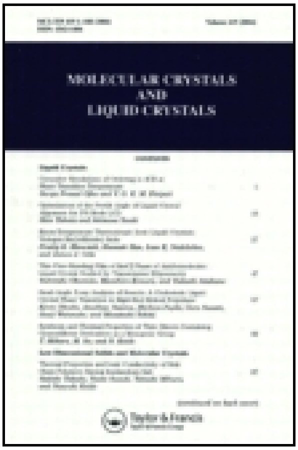

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Transitions and Relaxations in Mesophase Polymers: Thermotropic Liquid Crystalline Polyesters with Mesogenic Groups in the Main Chain

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Transitions and Relaxations in Mesophase Polymers: Thermotropic Liquid Crystalline Polyesters with Mesogenic Groups in the Main Chain[†]

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The thermal and dynamic viscoelastic behavior of some thermotropic liquid crystalline polyesters based on α, ω-bis(4-hydroxybenzoyloxy)alkanes and terephthalic acid is reported. Original samples obtained by solution polymerization followed by precipitation showed physical and dynamic-mechanical properties typical of semicrystalline polymers. Quenching of the polymers from the LC state gave rise to glass-like mesomorphic modifications that retained a glass transition at considerably higher temperature T_{g_m} than that of the corresponding amorphous material T_{g_a}. However, the formation of a new crystal form with respect to the original sample could not be prevented and the polymers so obtained were in fact partially mesomorphic and partially crystalline materials. All the quenched samples exhibited by dynamic-mechanical and calorimetric analyses a first order solid-solid transition independent of the length of the flexible spacer. Such a phenomenon was interpreted as an order-disorder transition of the material quenched from the LC state.

INTRODUCTION

Thermotropic liquid crystalline polymers frequently show in the solid state a rich variety of crystal phases depending on the thermal history of the

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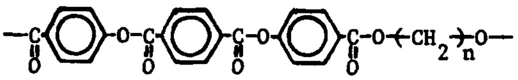
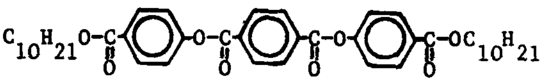
sample. Glass-like solid modifications with a structure very similar to that of the mesophase that is stable just above the melting temperature can also be obtained by quenching the samples from the liquid crystalline state. However, the identification of the supercooled mesophase by optical or diffractometric techniques is often complicated by the coexistence of crystalline and amorphous materials. Therefore, in spite of the extensive interest in the solid state physics of thermotropic polymers, there is very little known about the characteristic properties of the mesomorphic glassy state and the contribution that eventually such metastable structures can give to the physical and mechanical properties of the bulk polymer.

One of the most important characteristics of mesomorphic glasses is the possibility of giving rise to phase transitions at low temperatures.[1] In a recent paper,[2] we reported on the change in physical properties of some thermotropic liquid crystalline polyesters quenched from the anisotropic melt, as caused by a first order solid-solid transformation occurring well below room temperature. Whenever the observed transition is attributable to a metastable glass-like modification, a better understanding of formation, stability and structural characteristics of the mesomorphic glass can be gained by the investigation of that behavior. Yet another open question connected with the existence of a supercooled mesophase in liquid crystalline polymers is the glass transition behavior of the mesophase, as compared with the glass transition of the amorphous material.

In the present paper we wish to report on the dynamic-mechanical and differential thermal analysis of a series of thermotropic liquid crystalline polyesters based on α, ω-bis(4-hydroxybenzoyloxy) alkanes and terephthalic acid.



1(n = 3)
2(n = 4)
3(n = 10)



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EXPERIMENTAL

Materials

Polymer samples **1–3** were prepared by solution polymerization at room temperature from the corresponding α, ω-bis(4-hydroxybenzoyloxy) alkanes[3,4] and terephthaloyl chloride in 1,1,2,2-tetrachloroethane in the presence of dry pyridine according to a previous procedure.[5]

Bis(4-decyloxycarbonylphenyl) terephthalate **4**. A mixture of 28.0 g (0.20 mol) of 4-hydroxybenzoic acid, 120.0 g (0.76 mol) of n-decanol, 40 ml of benzene and 0.8 g of sulfuric acid was allowed to react for 3 h in a Dean-Stark apparatus. The reaction mixture was then washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$ and distilled in vacuo. The viscous oil remaining was twice crystallized from n-pentane to give 23.1 g (yield 41.4%) of decyl 4-hydroxybenzoate. A solution of 7.3 g (36 mmol) of terephthaloyl chloride in 80 ml of anhydrous dioxan was added in 2 h to a solution of decyl 4-hydroxybenzoate in 20 ml of dry pyridine. The mixture was stirred overnight at room temperature, the poured into 400 ml of cold 2 MHCl. The precipitate formed was filtered, washed with 5% $NaHCO_3$, water and crystallized three times from ethyl acetate to give 16.1 g (yield 76.8%) of **4**. ^{1}H-NMR ($CDCl_3$) : δ (ppm from TMS) = 8.5 (*s*, 2H, terephthalate), 8.2 and 7.4 (2 *d*, 4H, oxybenzoate), 4.4 (*t*, 2H, $COOCH_2$), and 2.1-0.6 (*m*, 19H, aliphatic).

IR (KBr) : $\bar{\nu}$ = 1730, 1710, 1605, 1280, 1270, 890, 760, 720, and 690 cm^{-1}.

Measurements

Inherent viscosities were measured using 10 ml of polymer solutions having concentration 0.6 g/dl in *p*-chlorophenol at 45°C by an Ostwald viscometer. Textures of thermotropic mesophases were observed by a Reichert Polyvar polarizing microscope equipped with a Mettler FP52 programmable heating stage.

X-ray diffraction spectra were obtained using a Phillips 1010/25 diffractometer with CuK_α radiation. X-ray spectra of the liquid samples were obtained by using a thermo-regulated sample holder.

Calorimetric measurements were made with a Perkin-Elmer DSC-2 instrument. All the runs were carried out under a nitrogen atmosphere with a heating rate of 20 °K/min. The maximum temperature of the enthalpy peak was taken as the transition temperature.

Thermal-optical analysis measurements were performed with the polarizing microscope in conjunction with the hot stage and a photometer.

