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Molecular analysis of the plastic deformation of amorphous semi-aromatic polyamides

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Paper dedicated to Professor Richard S. Stein on the occasion of his 75th birthday

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Abstract

The plastic behavior of a series of amorphous semi-aromatic polyamides (SAPA-A) was investigated in compression mode at temperatures ranging from −100°C to their glass transition temperatures. Data analysis was mainly based on the inspection of the temperature dependence of yield stress, σ_y, plastic flow stress, σ_{pf}, and strain softening, SSA $= \sigma_y - \sigma_{pf}$. The activation volumes, V_0, and the index of non-elastic behavior, I, were also determined, to account for the sensitivity of plastic deformation to strain rate and for the relative easiness of elastic and non-elastic processes, respectively. Some connections have been established between the nature of the molecular motions and the values of σ_y, σ_{pf}, SSA, V_0, and I, thanks to the knowledge of the relaxation behavior of these materials. The role played by the secondary relaxation motions (and especially by those presenting a cooperative character) was highlighted, in agreement with our conclusions in earlier reports on the subject. In addition, the molecular analysis proposed for describing the plastic deformation of the SAPA-A materials was shown to hold for other polymers also bearing phenylene rings in the main chain, namely some semi-aromatic polyamides of another series (SAPA-R) and aromatic polycarbonates. Interestingly, the line of reasoning proposed here proved to be suitable also to account for the plastic deformation characteristics of various vinyl polymers and copolymers.

Keywords: Plastic deformation; Yield; Plastic flow

1. Introduction

In recent years, a comprehensive study has been undertaken in our laboratory, with the aim of establishing connections between the chemical structure of amorphous thermoplastics and some of their mechanical properties, including yielding, crazing, shear banding, and fracture behavior. In agreement with earlier ideas and results [1–7], it has been shown that this goal can be achieved, provided a detailed analysis of the polymer chain motions involved in the main mechanical (α) and secondary relaxations (β, γ) is made.

Usually, the α motions involve conformational changes of the main chain bonds (for instance, *trans–gauche* changes). The perturbation induced by the conformational change of a given main chain bond is accommodated by a limited modification (say, from 10 to 60°) of the torsion angles of about 4–5 bonds on both sides of the jumping bond, as shown by computational modeling [8]. These results emphasize the cooperative character of the α motions. As far as β motions are concerned in methacrylate-based polymers, rotations of ester side groups around the C–CO bonds are involved. In the low temperature part of the relaxation, these motions do not implicate any modification of the torsion angles of the main chain bonds, as evidenced by NMR [9]. On the other hand, in the upper part of the β relaxation, side group rotations are shown to be accompanied by simultaneous modifications of the main chain torsion angles [9]. This latter case is referred to as α–β coupling, and the localized main chain torsion motions can be considered as precursors of the α motions. The γ motions are always isolated motions, occurring at quite low temperature. For example, in the methacrylate-based polymers, γ motions are special motions of lateral sub-units (alkyl residues, cyclohexyl rings) or rotations of the Cα methyl groups [10].

The effects of possible coupling between the α and β motions were emphasized in the case of polymethylmethacrylate [11,12] and methylmethacrylate-based random

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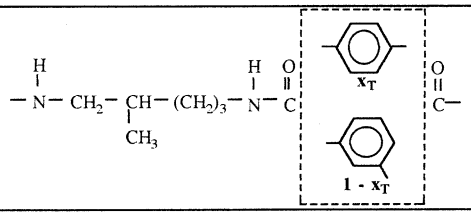
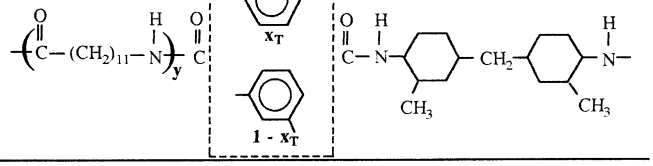
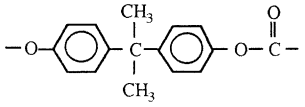
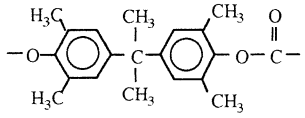
Table 1
Repeat units of the semi-aromatic polyamides and aromatic polycarbonates under study

Materials	Chemical formulae
SAPA-R	
SAPA-A	
BPA-PC	
TMBPA-PC	

copolymers including either styrene units [11] or *N*-substituted maleimide rings [11,12] or *N*-methyl glutarimide rings [12] as the comonomer. As a crucial result [12], the strain softening amplitude, SSA, which is defined as the difference between the yield stress, σ_y, and the plastic flow stress, σ_{pf}, both measured in uniaxial compression test, tends to vanish in the situations of α–β coupling. On the other hand, SSA presents large values when α and β motions do not involve the same units or sub-units. In these systems, similar correlations hold between the coupling and the nature of deformation micro-mechanisms, which develop upon thin film mechanical stretching [13,14]. Deformation zones are strongly favored at the expense of crazes as long as α precursor motions are active in the glassy state. Finally, the fracture behavior of bulk samples of these series was also shown to be influenced by the character of the β motions. Both the critical strain intensity factor, K_{Ic}, and critical energy release rate, G_{Ic}, increase from *N*-substituted maleimide copolymers (which are very brittle) to *N*-methyl glutarimide-rich methylmethacrylate copolymers, in relation to the augmentation of the degree of cooperativity of the β motions [15].

However, inspection of the data relative to aromatic polycarbonates (see for instance Ref. [16]) clearly shows that no α–β coupling can exist in such materials, in spite of the ductile character of polycarbonate of bisphenol-A. In other words, it was dubious that the above relationships may be extended at least in their present formulation to polymers whose chemical structure contains phenylene rings in the main chain. A first attempt to clarify this point has been made [17] by considering a series of semi-aromatic polyamides, so called SAPA-R, provided by Rhodia Co., and based on 2-methyl 1,5-pentanediamine and isophthalic and terephthalic acids (Table 1). In this series of materials, the choice of the relative mole fraction of terephthalic units, x_T, greatly affects the value of the main relaxation α (passing progressively from 142 to 160°C for x_T varying from 0 to 1). Unfortunately, both secondary relaxation and yield characteristics of the materials showed up slightly sensitive to x_T, so that the interest of the series SAPA-R as model systems was diminished. However, several interesting findings, although common to all samples, whatever their composition, resulted from this study. Firstly, a temperature gap larger than 200°C was shown to separate the secondary relaxation from the α relaxation, which means that the SAPA-Rs behave very much, with this respect, like bisphenol-A polycarbonate. Secondly, it turned out from the analysis of the values of yield stress, $\sigma_y(T)$, and modulus, $E(T)$, that the plastic behavior of these materials is controlled by the chain packing in the glassy state. Indeed, identical values of $\sigma_y(T)/E(T)$ were found irrespective of the chemical structure of the SAPA-Rs, when compared on the scale $(T - T_\alpha)$. And finally, very large values of SSA were obtained, as predicted in the poly(methyl methacrylate) series [11,12] by the absence of coupling between the α and β motions.

