released during annealing. Thus, calculation of ΔH_f from the d.s.c. curves of the annealed samples seems to yield fair estimates even at high grafting yields. Values of crystallinities of the annealed grafts, calculated from X-ray and from d.s.c. are in reasonable agreement, though the latter method yields

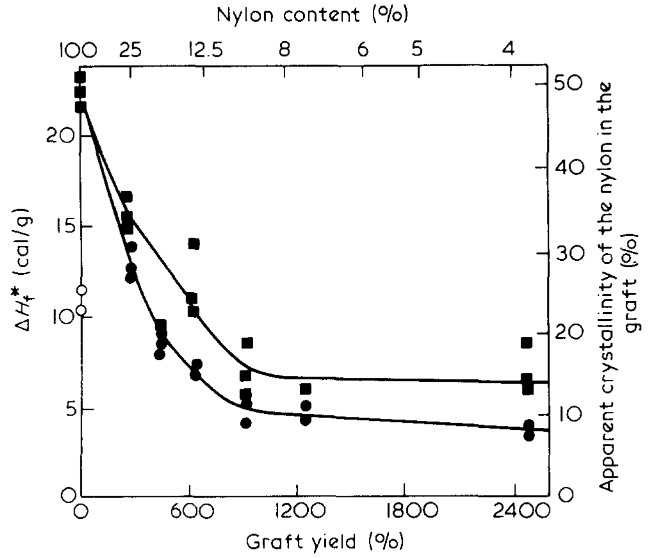

Figure 9 Values of ΔH_f normalized for the weight of nylon in samples obtained by grafting with AM, (on nylon-6 annealed by treatment with 65% formic acid); ● and ■ denote results obtained before and after annealing of the grafted samples, respectively

values which are consistently lower than those derived from X-ray. The d.s.c. measurements performed on grafted samples recrystallized from the melt provide an independent evidence that in the unannealed grafted samples their fusion endotherms are masked by the stress–release exotherms, since apparent values of ΔH_f increase strongly as result of such treatment. Obviously crystalline regions destroyed by grafting could not crystallize any more. Somewhat lower values of the ΔH_f of samples crystallized from the melt than of those annealed at room temperature indicate that the crystalline–amorphous interface may be modified during grafting and cannot participate in crystallization from the melt.

Part of the experimentally observed changes due to annealing, may represent a genuine increase in ΔH_f. It may reflect on the increase in the perfection of crystallites, distorted by stresses generated at their interfaces during grafting of the adjacent amorphous regions. An increase in the perfection of the crystallites is, indeed, indicated by the effect of annealing on the X-ray diffraction patterns of the grafted samples.

Our experimental findings prove, therefore, that crystallites of nylon-6 may resist quite successfully chemical attack, even when radiation grafted to very high grafting yields. The resistance must be due to the exclusion of the monomer, since radiation creates many centres of free radicals inside the crystalline regions[5].

Grafts on nylon-6 films annealed by treatment with formic acid

It has been pointed out in a preceeding section (see *Figure 3*) that the grafting rate of the annealed nylon-6 films is very fast. The fast reaction rate was attributed to the open structure of the amorphous regions of such materials, which has been induced by the decrease in the entanglement of polymeric chains in the amorphous phase of such materials. Our experimental results indicate that the crystalline regions of such samples are also more susceptible to chemical attack than those of the unannealed nylon-6. The value of ΔH_f of the nylon backbone of such materials (before and after repeated unannealing) is given as function of grafting yield in *Figure 9*. A decrease in the crystallinity of the nylon-6 backbone, due to grafting, seems to be evident. Apparently, the loose polymeric network of the amorphous regions enables dissolution of the grafted polymeric segments located at the surface of the crystallites. The interior layers of the crystallites become exposed to the chemical attack by the grafting monomer, when their exterior layer dissolves in the aqueous reaction medium.

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