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Synthesis and Characterization of a New Class of Fully Aromatic Liquid Crystal Polymers

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A new fully aromatic LCP, obtained by polycondensation of N-(4-carboxyphenyl) trimellitimide and tert-butyl hydroquinone (FAPT), was previously described. The polymer shows very interesting physical and mechanical properties but a very high glass transition temperature which does not allow a good processability.

In order to overcome this problem, a new class of LCPs, obtained by partial substitution of the dicarboxylic moiety with isophthalic acid, is described.

The new thermoplastic materials were characterized from the physicochemical and mechanical point of view.

All the polymers obtained with an isophthalic acid (FA-IA) content varying from 10 to 40% of the substituted moiety show a nematic mesophase.

Glass transition temperature and inherent viscosity are influenced by the presence of the modifiers but, surprisingly, the resulting effect is not proportional to their amount.

Thermal stability of the new polymers increases as the content of IA increases. The materials can be spun and the mechanical properties of the fibers were compared to those of a rigid commercial LCP.

Keywords: fully aromatic Liquid Crystal Polymers; mechanical and thermomechanical properties; structure

INTRODUCTION

Liquid crystal polymers (LCP) are a relatively new class of polymeric materials that can collect good processability and very high mechanical and thermomechanical properties[1]. All these characteristics derive from the particular structure of the macromolecules. Increasing the rigidity of the chains, the mechanical properties become better but the improvement of the

mechanical properties is not always accompanied by an easy processability that, on the contrary, can drastically worsen.

In a previous work [2] a new class of rigid liquid crystal polymers, named FAPT, has been described and characterized. This new fully aromatic LCP sample, synthesized from N-(4-carboxyphenyl) trimellitimide and ter-butyl hydroquinone, shows very interesting mechanical and thermomechanical properties, in particular high glass transition temperature, but a poor processability. This is a quite common feature for these fully aromatic materials and several strategies have been proposed to improve the processability[1], although some of these strategies lead to a decrease of the mechanical properties[1,3]

In this work the FAPT sample has been modified with the main aim to improve the processability. The polymerization has been carried out by substituting part of the carboxyimide with isophthalic acid. This new class of LCPs has been characterized both from a structural and mechanical point of view.

EXPERIMENTAL

Polycondensation reactions were carried out 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 (N-(4-carboxyphenyl) trimellitimide and ter-butyl hydroquinone and isophthalic acid) 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 6 - 8 hours after which vacuum was applied up to reach the maximum viscosity. The polymer production was about 100 g/run. 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 out using a vertical goniometer and nickel filtered CuKa radiation. Hot stage microscopy was used to recognize polymers mesophase.

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The samples for the tensile tests tests were obtained by compression molding and by melt spinning. The compression molding was performed in a laboratory Carver press at T ≈ 290 °C.

The samples for the flexural tests were obtained by injection molding in a Ray-Ran laboratory press. The melt temperature was about 300 °C and the mold temperature about 170 °C.

The fibers were prepared from the sample with a 0.15 molar fraction of IA using the tensile module of a capillary viscometer, Rheoscope 1000 (CEAST, Italy), with a capillary of 1 mm and length to diameter ratio of about zero. The extruded monofilament passes through a pulley system and is then drawn by two counter-rotating rolls, the rotational speed of which continuously increases with a linear acceleration of 1 rpm/s. The spinning temperature was about 320 °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 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 strain at break, FB, was calculated by using the usual equation for flexural deformation:

$$FB = 6\,d\,W/L^2$$

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

Tensile stress-strain curves were obtained using the same Instron model 1122. The tests were performed on fibers and on samples cut from compression moulded sheets.

RESULTS AND DISCUSSION

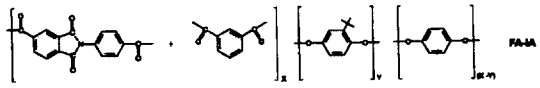
Structural Characterization

In a previous work[2], the preparation of a new fully aromatic LCP, obtained by polycondensation of N-(4-carboxyphenyl) trimellitimide (CI) and tert-butyl

hydroquinone (TBI), was described. The obtained polymer shows very interesting thermal and mechanical properties but a certain degree of stiffness and a too high processing temperature.

