Correlation between morphology and stress-strain properties of three block copolymers: 2. The hardening effect of the second deformation

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The discussion of the correlation between morphology and stress–strain properties of linear three block copolymers is centralized on the hardening effect which comes out at the highest values of the extension ratio when a deformation immediately follows another one. The experimental results support the hypothesis that this phenomenon is due to a kinetic effect. A model is proposed which involves the recovery of the original molecular conformations of the elastic central blocks of the chains between two successive deformations; on this basis the hardening is explained assuming that elastic chains partly stretched are present in the specimen.

The remarkable and unusual applications of the SXS three-block copolymers (S = polystyrene block; X = polybutadiene or polyisoprene block) as thermoplastic elastomers in the low temperature field justify the current renewed interest in these materials[1–3].

Our studies have been mainly devoted to correlating the mechanical properties with the morphological characteristics. It is well known that if the first deformation of the stress–strain plot is compared with the second one, a large influence of the previous treatment on the mechanical behaviour is observed; two very peculiar effects emerge, i.e. the stress softening and the hardening, that are apparent for low and high values of the extension ratio, respectively[4].

In recent papers[5–7] we have found a conclusive explanation for the stress softening. In this study some suggestions are given for the explanation of the hardening effect of the second deformation, which has been discussed only briefly elsewhere[6,7].

EXPERIMENTAL

The copolymers used in our experiments were commercial samples supplied by Shell Co. (Kraton) and labelled K 1101, K 1102 and K 1107. Their molecular characterization has been carried out with techniques already described in detail elsewhere[8–11].

Mechanical and morphological studies were made both on extruded plugs[5,6] and on solution cast or compression moulded films[6,7].

The stress–strain measurements were carried out by simple extension either at room or at controlled temperature (±0.02°C). The deformation rate was ~10 mm/min. Unless otherwise specified storage of the same specimen between subsequent deformations was at room temperature.

Birefringence measurements were carried out by stretching thin films step by step; the time interval between successive strains was ~2 min. Birefringence values were obtained measuring the retardation angle and following the Senarmont method[12]; the light used was 589 Å radiation of a sodium lamp, selected by a monochromator. Data were obtained at room temperature.

RESULTS AND DISCUSSION

The influence on the stress–strain curves of the storage time at zero load between the first and the second deformation for specimens of different copolymers prepared using various techniques (*Figures 1–3*) suggests that the hardening effect is reversible. This conclusion is strongly supported by the result obtained with the cyclohexane cast K 1107 film which, after one week of storage at room temperature, gives a second deformation curve practically coincident with the first one.

Other specimens show a smaller amount of recovery, which could be a consequence of different morphology and/or different chain mobility.

In fact K 1101 and K 1102 are styrene–butadiene–styrene linear three-block copolymers, but K 1107 has an isoprenic rubbery phase; in addition, there is a large difference in the block length and in the molecular weight of the elastomeric chains[8–11]. From the morphological point of view: (a) the slowly evaporated toluene cast K 1101 film is characterized by a polycrystalline structure where cylinders are hexagonally packed in the rubbery matrix[6]; (b) the slowly evaporated cyclohexane cast K 1107 film is characterized by an irregular distribution of well defined polystyrene spheres in the polyisoprene matrix[13]; (c) the extruded K 1102 filament shows a morphology where hexago-

