

# Rigid Chain Ribbon-like Metallopolymers

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**ABSTRACT:** A set of new copolymers is here reported in which the repeating units are connected each other through Cu(II) metal centers. The coordination link is based on the bis-chelating properties of salicylaldiminate groups of two different monomers. Due to their chemical structure, the two monomers afford, respectively, flexible and rigid repeating units in the metallopolymers constitution upon coordination to copper centers. All the copolymers were soluble and easily processable. As shown by XRD analysis, rigid units' rich copolymers adopt a ribbon-like structure in solid state in which highly planar strands of polymer stack thanks to  $\pi-\pi$

interactions, similarly to the polymer composed exclusively by rigid units. This behavior can be justified assuming the existence of a partial block character in copolymer constitution where long sequences of rigid units are alternated to sequences of flexible units. This assumption is supported also by DSC and UV-Vis analysis. © 2014 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2412–2421

**KEYWORDS:** copolymerization; differential scanning calorimetry; metal-polymer complexes; UV-Vis spectroscopy; X-ray

**INTRODUCTION** The search for novel organic materials able to replace traditional inorganic ones in different high tech applications is a general trend observed in the last decades. A huge number of studies has been published in this period which permitted the obtainment of materials with excellent performance in different fields of electronics such as photovoltaics,<sup>1–4</sup> field effect transistors,<sup>5–11</sup> and photonics, as for instance nonlinear optics (NLO),<sup>12–16</sup> by giving a better understanding of the physical mechanism underlying the activity of organic based materials. This interest stems first of all from the possibility of processing organic materials through solution techniques (spin-coating, inkjet printing, or roll-to-roll techniques),<sup>17,18</sup> deeply reducing in this way the cost of the device fabrication. The mechanical properties featured by organic materials, such as lightness and flexibility, open the way to new application possibilities not affordable for the heavy and rigid traditional inorganic ones. More recently, a growing interest has been observed for metal containing polymers with regard to their potential use in material science: the presence of metal centers may significantly

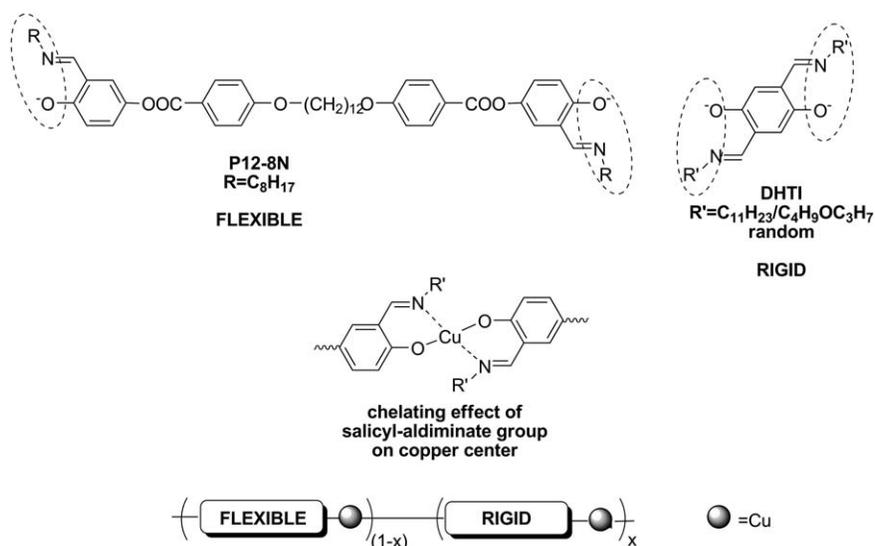
affect optical, electronic, and magnetic properties of the polymers.<sup>19,20</sup> As already proposed, this kind of systems can be considered the ultimate organic-inorganic hybrids, in which the two components are mixed at a molecular level.<sup>21</sup> They have been deeply investigated for what concerns their electrical properties (for application in photovoltaics<sup>22,23</sup> and sensors<sup>24,25</sup>), their electroluminescence activity,<sup>26,27</sup> their NLO properties<sup>28–30</sup> and liquid crystalline behavior.<sup>31</sup>

