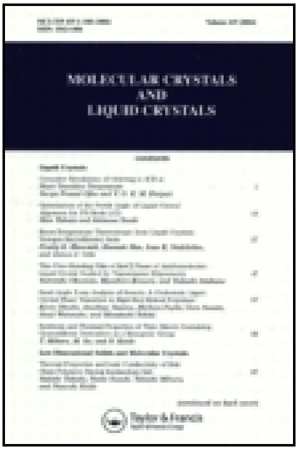

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Synthesis and Characterization of a New Fully Aromatic LCP

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SYNTHESIS AND CHARACTERIZATION OF A NEW FULLY AROMATIC LCP

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Abstract Liquid crystal polymers (LCP)are a relatively new class of polymers with very interesting and unusual properties. In particular, easy processability and outstanding mechanical and barrier properties make them very attractive. Unfortunately the high stiffness of their chains often leads to compounds having very high melting points and consequently to unprocessable materials. By adding a flexible segments in the chain backbone the LCPs become processable at lower temperatures but lower properties are displayed. A new rigid liquid crystalline polymer, having excellent physical properties, good processing temperature and a good cost/performance compromise, is described in this work. The properties of this liquid crystalline polymer are compared with those of a commercial rigid LCP and with those of a semirigid one.

INTRODUCTION

In the last decade the polymeric liquid crystalline structures have received the attention of the researchers worldwide because of their unusual physical properties, including mechanical, optical, electrical and rheological ones[1-4]. In particular thermotropic copolyesters, containing a rigid rod backbone, have been studied extensively by the academy and industry both as self reinforcing materials and as fillers for engineering resins. Unfortunately the high stiffness of their chains often leads to compounds having very high melting points and consequently to unprocessable materials. Moreover the cost of the monomers is often prohibitive for industrial applications. In previous years ENIRICERCHE has synthesized new classes of semirigid liquid crystalline polymers[5-9] where the presence of flexible segments in the rigid backbone reduces these shortcomings and, in particular, the crystal-nematic transition. The partly flexible nature of these LCPs gives rise to a better compatibility with flexible thermoplastics[10-13] but implies a decrease of mechanical and thermomechanical properties and of the chemical resistance.

In this work a new liquid crystalline polymer, having good physical properties, acceptable processing temperature and a good cost/performance compromise, is described.

EXPERIMENTAL

Polycondensation reactions were carried on in a 500 ml round bottomed glass reactor equipped with a stirrer, a gas inlet and outlet tube. The reactor containing the mixture of coreactants was placed in a bath preheated at 300 °C with stirring. In these conditions the polycondensation immediately starts with acetic acid production.

The reaction was normally carried out at room pressure over a period of 8 hours after which vacuum was applied up to the desidered molecular weigth.

Inherent viscosities were measured at 20 °C with an automated Ubbelohde viscometer in a CH_2Cl_2/trifluoroacetic acid solution (4/1 vol/vol).

Differential Scanning Calorimetry measurements were performed with a DSC 30 Mettler instrument in nitrogen flow. Thermogravimetric analyses were obtained with a TG 50 Mettler instrument in nitrogen flow. X ray powder analyses were carried on using a vertical goniometer and nickel filtered $CuK\alpha$ radiation.

The samples for all mechanical tests were obtained by injection molding in a Ray-Ran laboratory press. The temperature of the melt was 295 °C and the temperature of the mold 190 °C.

Before processing the LCP was dried in a vacuum oven for at least 24 hours to prevent hydrolitic scission of LCP.

Three-point flexural tests were carried out on an Instron machine mod 1122. The span to specimen depth (L/d) was about 10 and the cross speed was 1 mm/min. All the reported results are averages of at least seven measurements. The flexural stress has been evaluated at the maximum force that, for all the investigated samples, occurs at the breaking point. The elongation at break, FE, was calculated by using the usual equation for flexural deformation:

$$FE = 6\,d\,W/L^2 \qquad (1)$$

where d is the deformation, W and L is the width and the span length respectively

HDT values were determined following ASTM D648/82 (flexural load 1.8 MPa, rate of increase of the temperature 120 °C/h) using an automatic CEAST apparatus. During tests the deformation, directly read by means of a micrometer put on the sample, allowed the calculations of the flexural strain as a function of the temperature by using the same equation 1 for flexural deformation.

For comparison two other LCP samples were used: a semirigid LCP named SBH and a commercial rigid copolyester, Vectra A from Hoechst-Celanese.

The semirigid LCP was a liquid crystal polymer having the following composition: sebacic acid (S), 4,4' dihydroxybiphenyl (B) and 4-hydroxybenzoic acid (H). The molar ratio of the components (S:B:H) is 1:1:2.The LCP, synthesized by ENIRICERCHE, is known as SBH 112 and has been already characterized [5-9].