The dynamic elastic modulus and the mechanical damping were determined using a resonance electrostatic apparatus at frequencies of 10^3-10^4Hz, with specimens of the shape of circular plates of 36 mm diameter and 2 mm thickness.

TABLE I

Properties of thermotropic liquid crystalline polyesters **1**–**3** and model compound **4**

Sample	n	η_{inh}^{a} (dl/g)	Phase transition[b] (°K)
1	3	0.27	$k \xrightarrow{513} ? \xrightarrow{538} n \xrightarrow{585} i$
2	4	0.23	$k \xrightarrow{560} n \xrightarrow{630} i$
3	10	0.35	$k \xrightarrow{494} s \xrightarrow{533} i$
4	—	—	$k \xrightarrow{412} s \xrightarrow{420} i$

[a] In *p*-chlorophenol at 45°C.

[b] Determined by optical microscopy and DSC analyses: k = crystalline; s = smectic; n = nematic; i = isotropic.

Data relevant to the physical and thermo-optical characterization of both polymers and model compound are summarized in Table I.

RESULTS AND DISCUSSION

X-ray diffraction

Samples of the untreated original polymers showed wide angle diffraction patterns typical of semicrystalline polymers. In Figure 1 the powder diffraction spectrum recorded at room temperature for polyester **3** is reported as a typical example.

Melt crystallized specimens exhibited X-ray diffraction patterns different from those obtained from untreated original samples (Figure 1). The scattering patterns of samples quenched rapidly from the anisotropic melt in ice-water were, on the contrary, very similar to those of the samples slowly crystallized from the LC state. Thus X-ray data indicate that two different crystal forms are present in these polyesters at room temperature, depending on the procedure adopted for the crystallization of the samples. Form I is termed the crystal modification that is present in the original samples obtained by simple precipitation from solution, whereas form II corresponds to the crystal modification that is generated by crystallization from the melt. This kind of solid state polymorphism appears to be rather common in thermotropic polymers which contain mesogenic moieties in the main chain interconnected by flexible spacers.[6]

The X-ray spectra of the LC phase of polymer **1** recorded at 545°K, i.e., after the second DSC endotherm (see below), showed only two broad

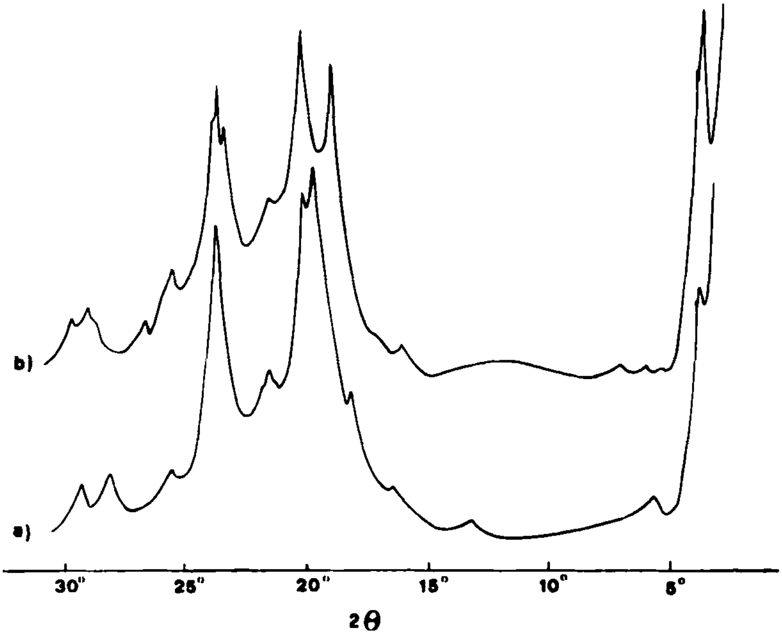

FIGURE 1 Powder X-ray spectra of original (a) and melt-crystallized (b) samples of polyester **3**.

haloes centered at $2\Theta \simeq 21°$ and $2\Theta \simeq 4.6°$. Similar results were obtained for the LC phase of polymer **2**. They are consistent with the occurrence of a nematic mesophase, as revealed by optical microscopy and in accord with previous indications.[5]

The X-ray diffraction pattern of the LC phase of polymer **3**, recorded at 513°K, showed instead a broad halo at $2\Theta \simeq 20°$ and a strong, sharp reflection at $2\Theta = 2.94°$ corresponding to a Bragg *d* spacing of 30.12 Å (Figure 2). The value of the lattice spacing correlates quite well with the length of the repeating polymer unit in the nearly fully extended conformation. X-ray data thus support the assignment of a smectic phase to the LC state of this polymer, although they do not provide any conclusive information about the nature of the smectic mesophase.

Differential scanning calorimetry

High temperature behavior The DSC heating curves of samples of polyesters **1–3** with different thermal history are reported in Figures 3–5.

Two or more endotherms are always present in the thermograms of these polymers. In any case the highest temperature transition is broad and

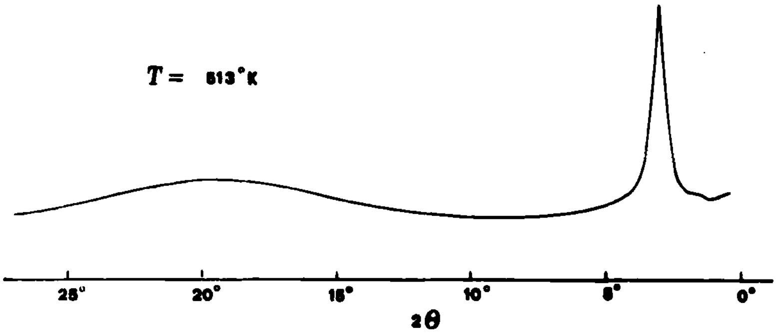

FIGURE 2 X-ray diffraction spectrum of the smectic phase of polyester **3** at 513°K.

corresponds to the isotropization of a LC phase. At lower temperatures polyester **1**, in addition to the crystal-mesophase transition, shows other transitions characterized by endothermic peaks in both the solid and fluid states (Figure 3). Polyester **3** exhibits multiple endotherms on melting and some of these appear as shoulders on both sides of the melting peak (Figure