Regarding the nature of the organic ligands, Schiff-bases have been widely investigated in the literature for the preparation of interesting metallo type assemblies, mainly because of their versatility, structural variety, and ease of preparation.<sup>32–35</sup>

In previous articles, the bis-chelating P12-8N ligand (whose structure is reported in Chart 1) was used in the preparation of linear metallopolymers.<sup>36,37</sup> P12-8N is characterized by two salicylaldiminate end groups separated by a flexible chain. Upon coordination with a metal a linear metallopolymer could be obtained, characterized by liquid crystalline properties due to the alternation, along the chain, of

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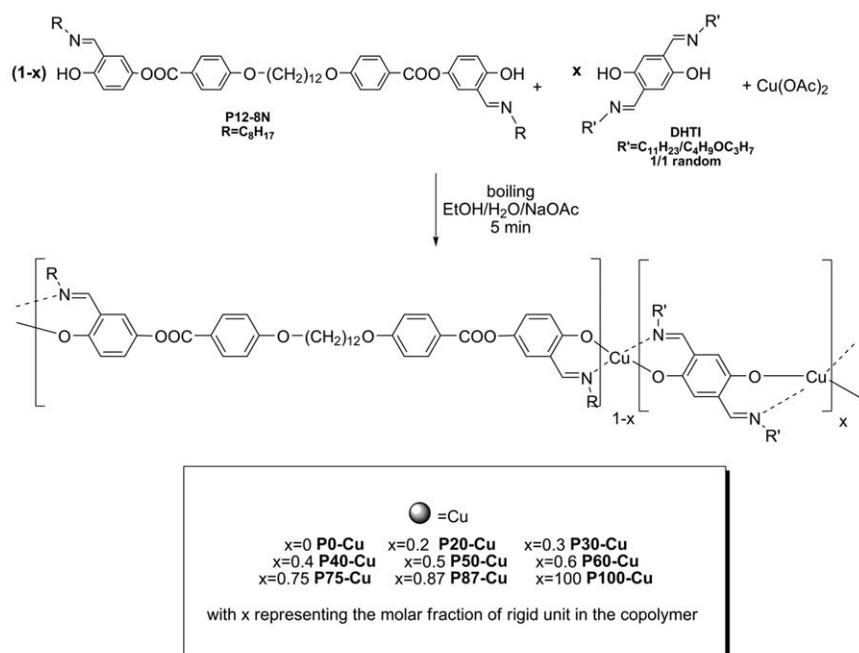
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**CHART 1** Schematic representation of the two type of repeating units and of the way they are linked through copper metal centers; in copolymer constitution drawing x represents the molar fraction of the rigid unit.

mesogenic aromatic groups with flexible groups. A new bis-chelating salicylaldimine type ligand, DHTI and metallopolymers based on it, are reported in this article. This ligand, DHTI, is a diimine derivative of 2,5-dihydroxyterephthalaldehyde and is characterized by two salicylaldimine functional groups sitting on the same aromatic ring (see Chart 1). In particular, a set of novel polymeric materials has been prepared, constituted by two different repeating units, deriving from P12-8N and DHTI respectively, and linked together by copper (II) metal centers, in a main chain covalent approach.

The prepared copolymers are hence characterized by flexible repeating units (deriving from P12-8N) and rigid units (deriving from DHTI). The insertion of DHTI type repeating unit was thought to increase the overall planarity of the polymeric systems, a desired feature for applications in fields like organic electronics or spintronics. It is worth to point out, in fact, that in the polymer containing exclusively rigid units, the metal based linkage is expected to induce a highly planar conformation of the polymer backbone as a consequence of the square planar coordination of the ligands around the copper centers (look for instance at the parent



**CHART 2** Synthetic pathway for polymers and copolymers preparation.

low mass compound reported by Carotenuto et al.<sup>38</sup> where the salicyl aldiminate group adopt a planar conformation around the copper center). We prepared a set of metal copolymers characterized by different molar ratio between flexible and rigid units with the aim of modulating the processability of the materials. Also the two homopolymers based exclusively on P12-8N ligand (already known in the literature but here presented with a slight modification in the synthesis) or on DHTI, were prepared. All the synthesized polymers and copolymers were carefully characterized for what concerns their thermal, structural, and optical properties; as discussed in the following sections, the results emerging from this combined analysis suggest a peculiar partial block character in copolymers chemical constitution.