Therefore, we decided to carry on this kind of studies by considering another series of amorphous semi-aromatic

polyamides, so-called SAPA-A, because the samples were provided by Atofina Co. As shown in Table 1, the chemical formulae of these materials include lactam-12 sequences, terephthalic and/or isophthalic residues and diamino dimethylcyclohexylmethane residues.

Choice of the series SAPA-A presents some potential interests:

(a) First of all, the molecular mobility of these samples has already been investigated extensively by Lauprêtre et al. [18–21], by using several techniques including dielectric analysis [18], high-resolution solid-state ^{13}C and ^{2}H experiments [19,20], and dynamic mechanical analysis [21].
(b) Decoupling of the α and β relaxations is observed, as in polycarbonates and in the series SAPA-R. In addition, and on the contrary to what has been regretted in the series SAPA-R, increase in the relative mole fraction of terephthalic units, x_T, allows the high temperature part of the β relaxation to present a cooperative character related to the occurrence of π-flip motions of the terephthalic rings [19].
(c) Presence of bulky cycloaliphatic residues prevents any crystallization to develop in the SAPA-A samples, whatever the values of x_T over the range 0–1 and of the length y of the lactam-12 sequence over the range 1–1.8 (the unique exception being the case $x_T = 1$; $y = 1$, not examined in this article). and
(d) some interesting industrial applications are expected from materials of the series SAPA-A, because of their toughness especially. Some of them are already commercial products, supplied by EMS Co. and Atofina Co.

With respect to our objectives, the yield properties, deformation micro-mechanisms, and fracture behavior of the SAPA-As have been investigated [22]. In the present publication, we concentrate on the plastic deformation of these materials. We also compare it with that of aromatic polycarbonates (Table 1) and with that of the amorphous thermoplastics which have been the subject of previous reports [11,12,17]. The other features of the mechanical behavior of these materials will be discussed in forthcoming publications.

2. Experimental

2.1. Materials

The nomenclature of the materials and their physical characteristics of interest here are listed in Table 2. It concerns mainly the samples of the series SAPA-A. However, data relative to some SAPA-Rs and polycarbonates, which are considered in this article for sake of comparison, are also reported. The number and weight average molecular weights, M_n and M_w respectively, were determined by steric exclusion chromatography. Measurements were carried out in benzyl alcohol at 120°C for the SAPA-As and SAPA-Rs and in tetrahydrofuran at room temperature for BPA-PC and TMBPA-PC. In relation to their methods of synthesis, all the samples present values of M_w close to 20 000 g/mol and large degrees of polydispersity (M_w/M_n around 3). The glass transition temperature, T_g, was determined by differential scanning calorimetry at a heating rate of 20°C/min. Conventionally, T_g was taken at the onset of the thermal transition, which was observed during the second scan. The main mechanical relaxation temperature, T_α, was arbitrarily taken at the maximum of the loss modulus traces at 1 Hz. In these conditions, T_α exceeds T_g by about 10°C. The amorphous character of all the samples listed in Table 2 was checked by the absence of endothermic peak on the differential scanning calorimetry traces at high temperature.

2.2. Sample preparation

Before use, all the materials were dried under vacuum at $T_\alpha + 20$°C for at least 2 days. Then, sheets of 3 mm in thickness were firstly compression molded under vacuum at $T_\alpha + 50$°C and then cooled down slowly through the glass transition region. Finally, samples of dimensions suitable for the compression tests ($3 \times 3 \times 6$ mm^3) were cut from the sheets with a diamond saw.

Prior to testing, samples were dried once more at $T_\alpha + 20$°C for 3 days. The purpose of this thermal treatment is double: firstly, it allows the elimination of the residual stresses induced by compression molding and saw cutting; and secondly, it permits removal of eventual moisture which is known to affect dramatically the mechanical properties of

Table 2
Nomenclature and characteristics of the materials

Nomenclature	y	x_T	M_w (g mol^{-1})	M_n (g mol^{-1})	T_g (°C)	T_α (°C)
SAPA-A/1.8*I*	1.8	0	22,000	8500	118	130
SAPA-A/1.8*T*	1.8	1	23,000	9000	124	137
SAPA-A/1*I*	1	0	21,000	8000	151	161
SAPA-A/1$T_{0.7}I_{0.3}$	1	0.7	23,000	8500	159	171
SAPA-R/M*I*		0	18,000	6000	134	141
SAPA-R/M$T_{0.5}I_{0.5}$		0.5	23,000	6500	137	145
BPA-PC			18,000	8000	145	150
TMBPA-PC			28,000	9000	192	200

such polyamides [23]. Therefore, all data reported in the present work (including the T_g and T_α values given in Table 2) refer to as the dry state of the materials.

Investigation on physical aging effects was performed on samples subjected to specific annealing. At the end of the above-given thermal treatment, the samples were slowly cooled down to $T_\alpha - 25$°C and maintained at this temperature for 100 h under vacuum.

2.3. Compression tests

Compression tests were carried out on a MTS 810 hydraulic testing system equipped with a temperature chamber. The regular deformation rate for the experiments was 2×10^{-3} s^{-1}. However, some additional measurements were performed over the range 4×10^{-5}–2×10^{-1} s^{-1}. Stress–strain curves were collected at temperatures ranging from −110°C to T_α. Before tests, samples were left at the chosen temperature for 30 min. Then stress–strain curves were obtained at different temperatures (from −110°C to T_α).

Because the levels of strain involved in the experiments are quite small (typically, less than $\varepsilon = 0.15$), the values of nominal stress calculated by the computer were supposed, as a first approximation, to be identical to the true stresses and used instead of them without further manipulation.