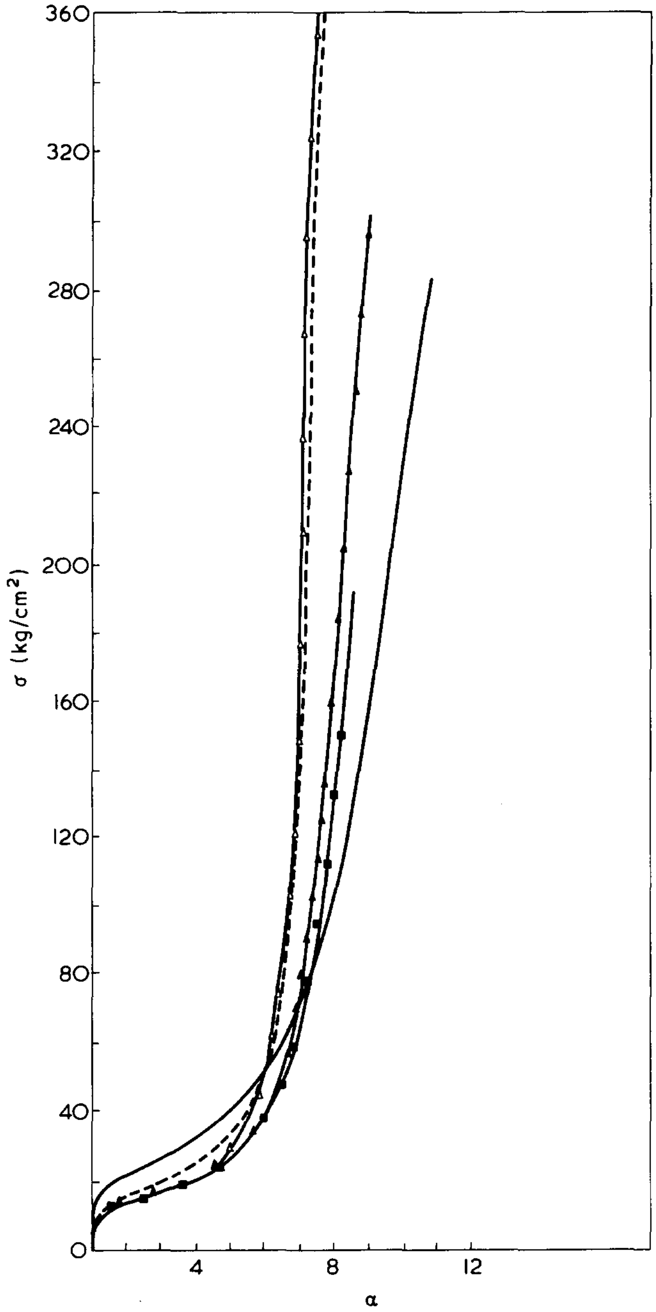

Figure 1 Simple extension stress–strain plot of slowly evaporated toluene cast K 1101 film[6]. ———, First deformation; – – – –, second and third deformation after 10 min of storage at zero load; ▲, second deformation after 1 day of storage at zero load; ■, second deformation after 1 week of storage at zero load; △, third deformation of the sample (▲) after 10 min of storage