## EXPERIMENTAL

### Synthesis

All the reagents and solvents were purchased from Sigma Aldrich and Carlo Erba Reagenti and used without further purification. P12-8N<sup>31</sup> and 2,5-dimethoxyterephthaldehyde<sup>39</sup> were synthesized according to procedures already reported in the literature. Two homopolymers and a set of copolymers were prepared, starting from two different bis-chelating monomers, one flexible (P12-8N) and one rigid (DHTI). The general name attributed to the prepared polymers is P $n$ -Cu (see Chart 2), where  $n$  is a number indicating the percent molar fraction of the rigid unit in the copolymer constitution. We report here in details the synthetic procedure of the two homopolymers, P0-Cu and P100-Cu. We also report the details of the preparation of P50-Cu, as an example of the copolymers synthesis; the procedure is the same for the other copolymers of the series except that, according to the desired composition, a different relative amount of rigid and flexible monomers was used.

### Synthesis of 2,5-Dihydroxyterephthaldehyde

2,5-Dimethoxyterephthaldehyde (5.00 g, 22.1 mmol) were refluxed in a solution composed of 48% HBr<sub>(aq)</sub> (200 mL) and glacial acetic acid (250 mL). After 20 h, the system was cooled to room temperature and poured in 400 mL of water. A precipitate formed, that was collected by suction filtration and purified by means of Soxhlet extraction with benzene. Upon cooling, the desired product crystallized in benzene and was then collected as gold crystals by filtration. Yield: 59%. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.25 (d, 2H,  $J$  = 4.0 Hz), 9.96 (s, 1H), 10.23 (s, 1H).

### Synthesis of P100-Cu

2,5-Dihydroxyterephthaldehyde (0.300 g, 1.80 mmol) was solved upon heating in ethanol (30 mL); to this solution, undecylamine (0.308 mg, 1.80 mmol) and 3-butoxypropylamine (0.236 g, 1.80 mmol) were added. The solution turned from yellow to orange. After 10 min at gentle boiling, an ethanol solution of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.396 g in 20 mL of solvent, 10% excess) was poured in this solution, followed by the addition of an ethanol solution of NaCH<sub>3</sub>COO (0.400 mg in 20 mL of 95% Ethanol). A dark precipitate

formed and the suspension was kept boiling for 5 min. Then the precipitate was collected by suction filtration, solved in chloroform (50 mL) and poured dropwise in 95% ethanol (150 mL) containing 0.200 g of sodium acetate. The formed solid was collected by suction filtration and washed twice with 50 mL of boiling ethanol; 0.738 g of a violet powder were recovered. Yield: 83%. IR (KBr, cm<sup>-1</sup>): 2922 (aromatic C—H stretching), 2852 (aliphatic C—H stretching), and 1610 (C=N stretching).

### Synthesis of P0-Cu

P12-8N (0.480 g, 0.53 mmol) was solved upon heating in 30 mL of ethanol. After 10 min at gentle boiling, an ethanol solution of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.116 g in 10 mL of solvent, 10% excess) was poured in this solution, followed by the addition of an ethanol solution of NaCH<sub>3</sub>COO (0.150 mg in 10 mL of 95% Ethanol). A light green precipitate formed and the suspension was kept boiling for 5 min. Then the precipitate was collected by suction filtration, solved in 50 mL of chloroform, and poured dropwise in 95% ethanol (150 mL) containing 0.200 g of sodium acetate. The formed solid was collected by suction filtration and washed twice with 50 mL of boiling ethanol; 0.399 g of a fibrous light green material were recovered. Yield: 78%. IR (KBr, cm<sup>-1</sup>): 2925 (aromatic C—H stretching), 2852 (aliphatic C—H stretching), 1722 (C=O stretching), 1619 (C=N stretching), and 1255 (esteric C—O stretching).