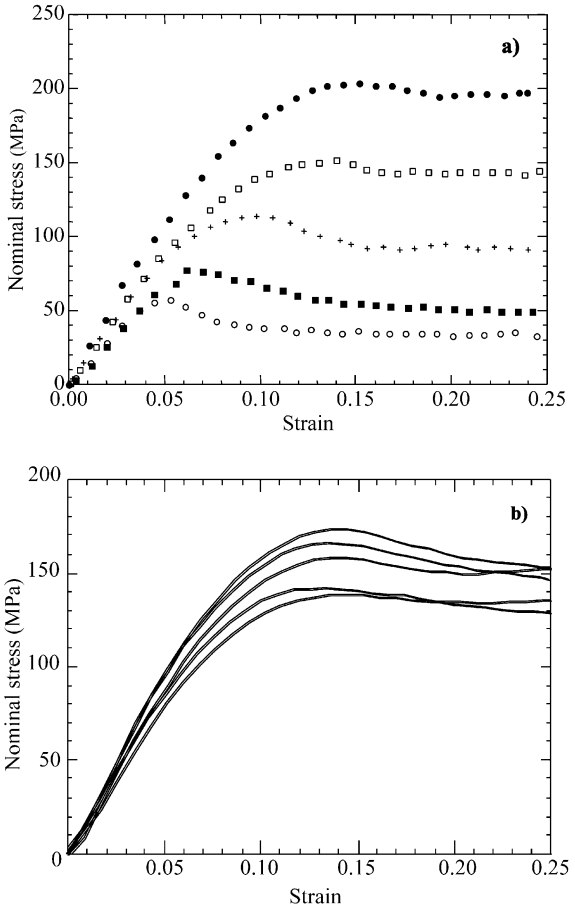


Fig. 1. Typical stress–strain curves relative to the sample SAPA-A/1$T_{0.7}I_{0.3}$. Plot (a): effect of temperature at a strain rate of 2×10^{-3} s^{-1}; (●): −80°C, (□): −40°C, (+): 20°C, (■): −100°C, (○): 140°C. Plot (b): effect of strain rate at a temperature of −40°C; from top to bottom: 2×10^{-1} s^{-1}, 2×10^{-2} s^{-1}, 2×10^{-3} s^{-1}, 2×10^{-4} s^{-1}, 4×10^{-5} s^{-1}.

2.4. Analysis of the stress–strain curves

Fig. 1 shows the general shape of the stress–strain curves of the materials under study. Irrespective of whether the variable under consideration is temperature (Fig. 1a) or strain rate (Fig. 1b), all curves present the same profile. Namely, an initial linear evolution, typical of the elastic response, then a curvature corresponding to the inelastic response before the yield point is attained at the maximum stress σ_y, and finally some strain softening until reaching the plateau, characterized by the plastic flow stress, σ_{pf}.

The present work deals mainly with the analysis of the three quantities σ_y, σ_{pf}, and SSA $= \sigma_y - \sigma_{pf}$ at the regular strain rate of 2×10^{-3} s^{-1}. These quantities were extracted from the stress–strain curves as illustrated in Fig. 2.

An account for the effect of strain rate is given by assuming the validity of an Eyring-type equation [24]:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp(-\Delta G_a/kT) \tag{1}$$

in which ΔG_a is the stress and temperature dependent activation free energy of deformation.

ΔG_a, in turn, obeys the equation:

$$\Delta G_a = \frac{\Delta H_0 + (T/\mu)(d\mu/dT)V_0\sigma}{1 - (T/\mu)(d\mu/dT)} \tag{2}$$

where ΔH_0 is the activation enthalpy, μ is the shear modulus, and V_0 is the activation volume. Basically, V_0 is an index of the sensitivity of the plastic deformation to strain rate, according to the equation:

$$V_0 = kT\left(\frac{\partial \ln \dot{\varepsilon}}{\partial \sigma}\right)_{T,\text{structure}} \tag{3}$$

Accordingly, V_0 was calculated from the slope of the plots of stress versus logarithm of strain rate. The calculations

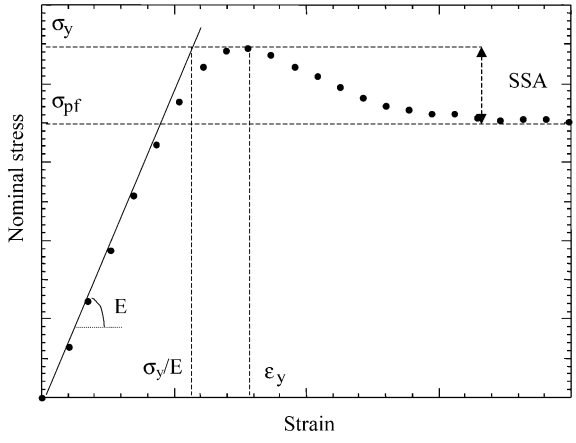


Fig. 2. Sketch of a typical stress-strain curve and visualization of σ_y, σ_{pf}, SSA and σ_y/E.

were performed systematically at the yield point ($\sigma = \sigma_y$). It was impossible to do the same at the plastic flow stress ($\sigma = \sigma_{pf}$), just because σ_{pf} could not be evaluated experimentally at high strain rate. Measurements were performed on samples subjected to the same thermal history in order to satisfy the requested iso-structural conditions.

And finally, the so-called index of non-elastic behavior, I, was deduced from the stress–strain curves. As introduced in previous reports [25,26], this quantity (see also Fig. 2) is defined as:

$$I = 100\left(\frac{\varepsilon_y - (\sigma_y/E)}{\varepsilon_y}\right) \quad (4)$$

3. Results and discussion

In this section, we will successively present and discuss the values of σ_y, σ_{pf}, SSA, V_0 and I relative to the samples SAPA-A. In each case, the general character of the proposed findings will be checked by considering the data relative to the samples of the SAPA-R series [17], to polycarbonates and eventually to polymethylmethacrylate and its copolymers [11,12].

3.1. Yield stress

Firstly, let us consider the global plots of σ_y versus temperature given in Fig. 3a. The influence of chemical structure on the values of σ_y appears clearly. Whatever the temperature and the nature of the acid residue, a systematic decrease of σ_y by about 20 MPa is observed when the lactam amount increases from 1 to 1.8 mol per repeat unit. However, one can wonder whether it has a physical meaning to perform such direct comparisons all over the glassy domain. It is recognized from previous studies, indeed, that the plastic deformation events are connected to the β relaxation motions at low temperature and to the α motions at the approach of the main relaxation. As a consequence, the systems do be compared with each other: (1) on the direct temperature scale at low temperatures (β region), and (2) on the $(T - T_\alpha)$ scale at higher temperatures to account for the differences of T_α from one polymer to the other (Table 2). More or less arbitrarily, we