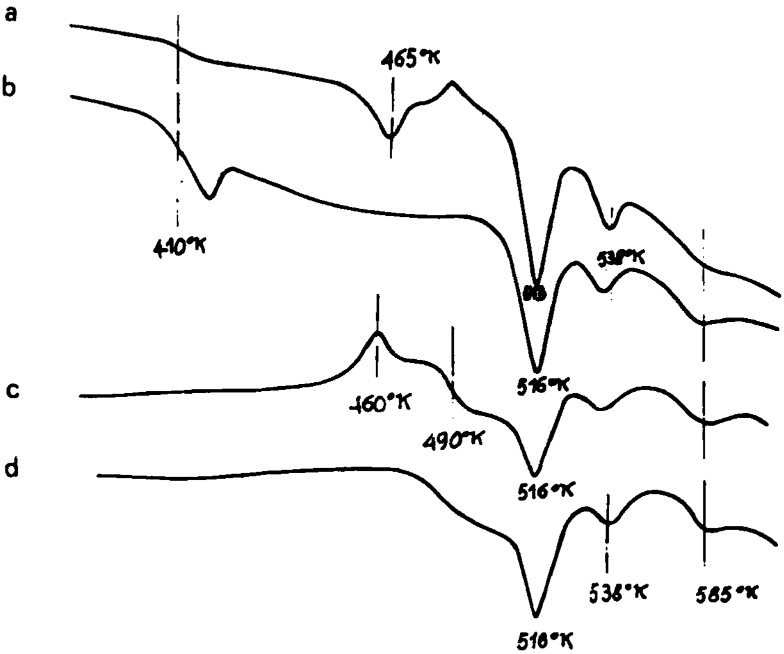

FIGURE 3 DSC heating curves of samples of polyester **1** with different thermal histories (high temperature): *a* original; *b* crystallized from the LC state; *c* quenched; *d* quenched and annealed at 460°K for 45 min.

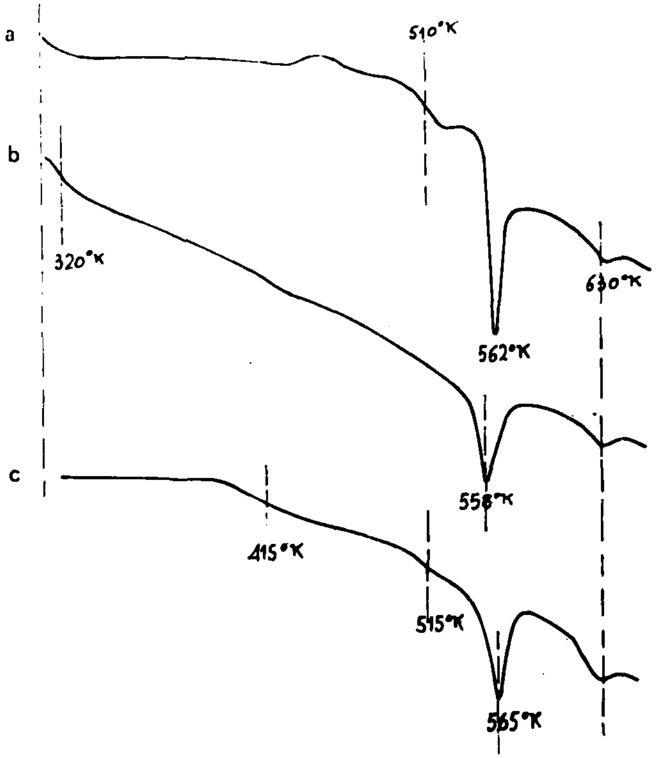

FIGURE 4 DSC heating curves of samples of polyester **2** with different thermal histories (high temperature): *a* original; *b* crystallized from the LC state; *c* quenched.

5). Such transitions may be due to different phenomena such as solid-solid phase changes, melting of various polymorphic forms stable in definite temperature ranges, or reorganization on heating of preformed crystalline entities.[8,9] This complex thermal behavior is characteristic for the majority of thermotropic polymers constituted of linear semi-rigid macromolecules and reflects their ability to crystallize in different crystal forms owing to the way by which they pack together in an ordered array.

However, apart from any consideration of the thermal behavior of these crystal phases, there are other points of interest concerned with the non-crystalline component of the polymers under investigation. One major question is connected with the identification and characterization of metastable glass-like modifications. A peculiarity observed in the thermograms of these polyesters is the marked difference in the behavior of samples with different thermal history. Original untreated and melt-crystallized samples

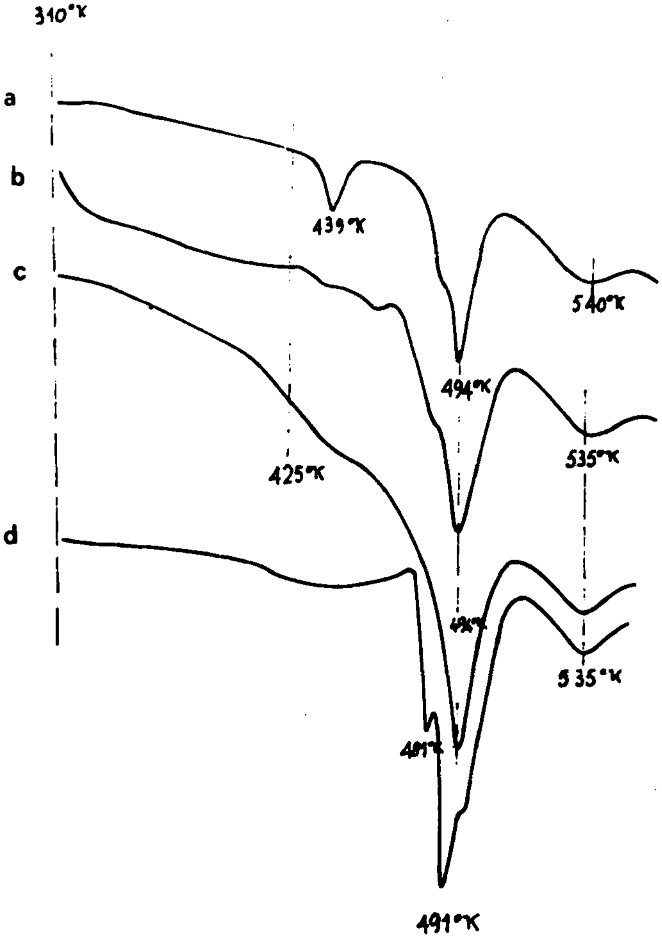

FIGURE 5 DSC heating curves of samples of polyester **3** with different thermal histories (high temperature): *a* original; *b* crystallized from the LC state; *c* quenched; *d* quenched and annealed at 473°K for 1 hr.

of polyester **1** show a heat capacity increase around 410°K, exactly corresponding to the amorphous glass transition of this polymer (Figure 3). This is evidenced by the presence of the hysteresis peak just above 410°K in the sample slowly cooled from the melt (Figure 3b). Hysteresis in heat capacity at the amorphous glass transition manifests itself in an endothermic peak in the glass transition region, and clearly appears when the sample is heated much more rapidly than it was previously cooled.