### Synthesis of P50-Cu

2,5-Dihydroxyterephthaldehyde (0.091 g, 0.55 mmol) was solved upon heating in ethanol (20 mL); to this solution, undecylamine (0.094 mg, 0.55 mmol) and 3-butoxypropylamine (0.072 g, 0.55 mmol) were added. This solution turned from yellow to orange and was then poured in a boiling ethanol solution of P12-8N (0.498 g, 0.55 mmol, in 20 mL of ethanol). After 10 min at gentle boiling, an ethanol solution of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.242 g in 10 mL of solvent, 10% excess) was poured in the first one, followed by the addition of an ethanol solution of NaCH<sub>3</sub>COO (0.300 mg in 10 mL of 95% Ethanol). A violet precipitate formed and the suspension was kept boiling for 5 min. Then the precipitate was collected by suction filtration, solved in 50 mL of chloroform, and poured dropwise in 95% ethanol (150 mL) containing 0.200 g of sodium acetate. The formed solid was collected by suction filtration and washed twice with 50 mL of boiling ethanol; 0.337 g of a violet material were recovered. Yield: 84%. IR (KBr, cm<sup>-1</sup>): 2923 (aromatic C—H stretching), 2852 (aliphatic C—H stretching), 1729 (C=O stretching), 1606 (C=N stretching), and 1254 (esteric C—O stretching).

### Chemical Physical Characterization

All compounds and polymers were characterized by standard techniques. DSC analyses were performed in dry ultrapure nitrogen flow using a DSC7 PerkinElmer apparatus at a scan rate of 10 K/min; DSC temperature calibration was made using a Fluka indium sample having 99.999% purity.

X-ray diffraction analysis was carried out by the photographic method on a flat film camera, using CuK $\alpha$  Ni-filtered

radiation. Phase transitions were observed with a Zeiss Axio-scope polarizing microscope equipped with a Mettler micro-furnace and an FP5 Mettler controller. The thermal stability of the polymers was monitored by thermogravimetric analysis (TGA) using a TA5000 apparatus at a  $20\text{ }^{\circ}\text{C min}^{-1}$  scan rate in air atmosphere.

FTIR spectra were recorded with a JASCO FT/IR 430 spectrometer on KBr pellets; solution and thin film UV-Vis spectra were recorded on a spectrophotometer Jasco F-530 (scan rate  $200\text{ nm min}^{-1}$ ). Thin film of polymers were prepared by spin coating of a chloroform solution ( $10\text{ mg mL}^{-1}$ ) on quartz substrates, using a Laurell WS-650Mz-23NPP spin processor.

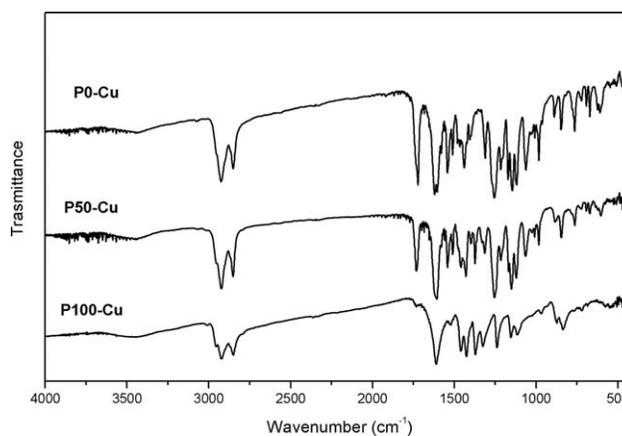
The characterization of the “apparent” molecular weight distribution (MWD) of samples was performed by using a multi-angle laser light scattering (MALS) absolute detector on-line to a size exclusion chromatographic (SEC) system. The SEC system consisted of an Alliance 2695 separation module from Waters equipped with two on-line detectors: a MALS Dawn DSP-F photometer from Wyatt Technology and a 2414 differential refractometer from Waters used as concentration detector. Specifically, we define the obtained MWD “apparent” because the absolute MALS detector measure the true molecular weight ( $M_w$ ) of the aggregate structures not of the single separated molecules. The experimental methodology for a reliable use of the SEC-MALS system has been described in literature.<sup>40,41</sup> The SEC-MALS experimental conditions were the following: 50% Chloroform + 50% Dichloromethane as mobile phase, 2 Styragel columns (500 and 100 Å) from Waters,  $35\text{ }^{\circ}\text{C}$  of temperature,  $0.6\text{ mL min}^{-1}$  of flow rate,  $100\text{ }\mu\text{L}$  of injection volume, about  $2\text{ mg mL}^{-1}$  of sample concentration.