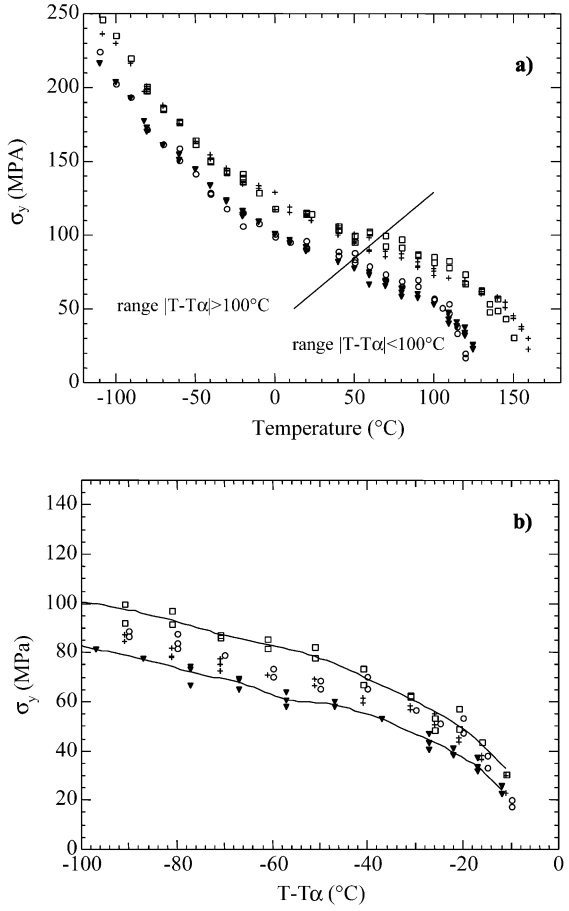


Fig. 3. Yield stress of the SAPA-A samples; (○) 1.8I, (▼) 1.8T, (□) 1I, and (+) $1T_{0.7}I_{0.3}$. Plot (a): σ_y versus temperature. Plot (b): σ_y versus $(T - T_\alpha)$ in the high-temperature range.

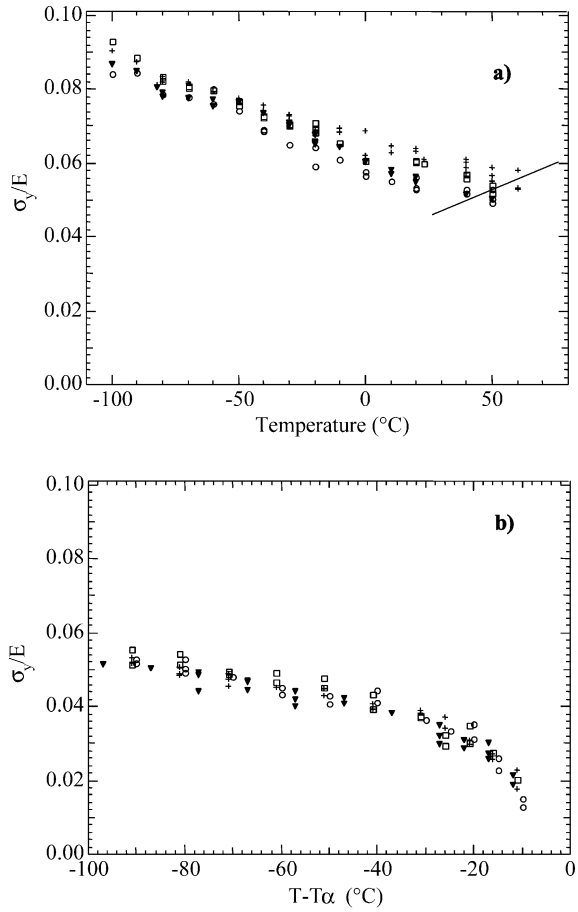


Fig. 4. Ratio yield stress/elastic modulus for the SAPA-A samples; (○) 1.8I, (▼) 1.8T, (□) 1I, and (+) $1T_{0.7}I_{0.3}$. Plot (a): σ_y/E versus temperature in the low-temperature range. Plot (b): σ_y/E versus $(T - T_\alpha)$ in the high-temperature range.

propose to fix the influence limit of the α motions at ($|T - T_\alpha|$) equal to 100°C in the case of the SAPA-As. Thus, the low-temperature region can be properly described by the left part of Fig. 3a, whereas the higher temperature region is concerned by the plot of σ_y versus ($T - T_\alpha$) (Fig. 3b). In each case, it turns out that σ_y actually decreases with increasing lactam amount. In addition, for a given lactam-12 content, the replacement of terephthalic acid by isophthalic acid does not influence the σ_y values in the β region, but induces an increase in σ_y in the α region.

In order to justify the sensitivity of yield stress to chemical structure, one can consider the Young's modulus values and assume that the higher the modulus, the larger the σ_y value. On this basis, if the values of σ_y are governed by the modulus only, then identical values of σ_y/E will be found whatever the SAPA under consideration. Such a situation is encountered for the series SAPA-A whatever the temperature range examined (Fig. 4a,b). Similar results have already been published for the series SAPA-R [17]. At this stage, it is interesting to compare the two series of semi-aromatic polyamides in order to check whether the observed differences in σ_y values (for example, σ_y(SAPA-R/MI) = 160 MPa and σ_y(SAPA-A/1I) = 110 MPa at ambient temperature) are exclusively related to differences of modulus. As reasonable master curves are obtained by normalizing σ_y by the modulus (Fig. 5a,b), it turns out that σ_y is governed by the compacity in these two series of SAPAs.

In the same way, it is impossible to distinguish TMBPA-PC from BPA-PC on the σ_y/E plots (Fig. 6a,b) whereas they differ markedly on the σ_y plots not shown here [22]. In other words, initiation of the plastic deformation occurs in all the samples under consideration here (semi-aromatic polyamides and polycarbonates, whatever the details of their chemical structure) when the effects of both applied stress and thermal energy equilibrate the cohesive strength. Such behavior seems to be a general rule valid for many other amorphous polymers including polystyrene [11], methylmethacrylate-*co*-maleimide random copolymers [11,12], epoxy networks [25], and even polymethylmethacrylate or methylmethacrylate-*co*-glutarimide [12] at sufficiently low temperature or after prolonged physical aging. The one exception on date deals with the cases where a strong coupling exists between the α motions and β motions, as in rejuvenated polymethylmethacrylate and in the methylmethacrylate-*co*-glutarimide copolymer 24:76 mol% [12].