The original, as well as the melt-crystallized samples, can then be considered as conventional semicrystalline polymers. Quenching of the polymer from the LC state causes the disappearance of the transition at 410°K, whereas a rapid increase in heat capacity is now observed at about 490°K (Figure 3). The occurrence of a marked change in C_p at high temperatures parallels the decrease in intensity of the endothermic peak due to the melting of the crystalline material, thus indicating that part of the LC phase is prevented from crystallizing and remains as a highly supercooled mesophase. Consequently, annealing of the quenched material at 460°K for 45 min. causes an appreciable reduction of ΔC_p at 490°K (Figure 3d), with the onset of a glass transition phenomenon connected with the existence of a supercooled mesophase. Therefore, the quenched polymer can be treated as a partially mesomorphic, partially crystalline material. Polyester **3** shows the same general trend (Figure 5). In fact, after quenching of the sample from the LC state and reheating, the glass transition shifts from about 310°K (Figure 5a,b) to about 425°K (Figure 5c),indicating that a supercooled glassy mesophase with a higher T_g is formed.

The behavior of polyester **2** is somewhat different, in that the original untreated sample shows two heat capacity changes at about 320° and 510°K (Figure 4a), with ΔC_p values higher for the high temperature transition than for the transition at lower temperature. The thermal behavior of the quenched sample **2** shows a major change in heat capacity at about 415°K (Figure 4c) intermediate between the 320° and 510°K transitions. At present no conclusive explanation for this complex behavior can be put forward, even though the formation of mesomorphic regions during the isolation and purification of the polymer cannot be completely ruled out.

Low temperature behavior The low temperature behavior of polyester **3** is represented in Figure 6. The other two polyesters **1** and **2** show very similar DSC traces. Original and melt-crystallized samples did not show any transition below 290°K. On the contrary, the quenched polymer displayed two endothermic effects occuring at 225° and 235°K. However, these transitions are strongly affected by the cooling temperature and cooling rate adopted for the further heat treatments of the quenched polymer. Very fast cooling of the mesophase of polyester **3** to 100°K causes a further supercooling effect of this structure, as demonstrated by the occurrence on the successive heating curve of two exotherms of different intensity at 145° and 183°K, respectively. These transformations are monotropic and correspond to transitions from a high energy state to a low energy one. From the above, it can be concluded that for this polymer one or more metastable modifications exist below 235°K.

Analogous conclusions can be drawn for polyesters **1** and **2**. The change in intensity of the two endothermic peaks as obtained by varying the cooling conditions (Figure 6c,d) is intriguing. In particular, the relative

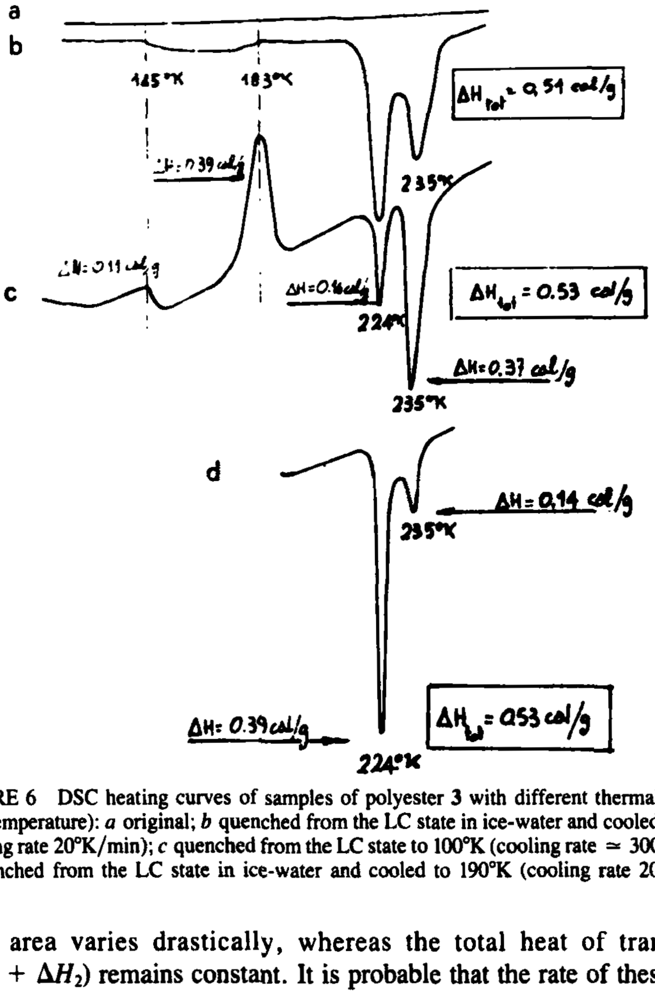

FIGURE 6 DSC heating curves of samples of polyester 3 with different thermal histories (low temperature): *a* original; *b* quenched from the LC state in ice-water and cooled to 100°K (cooling rate 20°K/min); *c* quenched from the LC state to 100°K (cooling rate ≃ 300°K/min); *d* quenched from the LC state in ice-water and cooled to 190°K (cooling rate 20°K/min).

peak area varies drastically, whereas the total heat of transitions ($\Delta H_1 + \Delta H_2$) remains constant. It is probable that the rate of these phase transitions depends on the cooling temperature and on the time the sample was maintained at this temperature.

The crystal phase (form II) does not appear to be involved in the observed transitions, since the same crystal phase exists in the slowly crystallized samples and the transitions are completely missing in the latter. The reported data would rather suggest that the metastable glass-like modification obtained by quenching from the LC state is transformed below 235°K into a more ordered, stable phase.