The inherent viscosities of the polymer solutions were measured in chloroform at  $25.0\text{ }^{\circ}\text{C}$  at a concentration of  $0.500\text{ g dL}^{-1}$  using an Ubbelohde viscometer.  $^1\text{H NMR}$  spectra were recorded on a Varian Gemini XL 200-MHz apparatus.

## RESULTS AND DISCUSSION

The synthesized polymers and copolymers are constituted by two different repeating units, P12-8N and DHTI, linked together through copper(II) metal centers, as schematically sketched in Chart 1. P12-8NCu was previously prepared by direct condensation of bis[N-[2,4-dihydroxyphenyl]-octylimino copper (II) with 4,4'-(dodecane-1,12-diylbis(oxy))dibenzoyl-chloride.<sup>36</sup> The so obtained polymer can be depolymerized in a  $\text{HCl}_{\text{aq}}/\text{CHCl}_3$  mixture to give P8-12N with high purity.<sup>31</sup> In the present work, the so obtained highly pure P8-12N was used for the synthesis of P0-Cu (and of the other copolymers) by reaction with  $\text{Cu}(\text{OAc})_2$  as described in Experimental Section.

DHTI was the monomer affording the rigid repeating unit in copolymers and has been formed *in situ* by adding two different amines, 1-undecylamine and 3-butoxypropylamine, in a 1:1 molar ratio, to 2,5-dihydroxyterephthaldehyde. The latter



**FIGURE 1** FTIR spectra of P0-Cu, P50-Cu, and P100-Cu; the spectra are vertically displaced to allow a better comparison.

was obtained from demethylation reaction of 2,5-dimethoxyterephthaldehyde; DHTI was not isolated and directly used for the next polymerization reaction step. The use of two different amines was thought to increase the solubility of the resulting polymers. The general procedure for polymers preparation is reported in Chart 2: an ethanol solution of DHTI prepared *in situ* was mixed with an ethanol solution of P12-8N and kept at gentle boiling; then copper acetate in ethanol was added, followed by sodium acetate.

The polymers so obtained immediately precipitated in the reaction media and were then filtered and purified by dissolving in chloroform and re-precipitating in ethanol twice. All the obtained polymers were soluble in chlorinated solvents.

FTIR analysis on KBr pellets were recorded on all the synthesized metallo polymers. In Figure 1, the FTIR spectra of the two homopolymers P0-Cu and P100-Cu, along with that of P50-Cu, are reported. In all the presented spectra, it is possible to identify the signals distinguishing the C–H stretching (at around  $2920$  and  $2850\text{ cm}^{-1}$ ) and the imine C=N stretching (at around  $1610\text{ cm}^{-1}$ ); in the spectra of P0-Cu and P50-Cu, moreover, other two significant signals are observed: in particular, carbonyl stretching at  $1720\text{ cm}^{-1}$  and ester C–O stretching at  $1255\text{ cm}^{-1}$ , associate to the flexible repeating units deriving from P12-8N, appear, while they are absent in the spectra of the fully rigid P100-Cu.

To assess their purity, the prepared polymers were investigated by means of TGA: the samples were heated in air flow up to a temperature of  $700\text{ }^{\circ}\text{C}$ , at which the polymers are transformed in copper (II) oxide.

As shown in Table 1, the measured residues are in good accord with the expected theoretical values, thus confirming the validity of the used synthetic methodology. The thermogravimetric graphs for all polymers are reported in the Supporting Information (Fig. S1).