An indirect validation of these ideas is given by looking at the effect of physical aging on the plastic behavior. In contrast to the case of polymethylmethacrylate, for which

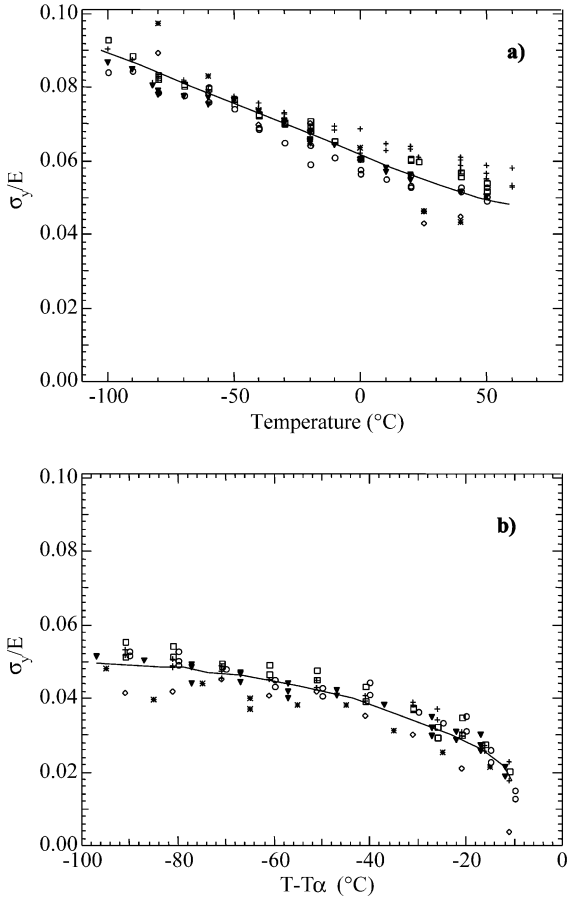


Fig. 5. Comparison of the ratio yield stress/elastic modulus in the series SAPA-A [(○) 1.8*I*, (▼) 1.8*T*, (□) 1*I*, and (+) $1T_{0.7}I_{0.3}$] and SAPA-R [(✧) M*I* and (✳) $MT_{0.5}I_{0.5}$]. Plot (a): σ_y/E versus temperature in the low-temperature range. Plot (b): σ_y/E versus ($T - T_\alpha$) in the high-temperature range.

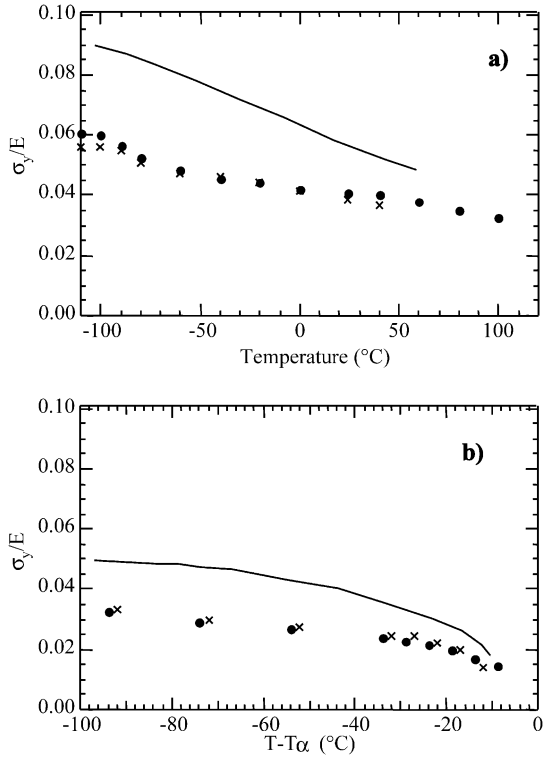


Fig. 6. Comparison of the ratio yield stress/elastic modulus for the SAPAs (solid line) and the polycarbonates [(×): BPA-PC, (●): TMBPA-PC]. Plot (a): σ_y/E versus temperature in the low-temperature range. Plot (b): σ_y/E versus ($T - T_\alpha$) in the high-temperature range.

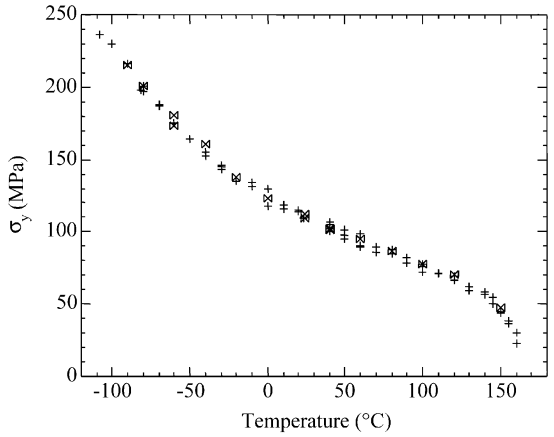


Fig. 7. Influence of physical aging on the yield stress of the sample SAPA-A/1$T_{0.7}I_{0.3}$; (+): fresh sample, (⋈) aged sample.

σ_y is substantially greater for the aged samples than for the fresh ones [11], the values of σ_y for physically aged and fresh SAPAs are quite similar (Fig. 7). Thus, the densification by physical aging would not hinder the motions promoting the yield phenomenon.

Further inspection of Fig. 6a,b also shows that σ_y/E is significantly smaller for the polycarbonates than for the amorphous polyamides, irrespective of the temperature under consideration. Among possible explanations, we would suggest that the increase in resistance to plastic deformation for the SAPAs may be related to the presence of hydrogen bonds. Hydrogen bonding would stabilize the low-energy stable chain conformations and, in turn, increase the energy gap between these conformations and the higher energy conformations which should be formed at the yield point, according to Robertson's ideas [3,4,6], and finally make the plastic deformation process more difficult.

3.2. Plastic flow stress

At the first sight, Fig. 8 reveals that σ_{pf} presents temperature and chemical structure dependence at variance from those of σ_y. Fig. 9a shows the evolution of σ_{pf} for different SAPA-As as a function of temperature. As mentioned and explained above, this representation is used to analyze the plastic behavior in the temperature range defined by ($|T - T_\alpha|$) > 100°C. These curves show up a marked change in slope around −20°C, a temperature closely related to the end of the β relaxation region [21]. Two conclusions can be inferred from this observation. Firstly, β motions are not precursors of the α motions. This statement is not surprising in the case of materials for which the β relaxation is separated from the α relaxation by about 200°C: typically, T_β = −60°C [21] and T_α varies from 130 to 171°C as a function of chemical structure (Table 2). Secondly, plastic flow is influenced by the β motions at low temperatures, i.e. below the end of the β relaxation. On the other hand, α motions are involved at higher temperatures, as confirmed by the master curve obtained by plotting σ_{pf} versus ($|T - T_\alpha|$) (Fig. 9b). In

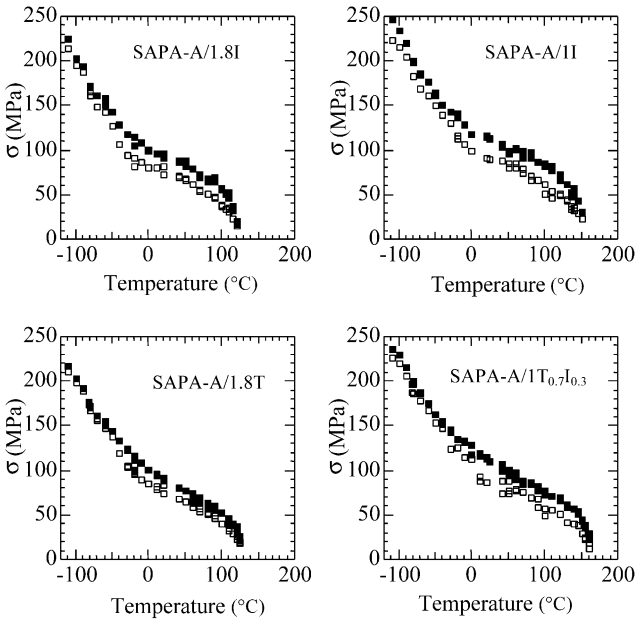


Fig. 8. Differences between σ_y (■) and σ_{pf} (□) for the SAPA-As as a function of temperature and chemical formula.