The calorimetric data so obtained make it possible to plot the temperature dependence of Gibbs' function, that shows the equilibrium conditions in each phase of the quenched polymer (Figure 7).

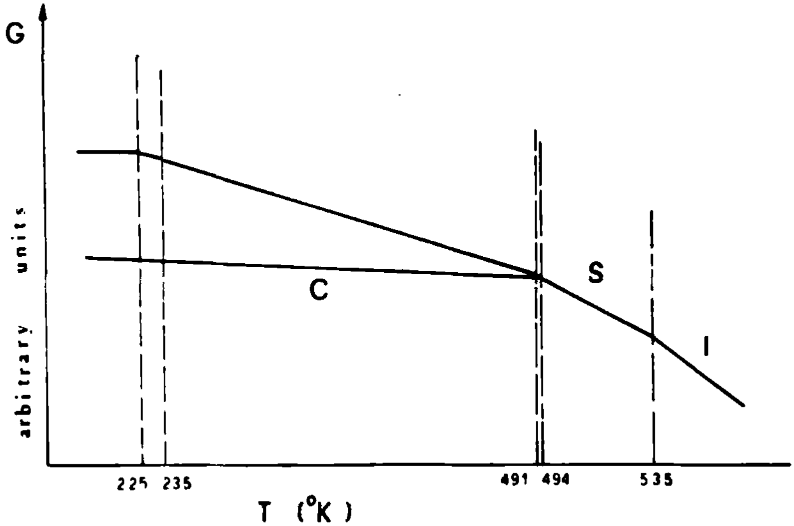

FIGURE 7 *G*-*T* dependence for polyester **3**.

Dynamic-Mechanical Measurements

Comparative plots of the dynamic viscoelastic parameters as a function of temperature for the original and quenched samples of polyesters **1–3** are reported in Figures 8–10, respectively.

High temperature behavior Original samples of polyester **1** display a pronounced inflection in the storage modulus E'-T curve at about 410°K. In the 410–550°K region, the modulus decreases steadily and in the vicinity of the melting point drops suddenly to very low values. In the same temperature range, two overlapping loss processes α_a and α' are observed. The α_a peak at about 450°K, accompanied by a six-fold decrease in modulus, is due to the main amorphous transition (T_{g_a}) of the polymer. The α' relaxation at higher temperature is connected with the onset of the melting process at about 510°K. The high temperature behavior of the original samples of the other polyesters is substantially similar to that already described. Differences are found in the temperature of the amorphous glass transition which is about 320° and 310°K for polymers **2** and **3**, respectively, and for the presence of another relaxation effect (α_c), intermediate between α_a and α'. Most probably the α_c relaxation originates within the crystal phase. It is well recognized that crystalline polymers can have crystalline relaxations that overlap pure amorphous relaxations, if the crystalline regions can provide *per se* a source of molecular motion. More-

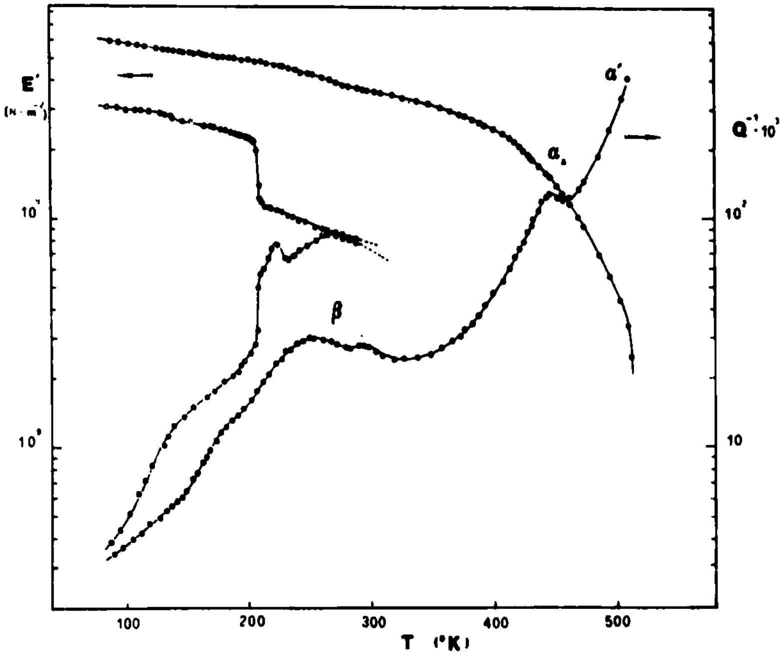

FIGURE 8 Dynamic-mechanical properties of original (●) and quenched (○) samples of polyester 1.

over, the crystalline α_c relaxation is usually found in linear polymers constituted by rod-like molecules, which at these temperatures can undergo low amplitude torsional or rotational oscillations in the crystallites without seriously disturbing the crystal structure.[9] In sample **1** the α_c relaxation is not observed due to the higher T_{g_a} value, as the α_a peak, correlated to the glass transition phenomenon, is shifted towards higher temperatures and submerges the α_c relaxation.

Melt-crystallized samples behave in the same fashion as the original samples.

The quenched samples, by contrast, present noticeable differences in the dynamic-mechanical behavior with respect to the original and melt-crystallized samples. Some peculiarities shown in their viscoelastic pattern deserve a particular comment.

Starting from sample **3**, we may note that the elastic modulus still shows a change in the slope in the region of the amorphous glass transition, whereas only a slight remnant of the α_a maximum is seen at about 350°K in the $Q^{-1} - T$ curve. The height of the loss peak in the loss modulus $E'' - T$ curve ($E'' = E' \cdot Q^{-1}$) can be taken as a qualitative