The thermal stability of the prepared polymers depends upon composition and in particular increases with the increase of

**TABLE 1** Thermal and Molecular Properties of the Synthesized Polymers

Polymer	%CuO calc.	%CuO exp. <sup>a</sup>	$T_d$ (°C) <sup>b</sup>	$\eta_{inh}$ (dL g <sup>-1</sup> ) <sup>c</sup>	$M_w$ (kg mol <sup>-1</sup> ) <sup>d</sup>	$M_w/M_n$ <sup>d</sup>	$T_g$ (°C)	$T_m$ (°C) <sup>e</sup>	$T_i$ (°C) <sup>e</sup>	$T_r$ (°C) <sup>e</sup>
P0-Cu	8.2%	8.2%	300	0.43	55.7	2.3	48	167	202.0	119
P20-Cu	9.1%	9.3%	300	0.43	64.3	2.4	47	–	191.0	–
P30-Cu	9.6%	9.9%	300	0.48	87.4	2.4	47	–	188.8	–
P40-Cu	10.2%	10.4%	289	0.51	106.7	2.0	43	–	182.6	198
P50-Cu	10.9%	11.2%	281	0.57	176.4	3.0	–	–	–	210
P60-Cu	11.6%	11.8%	266	0.59	300.2	3.1	–	–	–	218
P75-Cu	13.0%	12.8%	252	0.72	294.3	3.1	–	–	–	225
P87-Cu	14.3%	14.1%	252	0.84	308.9	3.1	–	–	–	225
P100-Cu	16.1%	16.0%	252	1.03	521.0	2.3	–	–	–	250 <sup>f</sup>
P'100-Cu <sup>g</sup>	18.8%	18.5%	260	–	–	–	–	–	–	–

<sup>a</sup> TGA run was performed in air atmosphere at a scan rate of 10 K min<sup>-1</sup>.

<sup>b</sup> Determined as the temperature corresponding to a weight loss of 5%.

<sup>c</sup> Inherent viscosity, determined by a Ubbelohde viscosimeter at 25 °C in chloroform solution at a concentration of 0.500 g/dL.

<sup>d</sup> Measured by SEC-MALS.

<sup>e</sup> Determined from DSC experiment performed in nitrogen atmosphere at a 10 K min<sup>-1</sup> scan rate.

<sup>f</sup> For P100-Cu, the recrystallization process overlaps in the last part with polymer decomposition.

<sup>g</sup> P'100 was synthesized with the same synthetic procedure used for P100-Cu, with the difference that 1-octylamine and 2-propyloxyethylamine were used as amines in the formation of the diimine.

flexible units molar fraction. It ranges from 252 °C, decomposition temperature of P100-Cu, P87-Cu, and P75-Cu, to 300 °C, for P0-Cu, P20-Cu, and P30-Cu (see Table 1).

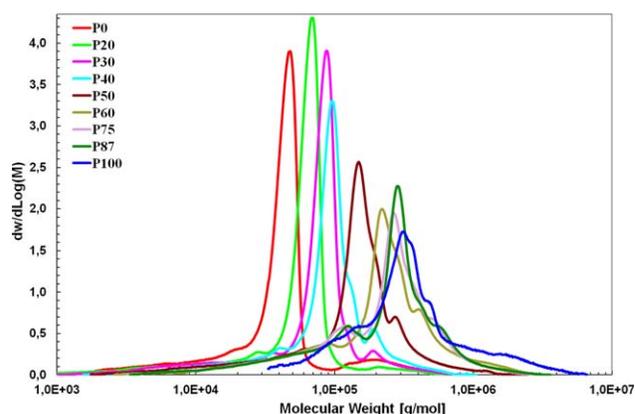
The apparent whole MWD, the weight average of the  $M_w$  and the polydispersity index ( $M_w/M_n$  where  $M_n$  denotes the numeric average) of the prepared polymers and copolymers were determined by using the absolute on-line SEC-MALS method. The inherent viscosity were measured off-line through a Ubbelohde viscometer at 25 °C of temperature in chloroform solvent. Very interestingly, the  $M_w$  and inherent viscosity values reported in Table 1 are consistent between them. Figure 2 shows the comparison of the differential whole MWD of all prepared polymers and copolymers.