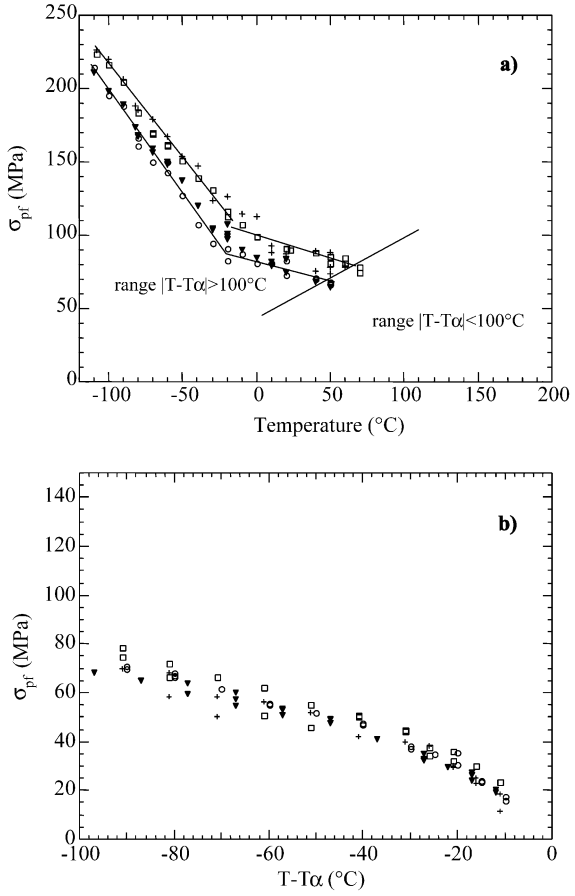


Fig. 9. Plastic flow stress of the SAPA-A samples; (○) 1.8I, (▼) 1.8T, (□) 1I, and (+) 1$T_{0.7}I_{0.3}$. Plot (a): σ_{pf} versus temperature in the low-temperature range. Plot (b): σ_{pf} versus ($T - T_\alpha$) in the high-temperature range.

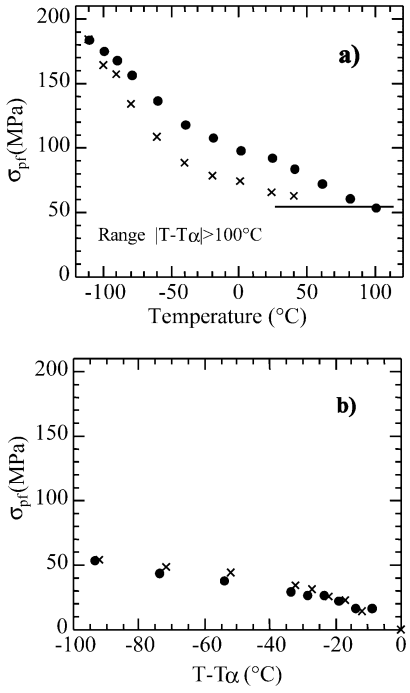


Fig. 10. Plastic flow stress of the polycarbonates [(×): BPA-PC, (●): TMBPA-PC]. Plot (a) σ_{pf} versus temperature in the low-temperature range. Plot (b) σ_{pf} versus $(T - T_\alpha)$ in the high-temperature range.

this temperature range, indeed, chemical structure influences the plastic flow stress by the departure from T_α, only.

The same arguments hold for justifying the similar trends observed in the case of the SAPA-Rs [17,22] (data not shown) and of the polycarbonates (Fig. 10a,b). On the other hand, the data available for polymethylmethacrylate and various methylmethacrylate-based random copolymers [11,12] reveal a quite different behavior, since the profiles of σ_{pf} versus temperature are linear all over the temperature range investigated. However, an explanation consistent with the above findings can be proposed. In the situations for which the cooperative β motions are hindered (maleimide copolymers) or at least 'diluted' due to the presence of the mechanically inactive comonomer (styrene copolymers), the secondary relaxation motions are not sufficiently efficient to allow plastic flow to develop, and therefore, only α motions can be involved. Alternatively, when the β motions are able to promote plastic flow (polymethylmethacrylate and glutarimide-rich methylmethacrylate-*co*-glutarimide copolymers), then they are indiscernible from the α ones, in the sense that they are their precursors.

3.3. Amplitude of strain softening

Temperature and chemical structure dependence of SSA is shown in Fig. 11 for the different SAPA-As. Let us analyze successively the influence of these two parameters by considering that the general shape of the four plots is the same.

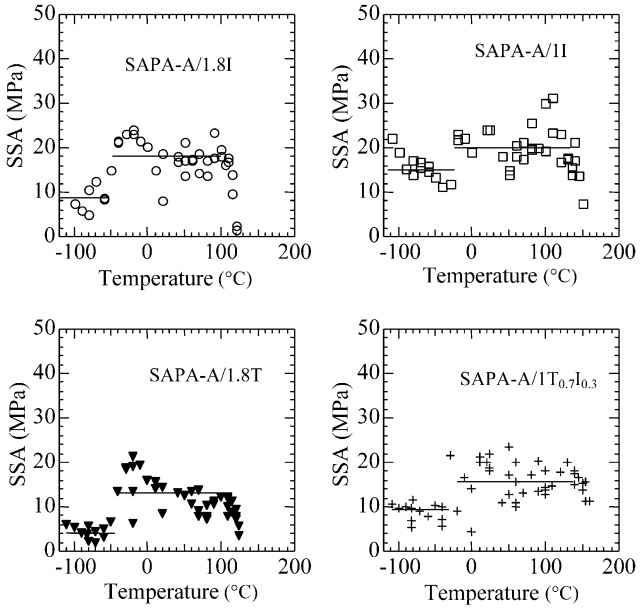


Fig. 11. Strain softening amplitude of the SAPA-A samples; (○) 1.8*I*, (▼) 1.8*T*, (□) 1*I*, and (+) $1T_{0.7}I_{0.3}$.