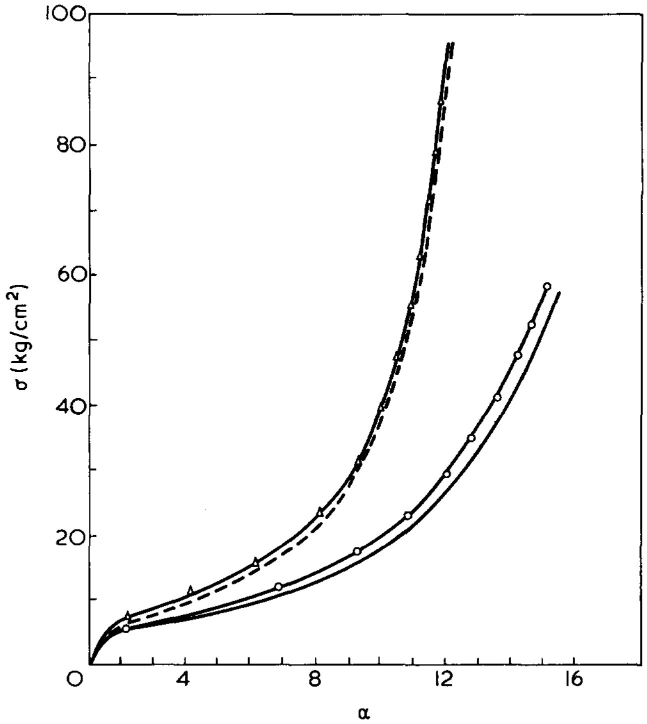

Figure 2 Simple extension stress–strain plot of slowly evaporated cyclohexane cast K 1107 film. ———, First deformation; – – – –, second deformation after 10 min of storage at zero load; ○, second deformation after 1 week of storage at zero load; △, third deformation of the sample (○) after 10 min of storage

nally packed polystyrene cylinders are oriented along the extrusion axis without any continuity[5].

However, this point is not discussed further since further investigations are required to separate the two effects.

The main result is that obtained by stretching the same sample three successive times. Consider a sample stored at zero load after the first deformation for more than one day, e.g., for one week; when it is strained (second deformation) we obtain a curve more or less similar to the original one, as seen before. If this sample is strained again immediately after the second deformation, we obtain the same plot for that without any storage between the first and the second run, i.e. a very large hardening effect. At the beginning of

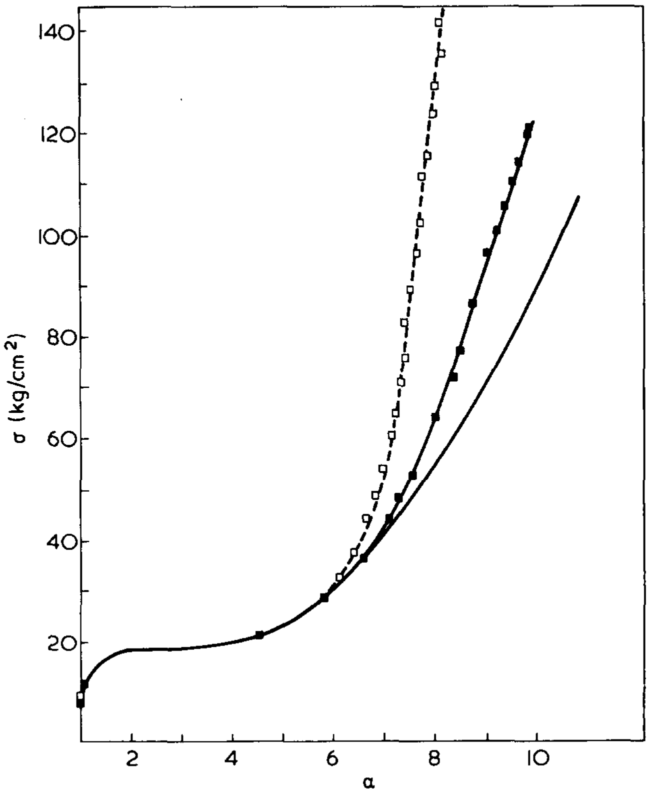

Figure 3 Simple extension stress–strain plot of extruded K 1102 filament. ———, First deformation; – – – –, second deformation after 10 min of storage at zero load; ■, second deformation after 1 week of storage at zero load; □, third deformation of the sample (■) after 10 min of storage