The analysis of the molecular results (see Table 1 and Fig. 2) clearly shows that, on average, a rise of the apparent  $M_w$  and of inherent viscosity occurs as the molar percentage of rigid units in the copolymeric systems increases. This behavior is not surprising: in P100-Cu, the polymer backbone conformation is highly planar because of the coordination geometry of the ligand DHTI on metal copper centers. In copolymers characterized by large molar fraction of rigid units, it can be expected that large segments of polymer backbone adopt a highly planar conformation thus favoring aggregation phenomena that result eventually in a inherent viscosity and apparent  $M_w$  increase.

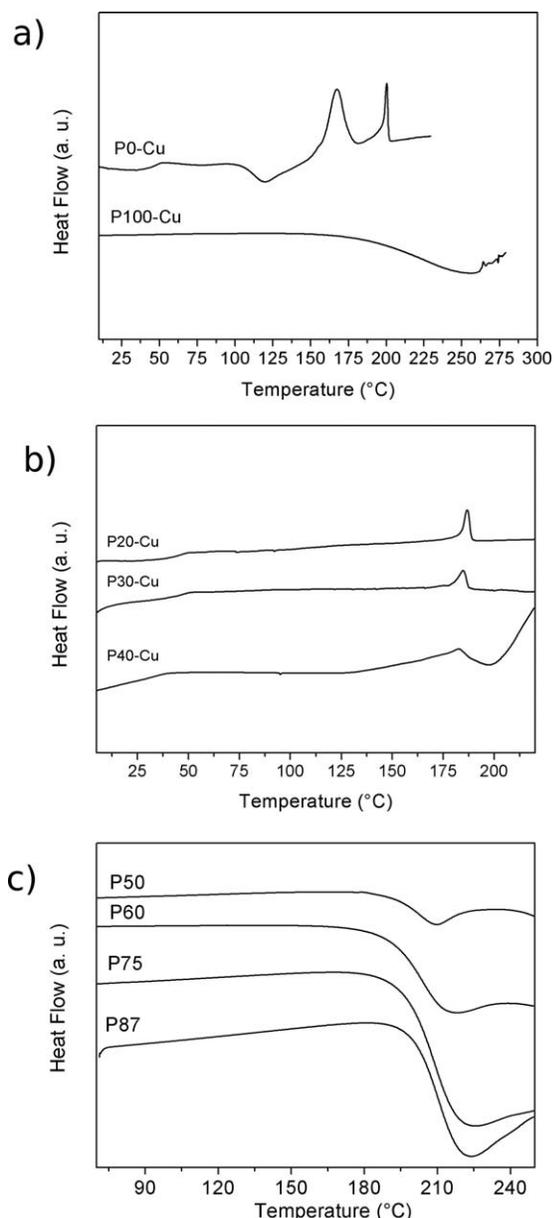
The thermal behavior of the synthesized polymers was checked by DSC analysis and the results are summarized in Table 1. The DSC thermograms of the homopolymers P0-Cu and P100-Cu are reported in Figure 3(a). Polymer P0-Cu shows a glass transition temperature ( $T_g$ ) value of 48 °C. As already known from the literature, P0-Cu gives rise to a

nematic liquid crystalline phase upon melting. Two endothermic peaks are in fact observed in the DSC trace of P0-Cu, one related to the melting of the polymer ( $T_m = 167$  °C) and the other to the isotropization of the liquid crystal phase ( $T_i = 200$  °C). An exothermic process occurs at about 120 °C, assignable to crystallization of amorphous zones of the polymer.

The phase behavior of P0-Cu was moreover observed through optical microscope analysis carried out in temperature and confirmed the interpretation given to DSC results. Upon melting at 167 °C P0-Cu afforded a nematic liquid crystal phase characterized by the typical Schlieren textures, which were preserved when the polymer was rapidly cooled down to room temperature; this liquid crystalline phase is



**FIGURE 2** Comparison of differential MWD of polymers and copolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**FIGURE 3** DSC traces for all the synthesized polymers.

stable up to  $\sim 200$  °C above which the melt sample turns isotropic. By shearing the liquid crystal phase, a well-defined band structure was produced.