To overcome these problems the chemical structure of the polymer was modified by partial substitution of the LCP dicarboxylic moiety with isophthalic acid (IA). It is well known in fact[2], that the use of "meta" linked aromatic rings causes sharp deviation of the chain axis allowing a lower processing temperature.

The new modified structure is reported below.



As already discussed in the previous paper[2], the presence of hydroquinone in the structure of this class of polymers is due to the partial decomposition of TBI during polymerization.

In Table I some experiments with different amount of (IA) in substitution of (CI) are summarized and compared with a sample of unmodified polymer (FAPT).

TABLE I Synthesis and properties of LCP obtained by partial substitution of (CI) with (IA)

Sample	composition (molar fraction)				
	CI	TBI	IA	Tg (°C)	[η] (dl/g)
FAPT	0.5	0.5	-	214	0.78
FA-IA 1	0.45	0.5	0.05	191	0.49
FA-IA 2	0.4	0.5	0.1	187	0.38
FA-IA 3	0.35	0.5	0.15	194	0.41
FA-IA 4	0.3	0.5	0.2	180	0.37
FA-IA 5	0.25	0.5	0.25	187	0.41

All the experiments were carried out in a glass apparatus under the conditions described in the experimental section and were continued up to reach the maximum viscosity.

The polycondensation reaction is not affected by the partial substitution of the carboxylic moiety with IA: when the coreactants are placed in a bath preheated at 300°C, the reaction immediately starts without significant loss of TBI; moreover the recovered amount of acetic acid is in accord with the reaction stoichiometry.

As already mentioned, glass transition temperature and viscosity of the obtained polymers are considerably influenced by the presence of "meta" aromatic units but, surprisingly, the resulting effect is not proportional to their amount. For both T_g and the inherent viscosity values reported in Table I, a sharp decrease of both characteristics is observed when small amounts of IA are added, while a further increase of IA content causes only some irregular changes. The change of the structure does not allow to state if this means a decrease of the molecular weight that, however, remains almost unchanged with increasing the IA content.

The structural characterization does not show any evidences of heterogeneous materials. XRD patterns show that the IA modified copolymers are almost completely amorphous while the original polymer shows, sometime, traces of crystallinity, probably due, as already discussed, to the partial decomposition of tert-butylhydroquinone to hydroquinone and to the growth of regular sequences[2].

Thermal stability is remarkably improved in comparison to unmodified polymer. In Fig. 1 the thermogravimetric curves of FAPT and FA-IA 5 (molar fraction of IA = 0.25) are reported.

The behavior of T_d (temperature at a weight loss of 5%) vs. molar fraction of IA in the polymers is reported in Fig. 2.

Thermogravimetric analysis evidences that decomposition temperature increases as the content of IA increases, according to the lower thermal degradation of the introduced comonomer.