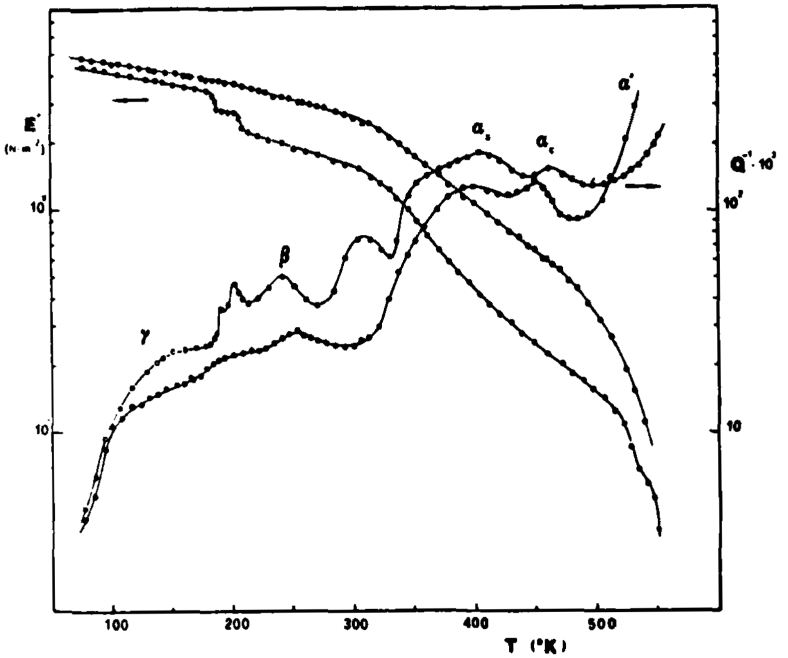

FIGURE 9 Dynamic-mechanical properties of original (●) and quenched (○) samples of polyester **2**.

measure of the relaxation strength. In order to determine the effect of heat treatments on the relaxation strength of the α process, comparative plots of E'' as a function of temperature for the original and quenched samples are reported in Figures 11 and 12.

As a result, the α_a maximum is no longer observed in the $E'' - T$ curve of the quenched polymer **3** (Figure 11). In this temperature range, the dynamic rigidity of the quenched sample is also lower than that of the original and melt-crystallized samples. These combined facts indicate that quenching from the LC state substantially reduces the relative amounts of amorphous and crystalline materials in favor of the formation of mesomorphic glass-like structures.

At about 420°K there is an appreciable decrease of the elastic modulus, that in a rather narrow temperature range changes from $1.3 \cdot 10^9$ to $5 \cdot 10^8$ N/m,^{2} which parallels the change in heat capacity observed by DSC analysis. Thereafter, the $E' - T$ curve describes a little plateau and finally the modulus drops quickly to very low values, as the melting point is approached. In the same temperature range where such a marked change in modulus occurs, there is evidence of a new loss peak (α_m), located between

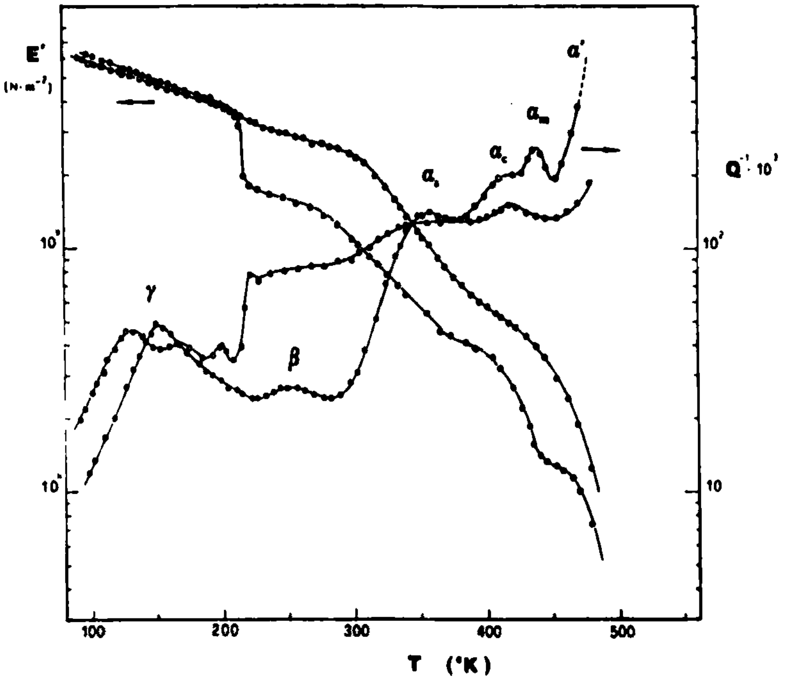

FIGURE 10 Dynamic-mechanical properties of original (●) and quenched (○) samples of polyester 3.

α_c and α' relaxations. This new relaxation, that was absent in both the original and melt-crystallized samples, shows that the inner mobility of the material is further increased as a consequence of the transition responsible for the abrupt drop in modulus. Most probably this phenomenon represents the unfreezing of the supercooled mesophase (mesomorphic glass transition T_{g_m}).

Likewise, the marked drop in modulus observed in polyester 2 at about 520°K (Figure 9) has to be associated with the mesomorphic glass transition of this polymer. In this case, the reduced temperature interval between T_m and T_{g_m} does not allow a good separation between the α' and α_m processes, which appear superimposed in the $Q^{-1} - T$ curve. Even for this polymer, the relaxation strength of the α_a process connected with the amorphous main transition is strongly reduced (Figure 12).

The origin of the secondary loss peaks at about 310° and 350°K (Figure 12) is unknown. The possibility exists that such peaks are not indicative

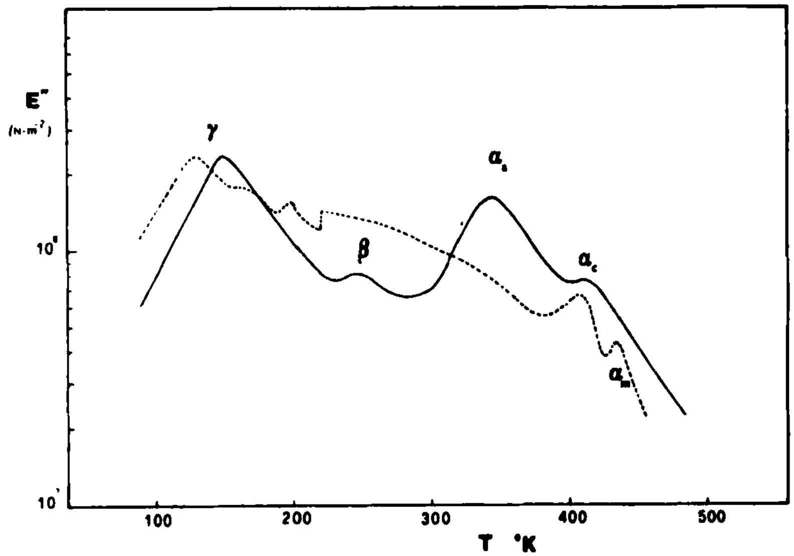

FIGURE 11 Loss modulus E'' as a function of temperature for original (—) and quenched (----) samples of polyester **3**.