3.3.1. Influence of temperature

Despite the large scatter of the data, three domains can be distinguished on the plots of SSA versus temperature. At low temperatures ($T < -40$ or -30°C), SSA takes a value, so-called SSA_0, which is independent of temperature within the experimental uncertainty. At intermediate temperatures (typically, between -30°C and $T_\alpha - 30$°C), another constant value, SSA_1 greater than SSA_0, is found. In a third domain, close to T_α, SSA values decrease as the temperature is raised. The latter feature has already been reported in the case of the members of the series SAPA-R [17]; it was correlated to the homogeneous deformation of the sample, due to creep near T_α.

The fact that SSA_1 is greater than SSA_0, irrespective of chemical structure, can be justified from the molecular description given for σ_y and σ_{pf}. The value of SSA_0 is small because the same kind of molecular motions, namely the β motions, are involved in this temperature range to pass the yield point and promote the plastic flow. On the contrary, at higher temperatures (case of SSA_1), β-type motions and α-type motions are concerned in yielding and plastic flow, respectively. Consequently, the stresses necessary to induce yielding and plastic flow have significantly different values in this temperature range, leading to a large value of SSA_1, greater than SSA_0.

3.3.2. Influence of chemical structure

The different values of SSA_0 and SSA_1, extracted from Fig. 11, are reported in Table 3. For a given lactam-12 content, the replacement of terephthalic acid by isophthalic acid leads to an increase in both SSA_0 and SSA_1. As far as the lactam-12 amount is the variable, its increase is

Table 3
SSA_0 and SSA_1 values for the SAPA-As

Sample	SSA_0 (MPa)	SSA_1 (MPa)
SAPA-A/1.8*I*	8	18
SAPA-A/1.8*T*	4	13
SAPA-A/1*I*	15	20
SAPA-A/1$T_{0.7}I_{0.3}$	9	16

accompanied by a decrease of SSA_0 whereas it does not notably affect the SSA_1 value.

In order to interpret these results, let us first recall that, in the low-temperature range (case of SSA_0), the molecular motions involved in yielding and plastic flow are β motions. On this basis, differences in SSA_0 values result solely from the variation of cooperativity of the motions. The larger the cooperative nature of the β-motions responsible for yielding is, the smaller SSA_0 value is. Therefore, SSA_0 value is expected to be smaller in the terephthalic SAPA-As, for which a motional cooperativity was detected in the high-temperature part of the β relaxation [21], than in the isophthalic ones for which no experimental evidence for cooperative β-motions was given. It was also shown [21] that the lactam-12 sequence does not affect the cooperativity of the β-motions. From this result, one might anticipate that SSA_0 does not depend on lactam-12 amount, which is in contradiction to the experimental measurements (Table 3). An alternative interpretation to the fact that SSA_0 value decreases as the lactam-12 amount increases could be given by paying attention to the γ relaxation, whose amplitude is mostly determined by the amount of lactam-12 units. As a result, the greater the intensity of the γ relaxation is, the smaller the SSA_0 value is. The influence assigned to the local γ-motions on the plastic behavior at low temperature may be a little bit surprising. However, this proposal sounds credible, at least in the case of the isophthalic SAPA-As in which the β relaxation refer to as localized motions [21].

In the high-temperature range (case of SSA_1), the molecular analysis is different: whereas large scale cooperative motions similar to those involved in the α process are concerned in the plastic flow phenomenon, yielding is essentially governed by the occurrence of β-motions. Even if the motions responsible for σ_y and σ_{pf} change in nature in this temperature range, a higher degree of cooperativity of β-motions involved in yielding should lead to smaller SSA_1 value. This assumption gives a reasonable molecular explanation accounting for: $SSA_1(1,8T) < SSA_1(1,8I)$ and $SSA_1(1T_{0.7}I_{0.3}) < SSA_1(1I)$ on the one hand, and $SSA_1(1,8I) \approx SSA_1(1I)$ on the other hand.

3.3.3. Extension to the case of polycarbonates

It is worth noticing that the temperature dependence of SSA for the BPA-PC (Fig. 12) is exactly the same as that observed and explained in terms of molecular motions in SAPAs. According to this interpretation, the transition temperature between SSA_0 and SSA_1 would be related to the β relaxation region. This is actually the case for BPA-PC: its β relaxation peak is centered at about −100°C [22], which is approximately the temperature at which the value of SSA begins to differ from zero. The most striking feature associated to the comparison between BPA-PC and TMBPA-PC is the difference observed between −110 and −90°C: SSA_0(BPA-PC) ≈ 1 MPa whereas SSA_0(TMBPA-PC) ≈ 15 MPa). If the conclusion established in the case of SAPAs is still valid for these other materials, the β relaxation of BPA-PC should involve a higher cooperativity of motions than that of TMBPA-PC. This statement is nicely supported by the determination of the activation entropy, ΔS_a, based on the Starkweather analysis [27] and derived from the equation:

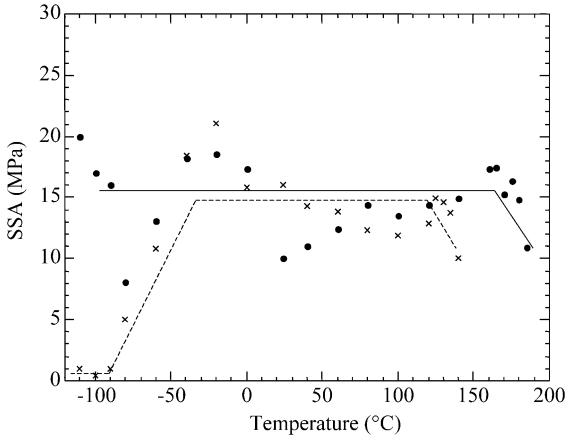


Fig. 12. Strain softening amplitude of the polycarbonates [(×): BPA-PC, (●): TMBPA-PC].

$$\Delta S_a = \frac{1}{T'}\left[E_a - RT'\left[1 + \ln\left(\frac{k}{2\pi h}\right) + \ln\left(\frac{T'}{f}\right)\right]\right] \quad (5)$$

in which T' is the temperature of the maximum of the β relaxation peak at $f = 1$ Hz and E_a is the activation energy of the β relaxation calculated from an Arrhenius relation.

According to this theory, low value of the activation entropy can be interpreted in terms of localized motions (case of TMBPA-PC, $\Delta S_a = 20\ J\ K^{-1}\ mol^{-1}$), whereas higher values correspond to cooperative motions (case of BPA-PC, $\Delta S_a = 110\ J\ K^{-1}\ mol^{-1}$). Therefore, one may interpret the high values of SSA of TMBPA-PC all over the temperature range investigated as resulting from localized motions assigned to the β relaxation, and responsible for yielding.