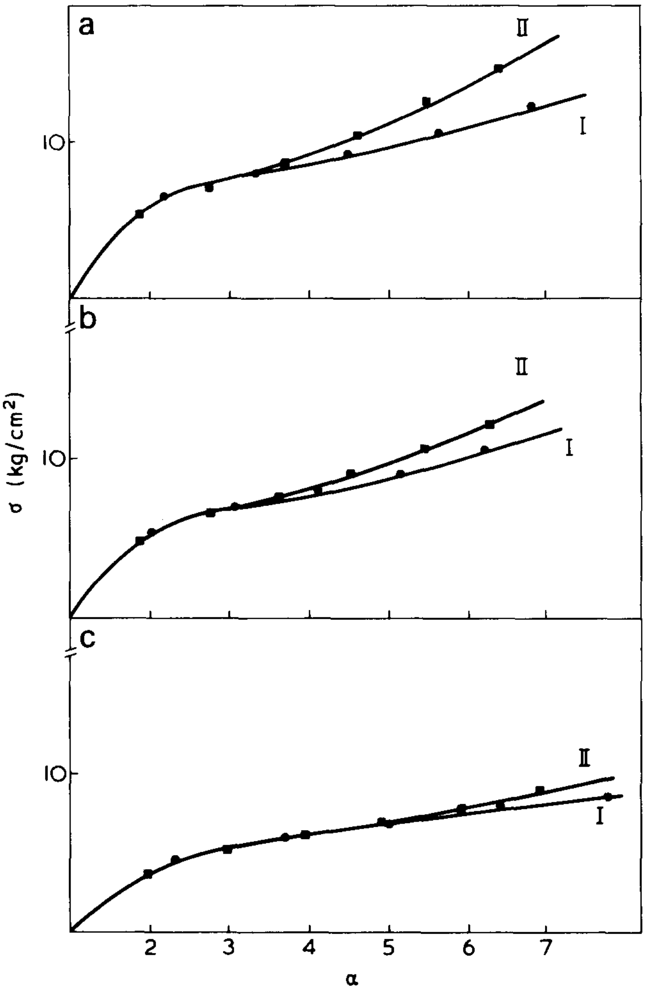

Figure 4 Simple extension stress–strain plot at different temperatures of compression moulded K 1107 film. Storage time at zero load, 30 min at the temperatures: (a) t = –10°C; (b) t = 0°C; (c) t = 40°C

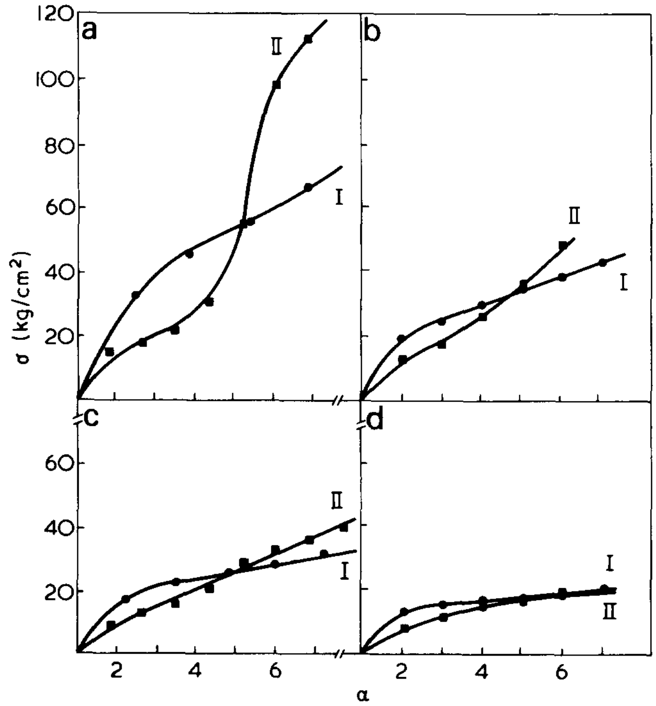

Figure 5 Simple extension stress–strain plot at different temperatures of compression moulded K 1101 film. Storage time at zero load, 30 min at the temperatures: (a) t = 0°C; (b) t = 20°C; (c) t = 50°C; (d) t = 60°C

our investigations[4] we showed that the second and the following deformations are perfectly coincident if they immediately follow each other.

We can therefore conclude that the hardening effect is a function of the time elapsed between the two following deformations.