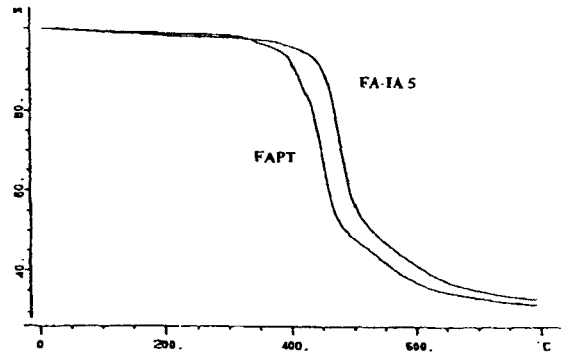


FIGURE 1 Thermogravimetric analysis of FAPT and FA-IA 5

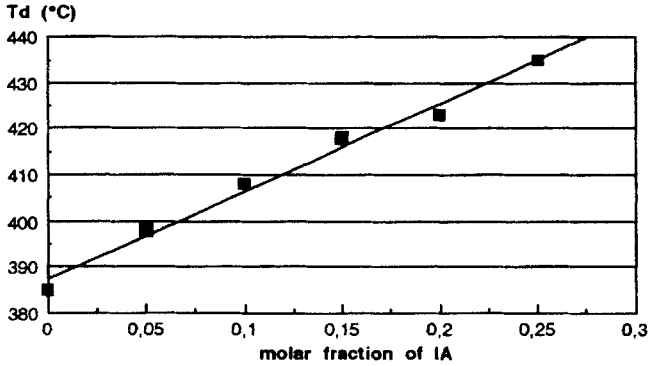


FIGURE 2 T_d as a function of the IA content

All the prepared polymers exhibit a nematic mesophase slightly above Tg while isotropization can not be observed because decomposition.

Mechanical Characterization

In Table II elastic modulus, FM, stress, FS, and strain at break, FB, in flexural tests are reported for all previous samples. All the curves show the same features. At very low content (less than 0.1) of IA the mechanical properties are almost independent on the composition and rather a slight decrease is observed.

TABLE II Mechanical properties in flexural tests

Sample	FM, GPa	FS, MPa	FB, %
FAPT	5.2	38	0.6
FA-IA 1	5.1	37	0.6
FA-IA 2	5	36	0.5
FA-IA 3	5.8	80	1.7
FA-IA 4	5.7	75	1.5
FA-IA 5	5.65	75	1.6

On the contrary, the flexural properties significantly increase when the content of IA ranges from 0.1 to 0.2. Finally, all these mechanical properties level off with increasing the IA content. The best composition is that with 0.15 mole fraction of IA.

Similar behaviour is shown by the tensile properties. It is however worth to notice that the tensile properties cannot be measured for the sample without IA. Indeed, the specimens of this sample, as already discussed in a previous paper[2], cannot be tested in tensile mode because of their very high brittleness that does not allow even to cut the specimen. The presence of IA improves, therefore, the processability and the ductility of these polymeric materials.

The tensile properties of compression molded specimens of the sample with 0.15 molar fraction of IA are reported in Table III together with the tensile properties of a specimen of a commercial sample of a fully aromatic LCP known as Vectra A processed in the same conditions. The tensile elastic modulus is about 3.1 GPa and then higher than that of Vectra (about 2.4 GPa) while both tensile stress and elongation at break show lower values. Also for this composition, therefore, some brittleness remains with respect to the commercial Vectra sample.

The improved processability is better put in evidence by the fact that the samples with a content of IA less than 0.1 cannot be significantly spun while at higher content of IA the spinning become easy and very high draw ratio values are obtained. In the same Table III the maximum values of the tensile properties for the fibers of the sample with 0.15 of IA are reported with the values of fibers of Vectra A obtained in the same conditions.

TABLE III Elastic modulus, E, Tensile stress, TS and elongation at break, EB, of isotropic and anisotropic specimens

Sample	E, GPa	TS, MPa	EB, %
FA-IA3	3.1	27	1.3
Vectra A	2.4	57	3.6
FA-IA3 fiber	58	450	1.1
Vectra A fiber	60	810	1.9

The values of the tensile properties strongly increase with the spinning due to the good orientation achieved by these LCP samples. Also for these specimens the Vectra A sample shows better values of the ultimate properties while the two elastic moduli are very similar. These data seem to suggest a slightly better orientability of Vectra A

CONCLUSIONS

A new fully aromatic LCP has been synthesized and characterized both from a structural and mechanical point of view.

The structural characterization shows that the material is a true copolymer, almost completely amorphous, with lower processing temperature and improved thermal resistance in comparison to the unmodified polymer. The presence of IA strongly improves the processability and the ductility of this class of LCPs with respect to the unmodified sample. In particular, these samples can be spun and oriented. Finally, the elastic modulus of both isotropic and anisotropic samples are very similar, and in some cases higher, than those of a commercial fully aromatic LCP, while the ultimate properties are lower.

Acknowledgments

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