3.4. Activation volumes

The activation volumes of the SAPAs, determined at the yield point according to the Eq. (3) (with $\sigma = \sigma_y$), are given in Table 4. The region of temperatures higher than 40°C has been disregarded, on account to the fact that the temperature

Table 4
Temperature dependence of the activation volumes, V_0, (nm^3) of the SAPA-As

Sample	−80°C	−60°C	−40°C	−20°C	0°C	20°C	40°C
SAPA-A/1.8*I*	0.8	0.8	0.7_5	1.0_5	1.2	1.2	1.4_5
SAPA-A/1.8*T*	0.9	0.9	1.0	1.1	1.5_5	2.0	2.0
SAPA-A/1*I*	0.7	0.7_5	0.7_5	0.9	1.2_5	1.3_5	1.3
SAPA-A/1$T_{0.7}I_{0.3}$	0.9	0.8_5	0.8_5	1.0_5	1.4	1.6_5	1.9

dependence of strain rate has no longer the meaning of an activation volume when large values are obtained at the approach of T_g [28]. Three main features result from the inspection of the V_0 values. Firstly, large values (1 nm^3 in order of magnitude) are obtained, even at low temperatures. This situation, which means a rather weak strain rate dependence of σ_y, is in contrast to that encountered in the case of some vinyl polymers such as polystyrene or polymethylmethacrylate. In these cases, values from 0.1 to 0.4 nm^3 are found [29]. On the other hand, the situation of the PASA-As seems to be usual for polymers bearing a phenylene ring in their main chain. Thus, V_0 equals about 1.2 nm^3 at 40°C for SAPA-Rs and 1.2 nm^3 and about 2.5 nm^3 for BPA-PC [30], at −40 and 40°C, respectively. Secondly, a marked increase in V_0 is observed for all the SAPA-As at temperatures higher than −40°C, i.e. in the high temperature part of the broad β relaxation. There, the spatial extent of the motions is assumed to increase substantially [21], whatever the chemical structure of the materials. Finally, looking at the quantitative effects of chemical structure, it turns out that the values of V_0 are unaffected, within the experimental uncertainties, by changes in length of the lactam unit; in other words, the activation volumes should be insensitive to the γ relaxation motions. At temperatures equal or higher than −40°C, the increase in the relative amount, x_T, of terephthalic units at given length of the lactam unit is accompanied by the increase in V_0. This observation can be related to the observed increase of the E'' damping peak area (see Fig. 5 of Ref. [21]). It would result either from the augmentation of the number of β motions, or, as above, from the cooperative character of the π-flip motions of the terephthalic units involved in the β relaxation.

Table 5
Values of the index of non-elastic behavior *I* (%)

Sample	*I*	Reference
SAPA-A/1.8*I*	35	
SAPA-A/1.8*T*	45	
SAPA-A/1*I*	35	
SAPA-A/1$T_{0.7}I_{0.3}$	40	
Polymethylmethacrylate ($T < T_\beta$)	40	[22,25,26]
Methylmethacrylate-*co*-maleimide copolymer 75:25 mol%	45	[22,25,26]
Polymethylmethacrylate ($T > T_\beta$)	60	[22,25,26]
Methylmethacrylate-*co*-glutarimide copolymer 24:76 mol%	55	[22,25,26]
BPA-PC	45	[30]

3.5. Index of non-elastic behavior

By contrast to the quantities analyzed in the above paragraphs, to which it is possible to associate a direct physical meaning, the index of non-elastic behavior, *I*, defined by Eq. (4), may be regarded as a purely phenomenological parameter, which accounts for the shape and curvature of the stress–strain curves. As a matter of fact, *I* permits cross-check, and, to some extent, summing up of some general features of the plastic behavior [25,26].

For the SAPA-As, the parameter *I* may be considered as independent of temperature over the range −100°C/+100°C. At higher temperatures, it cannot be determined with confidence, because of the dramatic decrease of both σ_y and ε_y and of the drop of modulus at the approach of T_α. Table 5 gives the values of *I* thus determined. Values available for some other polymers are also given in this table for sake of comparison. *I* does not seem to depend on the amount of lactam-12 in the SAPAs, whereas it increases, at given length of lactam unit, with the relative fraction, x_T, of terephthalic units. In other words, the parameter *I* presents the same sensitivity to chemical structure as the activation volume V_0. Therefore, the transition from 35 to 40–45 in the SAPA-As may be regarded as the contribution of the cooperative motions.

This result is corroborated by the case of BPA-PC [30], which behaves just as SAPA-A/1.8*T*. Such findings are consistent with the data available for polymethylmethacrylate and related copolymers, as recalled in Table 5. Large values of *I* are observed as long as cooperative motions are involved at the yield point. Such is the case for polymethylmethacrylate at sufficiently high temperature and for the copolymer methylmethacrylate-*co*-glutarimide 24:76 mol%. When motion cooperativity is lacking, lower values of *I* are obtained. Polymethylmethacrylate at temperatures typical of isolated β motions and the copolymer methylmethacrylate-*co*-maleimide 75:25 mol% are representative of this behavior.

4. Conclusions

This study, based on amorphous semi-aromatic polyamides, confirms the findings of our previous works on vinyl copolymers. Suitability of the connections proposed between the details of the polymer chain dynamics (and especially the characteristics of the secondary relaxation)

and such macroscopic quantities as σ_y, σ_{pf}, SSA, V_0 and I is confirmed. This approach agrees well with the concepts popularized for instance in Robertson's theory.

The main peculiarity of the SAPAs and of the BPA-PC as well is to present at very low temperature a secondary relaxation which strongly influences the yield behavior over a large domain of the glassy state. The most direct illustration of this statement is given by considering the activation volumes, which take very large values, as compared to the vinyl polymers. As a consequence, one may suggest, as a touch of difference with Robertson's model, that the occurrence of very active β motions would allow appearance of plastic deformation at temperatures sufficiently low in these cases so that the α relaxation motions are not concerned.

Whatever the type of polymer under consideration, our data validate definitely the idea that the amplitude of strain softening reflects the difference in nature of the motions involved at yield point and plastic flow. When they are of similar nature (as in polymethylmethacrylate at high temperature or in polycarbonate and SAPAs at low temperature), then SSA is small. Alternatively, when the former are of β type and the latter of α type, then a noticeable SSA is observed (as in polymethylmethacrylate at low temperature or in polycarbonate and SAPAs at high temperature).

Now, these findings could be extended to a broader range of materials, provided a detailed description of their viscoelastic properties, especially in the secondary relaxation region, and of their compression yield behavior are available.

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