This behaviour is general; mechanical tests on specimens prepared from different copolymers and with various procedures show that it does not depend on: (a) the chemical nature of the elastic block: linear three-block copolymers having both a polybutadiene and a polyisoprenic central block give the same qualitative results; (b) the amount of polystyrene, at least up to 33% by wt; (c) the molecular weight and the length of the blocks; (d) the technique used for the specimen preparation, i.e. extrusion, compression moulding, solvent casting; (e) the morphology of the specimen.

These observations suggest that the hardening effect of the second deformation could be explained on a kinetic basis. This is in agreement with the results of *Figures 4* and *5*, which show the influence of temperature on the stress–strain plot (both deformations and storage were carried out at the indicated temperatures). In fact the relaxation phenomena are governed by the physical correspondence between time and temperature[14]. Therefore the stress–strain plots carried out at low temperatures can be considered as obtain-

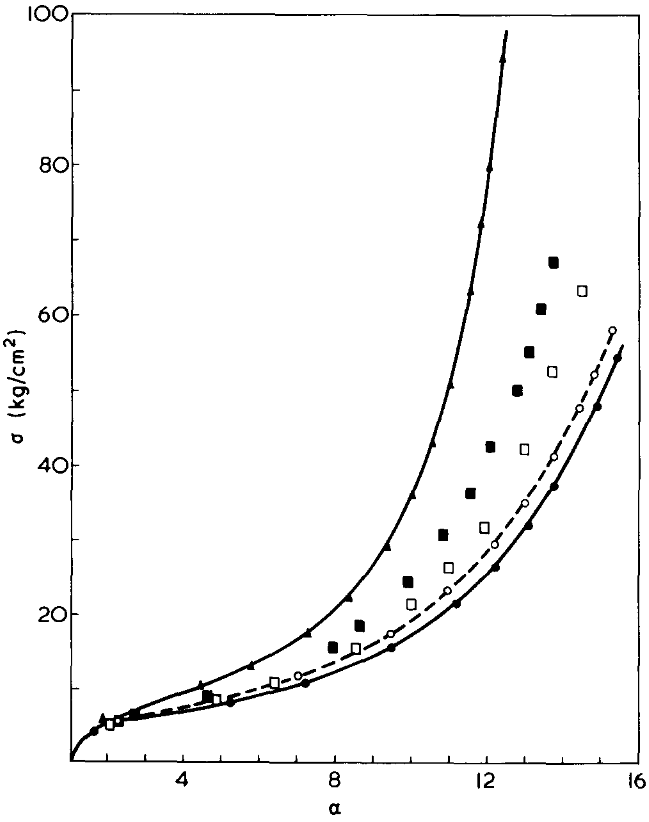

Figure 6 Simple extension stress–strain plot, at room temperature, of slowly evaporated cyclohexane cast K 1107 film stored at different temperatures for 1 week between the first and the second deformation: ●, first deformation; ▲, second deformation after 10 min of storage at room temperatures; ○, second deformation after 1 week of storage at room temperature; ■, second deformation after 1 week of storage in liquid nitrogen; □, second deformation after 1 week of storage in acetone–dry ice mixture.

ed with short storage times between successive mechanical treatments; on the other hand the stress–strain plots at high temperatures must be correlated with results obtained with long storage times. These latter results correspond to storage times longer than those used in our experiments reported in *Figures 1–3*.

On this basis we would expect that the second stress–strain plot of a sample frozen in liquid nitrogen or in dry ice–acetone mixture for one week after the first deformation, would be rather similar to that observed when the second deformation immediately follows the first one at room temperature. This is because the relaxation of the macromolecules will be more difficult on cooling down the sample. Experimentally (*Figure 6*), we observed a recovery that was roughly one half of that obtained when the storage was carried out at room temperature and there was no significant difference between the liquid nitrogen and the dry ice–acetone curves. It is believed that in order to understand these results one must take into account that about ½ h is necessary to remove the specimen from the clamps of the stress–strain apparatus, to clamp it again after the freezing and, mainly, to warm it up spontaneously from freezing to the room temperature. In addition, we would emphasize that, when the specimen is frozen, we have a macroscopic contraction of the lateral dimensions which improve the recovery.