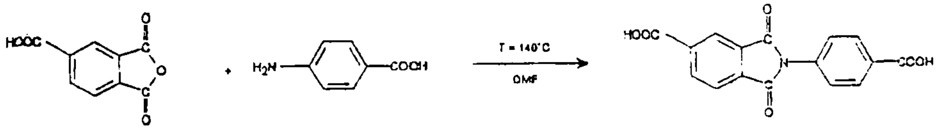
Vectra A is a rigid copolyester made from HBA (73%) and HNA (27%) and well characterized in the literature[14-16].

RESULTS AND DISCUSSION

Synthesis and Structural Characterization

The polymers were obtained by polycondensation of N-(4-carboxyphenyl)trimellitimmide (CI) and tert-butyl hydroquinone diacetate (TBI), in presence of MgO as catalyst.

Synthesis of CI has been achieved by literature methods as reported in the following scheme.



The main difficulties in the preparation of FAPT are due to the very high melting point of CI (about 375 °C), and to the weight loss at relatively low temperature of TBI. This means that the reaction does not take place in melt conditions and there exists the possibility of uncorrected reacting composition.

Because of these problems, two different approaches have been attempted:

1- the preparation of CI derivatives with lower melting point

2- the use of experimental conditions that allow an homogeneous reaction to occur also in non-melt but sintering conditions.

As regards the first approach, the dimethyl ester of CI has been prepared by reaction of CI with methanol in acid medium. The resulting melting point (196 °C) allows melt condensation at lower temperatures, but preliminary attempts have shown that the polycondensation does not take place in 230-250 °C temperature range. When the temperature has been raised to 280 °C a noticeable loss of (II) has been occurred before the polycondensation has slowly started. This synthetic route has been abandoned.

As regards the second approach, it has been found that, when the mixture of coreactans are placed in a bath preheated at 300 °C, the polycondensation immediately starts without significant loss of TBI.

Some of the most significants runs, made in different experimental conditions are reported in Table 1. The best results, in terms of molecular weight, are obtained with the highest reaction temperatures and a period of at least 3 hours of polycondensation under vacuum conditions.

TABLE 1 Synthesis conditions and properties of some FAPT samples

Sample	Ambient Pressure		Vacuum		Tg, °C	[η], dl/g
	T, °C	t, h	T, °C	t, h		
FAPT6	270	7	280	3.5	187	0.45
FAPT7[a]	280	8	280	4	193	0.86
FAPT9	295	8	300	3	221	1.08
FAPT10	300	8	300	3	214	0.78
FAPT14	310	9	250-280	1	176	0.14
FAPT 21[a]	310	6	310	2	210	0.68

a) after annealing (96 h at 195 °C under N_2 flux).

The behaviour of the glass transition temperature, Tg, and inherent viscosity, [η], of a typical polycondensation (FAPT9) is plotted in Figure 1 where the reaction time (in minutes) is also reported.

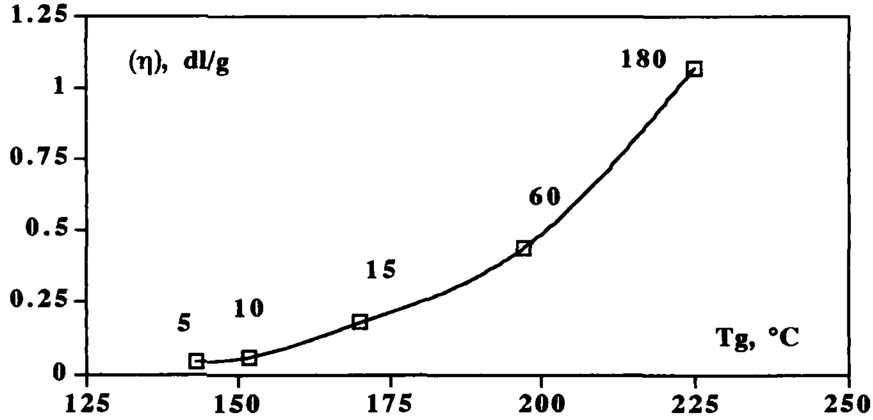


FIGURE 1 Inherent viscosity as a function of the glass transition temperature

It is possible to note that Tg increases less than linearly at high values of inherent viscosity. By changing the synthesis parameters it is then possible to obtain samples with Tg ranging from 140 to 230 °C.

XRD patterns of FAPT LCPs, Figure 2, show a broad halo, typical of disordered materials. This property is probably due to head-to-head and head-to-tail disordered sequences of the asymmetrical utilized monomers. In addition the steric hindrance of the lateral tert-butyl group seems able to prevent paracrystalline order.