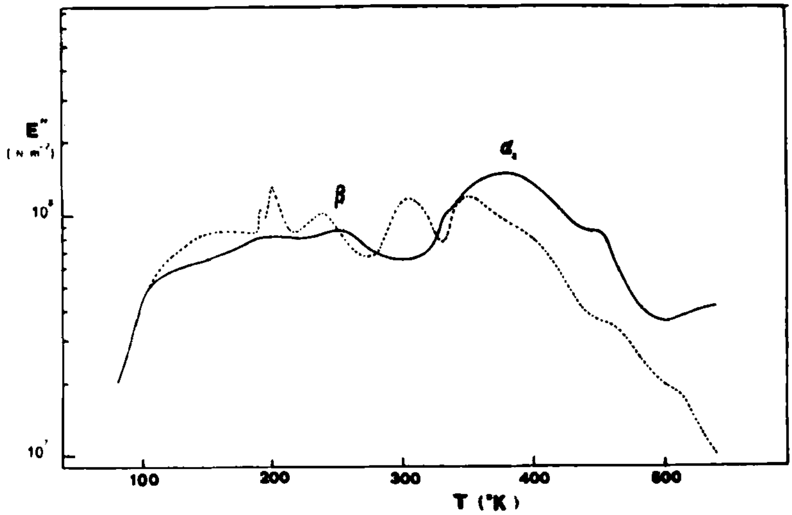

FIGURE 12 Loss modulus E'' as a function of temperature for original (—) and quenched (----) samples of polyester **2**.

TABLE II

Glass transition and melting temperatures of thermotropic liquid crystalline polyesters **1–3**

Sample	n	$T_{g_a}^a$ (°K)	$T_{g_a}^b$ (°K)	$T_{g_m}^a$ (°K)	$T_{g_m}^b$ (°K)	T_m^a (°K)
1	3	410	400	490	490	513
2	4	320	320	510	520	560
3	10	—	310	425	420	494

[a] Determined by DSC analysis.
[b] Determined by dynamic-mechanical measurements.

of molecular relaxation effects but rather arise from changes in the background loss caused by either crystallization or reorganization processes taking place during the heating of the sample in the course of the measurements.

In sample **1** the difference between T_m and T_{g_m}, as determined by calorimetric data, is only 23°K. Under such circumstances, not only the α_m peak, but also the transition in the $E' - T$ curve that does interrupt the smooth decrease of the modulus in the high temperature region, are no longer detectable.

In Table II are collected the glass transition temperatures and the melting temperatures for polyesters **1–3**, as determined by calorimetric and dynamic-mechanical measurements.

Low temperature behavior Original samples of the three polyesters show different dynamic-mechanical behavior in the low temperature region.

Polymer **1** exhibits a β loss peak at about 260°K, typically characterized by a very broad distribution of relaxation times (Figure 8).

In polyester **2** the β dispersion is resolved into a double or triple peak ranging from 180° to 320°K. In addition to the complex β relaxation, there is an additional γ relaxation, that appears as a large shoulder on the low temperature side of the β peak (Figure 9). The γ relaxation is seen to occur in polymers containing $\leftarrow CH_2 \rightarrow_n$ sequences with $n \geq 4$, and is universally attributed to motions of these methylene units, mainly in the amorphous polymer phase.[10]

In polymer **3**, the γ relaxation appears as a single loss peak centered at 150°K (Figure 10). For this sample containing $\leftarrow CH_2 \rightarrow_{10}$ sequences, the γ peak is strongly enhanced and is characterized by a much higher intensity than the β peak at about 260°K.

The dynamic viscoelastic behavior of the quenched polymers shows very unusual features. In all polyesters, there is a remarkably sharp change in the elastic modulus at 210°K. The change of modulus is always accompanied by an abrupt change of damping, that varies by a factor of three or four. In all cases, temperature and magnitude of the mechanical transition are perfectly reproducible, independent of successive cooling and heating cycles through the transformation range. Sometimes the transformation was completed within 2°K.

In sample **2**, the mechanical transition appears to be split into two steps (Figure 9), in conformity with the existence of two endotherms in the DSC thermograms.

A possible explanation for the observed phenomena is that in the lattice of the glass-like modification, molecular segments, which possess a high symmetry around one axis (i.e., the aromatic linkages forming the rigid core), can undergo relatively free rotation around this axis. This is supported by the fact that the modification formed by quenching has a highly dissipative structure, that at low temperature undergoes a transition at which damping suddenly falls to values characteristic of rigid solids. Such a transformation could be then considered as a transition between a rotator and a non-rotator phase (rotational transition). In this instance, rotation can be described in terms of orientational disorder within the molecules vibrating among two or more discrete positions in the lattice and reorienting with a very high frequency. Hence, the segmental motion is pretty much different from conventional rotation, resembling more a restricted rotation from a preferred orientation to another.

It is worth noting that a mechanical transition strictly resembling that occurring in the investigated polymers was observed in the LC low molecular weight model compound **4**. In this case, the transition is seen to occur in the sample obtained by slow crystallization from the melt (Figure 13), whereas it is lacking in the sample crystallized from solution. The step change in the viscoelastic parameters of **4** at 200°K is certainly connected with the same molecular motions that are responsible for the transition observed in polymers, thus supporting the idea that the order-disorder phenomenon might be due to conformational changes of a specific group in the molecule.

However, it should be noted that in the case of **4**, the metastable phase was obtained at a moderate cooling rate; under such conditions, a crystalline modification, rather than a glass-like modification, is conceivably formed. Therefore, in the light of these results, the assignment of the observed transition to the existence of a glass-like modification is not yet unequivocal.

Another peculiar feature resides in the differences observed in the loss patterns of the low temperature phase of the quenched, original and melt-crystallized samples of polyester **3**.