In *Figures 7* and *8* the kinetic model is further supported by the birefringence data, which are more directly related to the fine structure of the specimen.

The plots of birefringence as functions of the extension ratio α indicate that the optical anisotropy, i.e. the orientation in the strain direction, increases going from the first to the second deformation run. It is well known that the form contribution, related to the distribution of the glassy phase inside the specimen and to its shape, is very low in comparison to the conformational contribution, due to the orientation of the rubbery chains; our results indicate that in the course of the second deformation the orien-

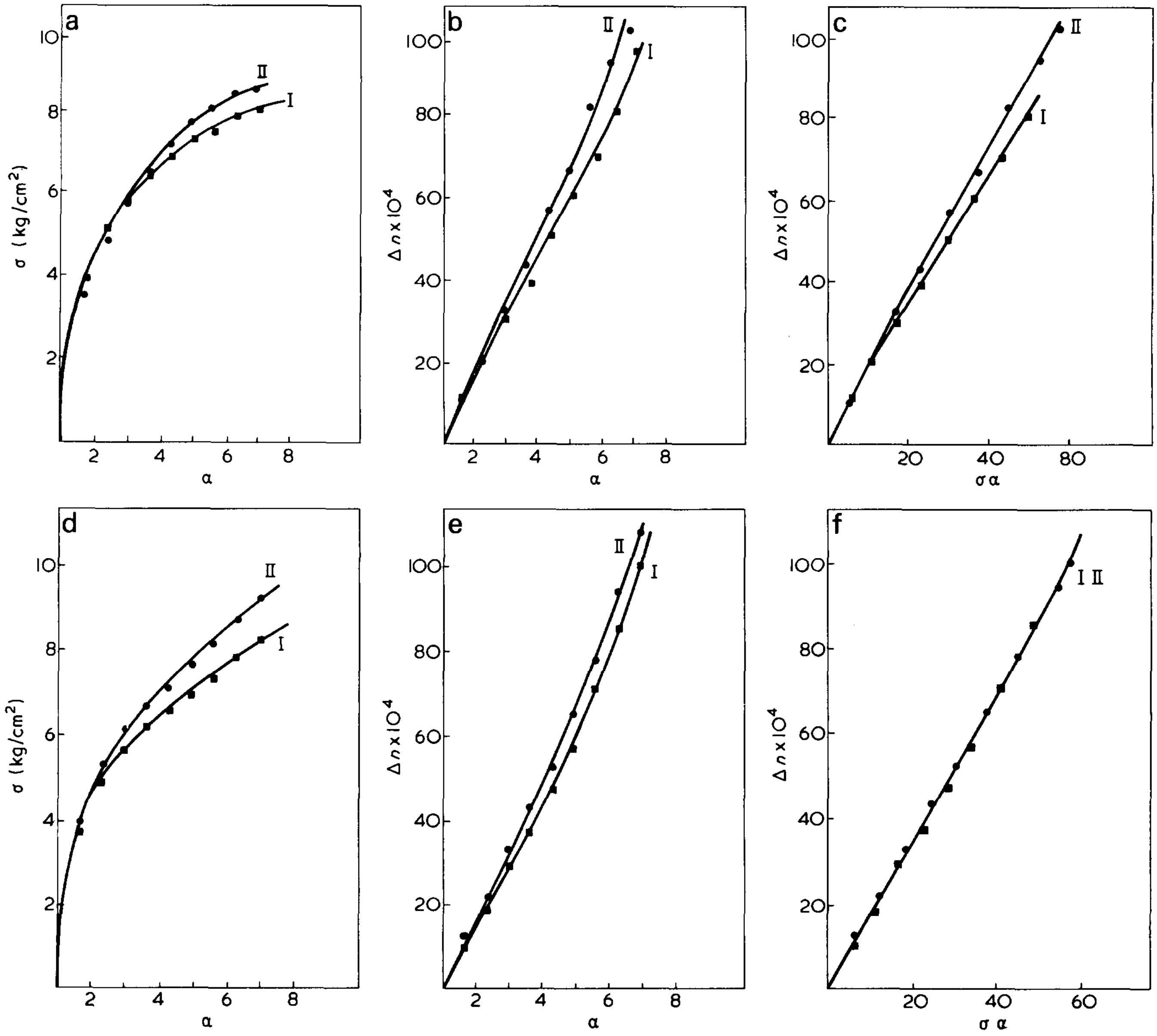

Figure 7 Simple extension stress–strain plot and birefringence curves of compression moulded K 1107 film. Storage time at zero load between the first and the second deformation: (a)–(c) 10 min; (d)–(f) 24 h