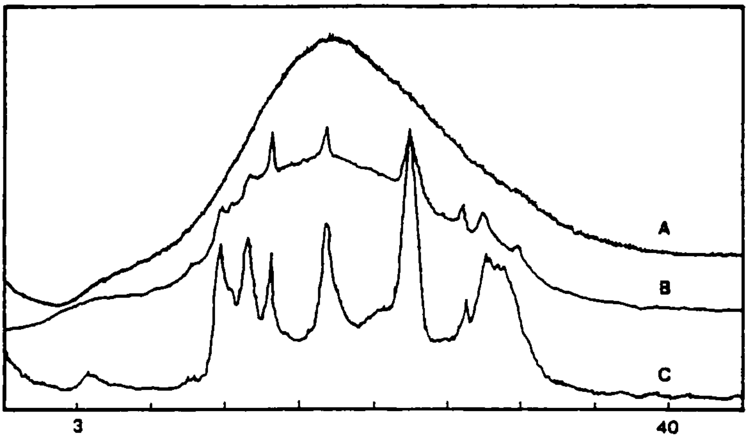
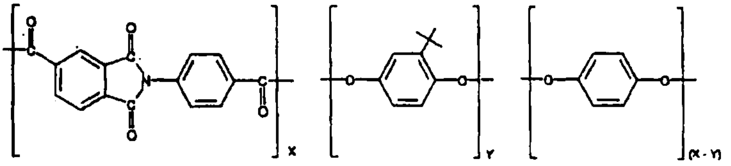


FIGURE 2 XRD patterns of: (A) FAPT21[a], (B) FAPT6, (C) FAPT8.

Traces of crystallinity are often visible in FAPT, showing a pattern quite similar to that one observed in polyesters, when the samples are obtained by partial substitution (50%) of TBI with hydroquinone diacetate, ID, Figure 2. The crystalline phase is probably due to the partial decomposition of tert-butylhydroquinone to hydroquinone and to the growth of regular sequences. The general formula of this polymer is then:



The crystallinity index (Icr) has been calculated as the ratio between the scattered intensity of the crystalline fraction and the total scattering. In Table 2 some results are reported indicating that the crystallinity is strongly enhanced by using ID instead of TBI.

TABLE 2 Structural characteristics of some FAPT samples

Sample	Composition			Icr	ΔH, J/g	$T_{k\text{-}m}$, °C	T_d, °C
	CI	TBI	ID				
FAPT6	0.5	0.5	-	0.17	11	313	387
FAPT7[a]	0.5	0.5	-	0.2	10	313	400
FAPT8	0.5	0.25	0.25	0.53	32	332	-
FAPT9	0.5	0.5	-	0.09	3	306	-
FAPT10	0.5	0.5	-	0.10	5	285	-
FAPT 21[a]	0.5	0.5	-	0.0	2	280	430

[a] see Table 1

DSC thermograms of these LCPs show a glass transition temperature, as has already been mentioned, depending on the molecular weight and of the crystal-to-mesophase transition temperature, $T_{k\text{-}m}$, ranging from 280 to 330 °C whose heat of melting (ΔH) is proportional to Icr. For example in Figure 3 the DSC trace of the FAPT7 sample show a Tg of about 190 °C and a melting endotherm peak at about 315 °C.

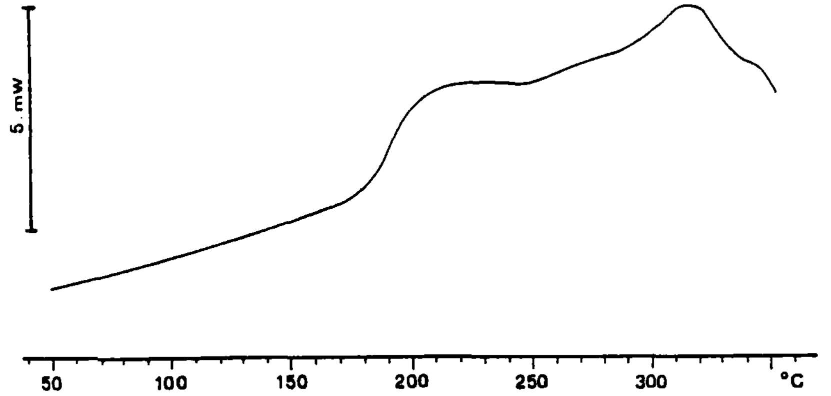


FIGURE 3 DSC trace of a FAPT sampe

The FAPT LCPs exhibit a nematic phase at temperatures slightly above Tg in which the crystalline phase is dispersed as separated particles that start to melt at temperatures near to $T_{k\text{-}m}$. Such a morphology is probably due to the precipitation of low molecular weights of CI and ID in the first steps of the polycondensation. The isotropization can not be observed because of the decomposition at high temperatures.