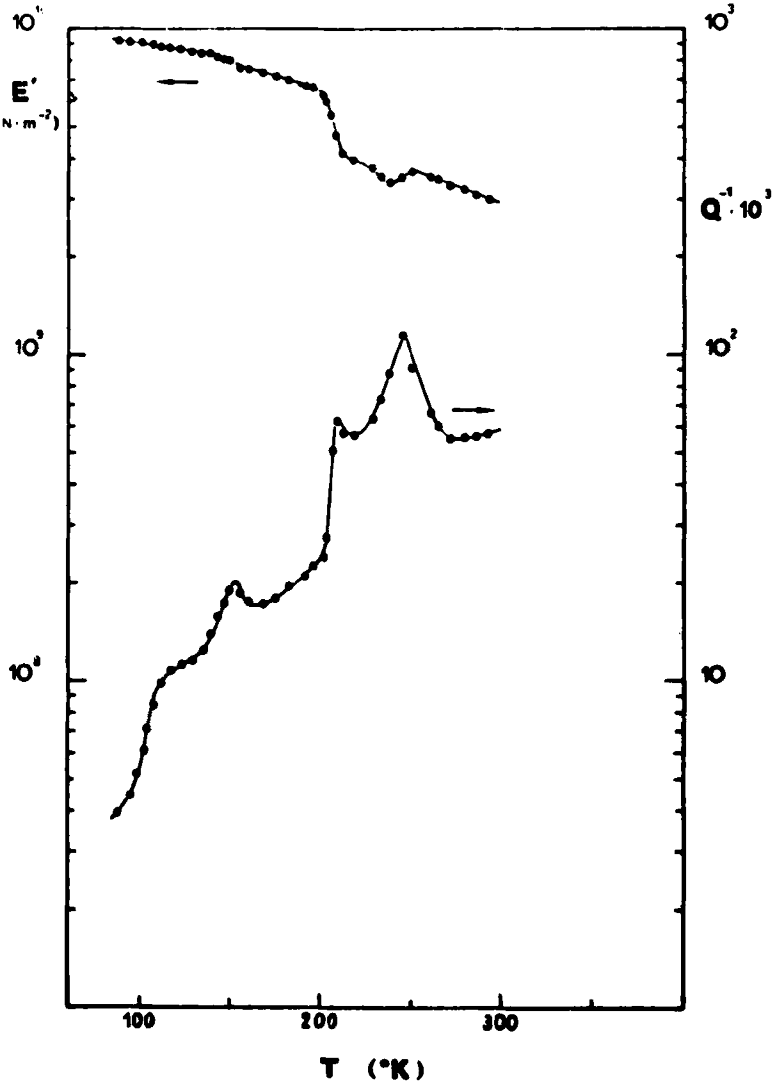

FIGURE 13 Dynamic-mechanical properties of the low molecular weight model compound 4.

In the lower temperature region, the loss trace is dominated by the occurrence of the γ relaxation. In the original sample, the γ peak is situated at 150°K, whereas in the quenched sample it occurs shifted by 20°K toward lower temperatures and its area is decreased. It has been reported that in semi-crystalline polymers, the γ relaxation is a composite phenomenon, consisting of at least two distinct processes.[11] The lower temperature one (γ_1) is attributed to motions of methylene sequences in the crystal phase (crystalline lattice relaxation), whilst that occurring at higher temperature (γ_2) is related to motions of the same sequences in the amorphous regions. Generally, the amorphous relaxation γ_2 is the prominent phenomenon obscuring the γ_1 relaxation effect. Generally, the separation of the two processes in two distinct peaks is not possible, owing to the difficulty in preventing the formation of amorphous regions in the bulk polymer. Here the absence of the γ peak at 150°K (γ_2 relaxation) in the quenched sample might relate to the drastic reduction of the amorphous material. Conversely, the presence of the γ peak at 130°K (γ_1 relaxation) would be interpreted as a crystalline relaxation, which can take place in either the pre-existing crystal phase or in the new phase generated by the transformation of the supercooled mesophase, *via* the first order transition close to 220°K.

CONCLUSIONS

A first order solid-solid transition was found in samples of thermotropic polyesters quenched from the liquid crystal state. The transition was observed by mechanical measurements at 210°K for all three polyesters examined. Calorimetric data confirmed the existence of the transition which appeared in all cases as a double endothermic peak at 225° and 235°K.

The quenched samples still possessed a definite degree of crystallinity observable by X-ray analysis. The degree of crystallinity can be evaluated approximately from the values of elastic moduli above T_{g_m} on the basis of the logarithmic rule of mixtures suggested by Nielsen[12,13] and was found to be about 30–40%. The crystal form of the quenched samples was nearly the same as that found in the sample crystallized slowly from the melt. However, in the latter no indication of the transition at low temperature was gained by both calorimetric and dynamic-mechanical investigations. Such results strongly suggest that this transition concerns the supercooled mesophase rather than the crystal phase.

The starting point for the interpretation of the phenomenon on a molecular basis is represented by the interesting finding that such a transition is independent of the length of the flexible polymethylene spacers interconnecting the rigid anisotropic moieties. Since the rigid core of the mesogenic unit is the same in all the samples, it may be concluded that the transition has most probably to be ascribed to the intrinsic characteristics of the aromatic part of the mesogenic units.The apparent enthalpy of transition in polyester **3** was found to be 0.53 cal/g. If the polymer is adequately represented by a two-phase system, the amount of the supercooled mesophase can be estimated to be as high as 60–70%. The resulting enthalpy of transition for the 100% mesomorphic polymers is ≃80 cal/g, corresponding to a $\Delta H \simeq 300$ cal/mol of rigid core unit. The entropy of transition is thus $\Delta S \simeq 1.29$ cal/mol · °K. Since this value is very close to $R \cdot \ln 2 = 1.38$ cal/mol · °K, the entropy change could be tentatively rationalized on the basis of an order-disorder transition of rigid segments between two equivalent sites.

The rotational character of the transition is further supported by the results of the dynamic-mechanical analysis. Moreover, the experimental data indicate that the loss pattern of the low temperature phase in the quenched sample is different from that of the original and melt-crystallized samples. This suggests that the mobility of the polymethylene sequences, that is responsible for the occurrence of the γ relaxation, is also affected by the type and extent of structural organization in the various polymorphs.

Finally, two glass transitions T_{g_a} and T_{g_m} were detected. The former, in the intermediate temperature range, is the glass transition of the amorphous phase which is always present in both the original and melt-crystallized samples. The latter, occurring at higher temperatures, is connected with the unfreezing of the supercooled mesophase and is observed in samples quenched from the liquid crystal state.

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