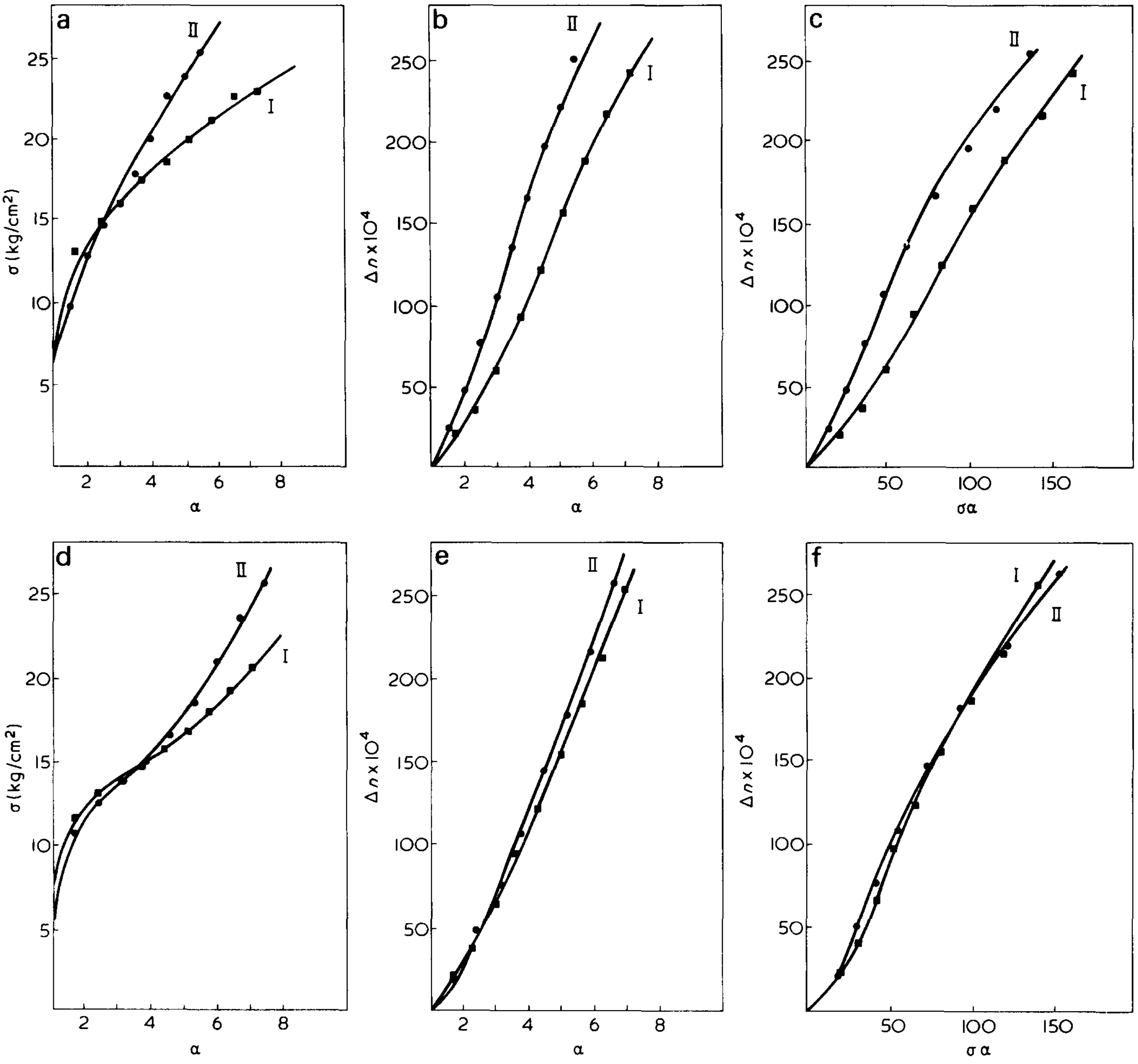

Figure 8 Simple extension stress–strain plot and birefringence curves of compression moulded K 1101 film. Storage time at zero load between the first and the second deformation: (a)–(c) 10 min; (d)–(f) 24 h

tation of the rubbery phase increases remarkably. The effect observed is related to the storage time at zero load and to the molecular characteristic of the copolymer; the latter conclusion is shown if data obtained with K 1107 are compared with those obtained with K 1101.

Moreover plots of the birefringence as functions of the true stress $\sigma\alpha$ give other important information since it is well known that the ratio $\Delta n/\sigma\alpha$ is a measure of the photoelastic coefficient, which is constant for any given system[15]. When short storage times are considered, data of *Figures 7* and *8* indicate that the ratio is different in the two runs; it suggests that some structural change occurs. On the other hand the effect practically disappears for long storage times.

This result could be consistent with the phenomenon of crystallization of the rubbery phase induced by the strain, but it is difficult to understand why the hardening is so greatly increased by a deformation which follows immediately after the previous one.

We believe that some structural change occurs inside the specimen in the course of the first deformation and that some kinetic phenomena do not allow the recovery of the original structure; consequently in the second deformation the structural modification can be more relevant.

We can reasonably assume that, when the load is removed, the recovery of the original conformations of the rubbery phase takes time following a correlation with the irreversible disruption and/or deformation of the glassy phase. For instance, consider two polystyrene domains connected by thin ties; when they are separated by the deformation of the specimen, the space between them must be occupied by elastic segments and it is clear that there is a modification of the coarse morphology of the