The FAPT polymers show, moreover, a remarkable thermal resistance and the thermogravimetric tests evidence that the decomposition temperature, T_d, taken as the temperature at which the weight decreases of 5%, is not less than 370 °C and increases with increasing Tg and then with increasing the molecular weight, see Table 2 and 1 respectively.

Mechanical and Thermomechanical Properties

In Table 3 the value of the modulus, E, the flexural stress, FS and of the flexural elongation, FE, for the three pure LCPs are reported. Both the E and FS of the semirigid sample, appear lower than those of the two rigid samples. For VA, the modulus is about five times and the FS is about seven times with respect to the value shown by SBH.

TABLE 3 Flexural properties and HDT values of pure polymers

Sample	E, GPa	FS, MPa	FE, %	HDT, °C
FAPT21	5.2	38	0.6	193
SBH	1.1	24	2	61
VECTRA A	5	155	7.6	175

For the FAPT sample the situation is similar but some differences should be noticed. The modulus of FAPT is about five times than that of SBH and similar to that of VA, but FS is only about 50% higher. This difference between the two rigid samples should be attributed to differences in structure, composition (aromaticity and then rigidity of the chains) and, perhaps, in molecular weight. A strong difference in FE is observed too. The flexible spacers present in SBH allow it to reach higher values of FE (2%) with respect to that of FAPT (0.6%) that is a wholly rigid copolyester, but lower than that of the other rigid copolyester. This latter result is quite surprising and perhaps depending on the kind of the mechanical test. In tensile tests in fact the best flexibility of SBH allows it to reach an elongation at break of about 8% [17] while the rigid VA reach only 3.6% [18].

In Figure 4 the curves of flexural strain, FS, as a function of the temperature for the three LCP samples are reported. the small negative strain observed for the FAPT sample can be due to residual internal stresses induced by the preparation of the samples (injection molding).

The semirigid SBH shows a rapid increase of the strain at low temperature because of its low glass transition temperature. At about 60 °C it reaches a strain value of about 0.2% which corresponds to the HDT value, see Tab. 3. The behavior of the rigid LCPs is completely different. The deformation of VA grows gradually with temperature; at about 130 °C the strain is about 0.1% and the HDT value is 176 °C. On the contrary, only above 150 °C the FAPT sample shows a significant deformation while the HDT value is more than 190 °C.

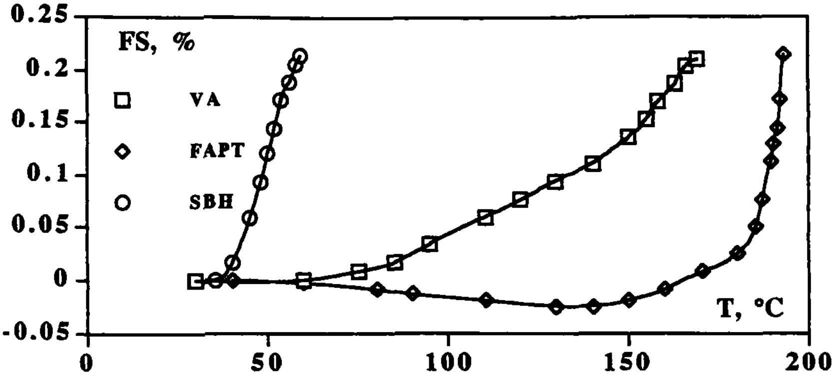


FIGURE 4 Flexural strain as a function of the temperature for the three LCP samples

The semirigid SBH shows a rapid increase of the strain at low temperature because of its low glass transition temperature. At about 60 °C it reaches a strain value of about 0.2% which corresponds to the HDT value, see Tab. 3. The behavior of the rigid LCPs is completely different. The deformation of VA grows gradually with temperature; at about 130 °C the strain is about 0.1% and the HDT value is 176 °C. On the contrary, only above 150 °C the FAPT sample shows a significant deformation while the HDT value is more than 190 °C.

CONCLUSIONS

A new fully aromatic LCP has been synthesized and characterized from both a structural and mechanical point of view. This polymer exhibits a very high glass transition temperature, strongly dependent on the synthesis conditions, and very interesting physical and mechanical properties.

To compare the properties of this material with other commercial ones belonging to the same class, a rigid LCP (VA) and a semi rigid LCP (SBH) were also investigated.

This fully aromatic LCP present good mechanical and thermomechanical properties if compared with the other LCPs. The elongation at break is very small, but both the modulus and the tensile stress assume good values.

HDT is very high not only if compared with that of the SBH but also if compared with that of VA.

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