specimen, which also involves the rubbery phase. Since the disruption of the continuous polystyrene phase is an irreversible process at room temperature, the structure of the elastic phase also undergoes a modification which is not completely reversible and consequently the elastic macromolecules assume conformations different from the original ones. A quite similar process occurs when the polystyrene domains are simply deformed by the strain.

On this basis two phenomena can be reasonably explained. First of all, when a stretching is followed immediately by another one, macromolecules that are still partly strained by the previous deformation are stretched again and higher loads are necessary to reach the same values of the deformation. On the other hand the different mobility of the elastic blocks and the different amount of disruption and deformation of the glassy phase, derived from the various morphologies of the specimens, could account for the amount of recovery between the first deformation and the second one after one week of storage at zero load.

Following another hypothesis it can be assumed that the hardening is not due to the rubbery phase (which does not give any contribution because the recovery of its original conformations is very fast) but to the glassy phase: in order to explain the phenomenon it is sufficient to note that when the second deformation starts the polystyrene domains are closer than they were initially.

We would finally remark that *Figures 4* and *5* give evidence of a large decrease in the elastic modulus with temperature. This is consistent with a deformation mechanism mainly energetic in its thermodynamic nature. In fact, orientation, deformation and breaking of the glassy domains, followed by strong effects at the interface, must give a relevant contribution to the energetic component of the total retractive force. This means that also in the course of the first deformation we must have hardening phenomena, which account for the kinetic effect discussed before.

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