No glass transition or melting is instead observed for the rigid P100-Cu. The thermogram of P100-Cu, shown in Figure 3(a), is characterized by an exothermic phenomenon, associable to the crystallization of amorphous phase of the polymer, having its onset around 200 °C and reaching its maximum at around 250 °C; considering the fact that this polymer has a  $T_d$  of 255 °C, as determined by TGA, it can be assumed the recrystallization process overlaps, in the last part, with the decomposition process of the polymer. When analyzed at the optical microscope, no phase transitions could be observed for P100-Cu; a concentrated chloroform

solution of this polymer afforded instead a lyotropic mesophase as deduced from the observation of shear bands on films obtained from shearing and fast evaporation of the solvent.

For what concerns the copolymers series, depending on their composition, they feature a behavior typical of P0-Cu or P100-Cu. Up to a rigid units percentage of 40%, copolymers show a glass transition occurring at temperatures similar to the  $T_g$  of P0-Cu. We assume the presence of long sequences of flexible units in these copolymers that gives rise to thermal behavior similar to that of the fully flexible homopolymer P0-Cu. This assumption is also validated by the observation of an endothermic peak at around 190 °C in the DSC analysis [see Fig. 3(b)], corresponding roughly to the isotropization temperature of P0-Cu: hence, the long sequences of flexible units in P20-Cu, P30-Cu, and P40-Cu do not crystallize but adopt the liquid crystalline arrangement typical of P0-Cu and isotropize at 190 °C.

The thermal behavior of copolymers with lower content of rigid units was then observed at the optical microscope. P20-Cu was completely fluid at 170 °C and shear bands, typical of a nematic phase, could be induced (see Fig. 4). Beyond the isotropization temperature determined from DSC, all the sample became isotropic. Similar behavior was shown by P30-Cu even if, after the isotropization temperature, a slightly anisotropic field was observed. For P40-Cu, it was not possible to induce shear bands and largely anisotropic zones were observed above the  $T_i$ .

As far as the copolymers with higher content of rigid units are concerned, also in this case, it is possible to interpret their thermal behavior of these copolymers by assuming the presence of long sequences of all flexible units and of all rigid units.

The glass transition associable to the flexible units, is no more observed, probably because the rigid units domains act as physical crosslinks that hinder the chain mobility: we



**FIGURE 4** Optical microscope photograph for P20-Cu: shear bands induced on the melt polymers and preserved at room temperature.

**TABLE 2** d Spacing of the Synthesized Polymers Determined by XRD Analysis

	$2\theta/d_1$ (Å)	$2\theta/d_2$ (Å)	$2\theta/d_3$ (Å)	$2\theta/d_4$ (Å)	$2\theta/d_5$ (Å)	$2\theta/d_6$ (Å)
P0-Cu <sup>a</sup>	4.79/18.46 <sup>b</sup>	–	–	20.65/4.30 <sup>c</sup>	–	–
P20-Cu <sup>a</sup>	4.79/20.23 <sup>b</sup>	–	–	20.29/4.39 <sup>c</sup>	–	–
P30-Cu <sup>a</sup>	4.31/20.50 <sup>b</sup>	9.04/9.78 <sup>d</sup>	13.20/6.71 <sup>d</sup>	20.65/4.30 <sup>c</sup>	–	–
P40-Cu <sup>a</sup>	4.31/20.50 <sup>b</sup>	9.04/9.78 <sup>d</sup>	13.19/6.70 <sup>d</sup>	20.65/4.30 <sup>c</sup>	23.93/3.72 <sup>d</sup>	–
P50-Cu <sup>a</sup>	4.31/20.50	8.57/10.31 <sup>d</sup>	13.20/6.71 <sup>d</sup>	20.23/4.39 <sup>c</sup>	24.33/3.66	–
P60-Cu <sup>a</sup>	4.31/20.50	8.57/10.31 <sup>d</sup>	12.97/6.82 <sup>d</sup>	18.74/4.73 <sup>d</sup>	23.93/3.72	–
P75-Cu <sup>e</sup>	4.31/20.50	8.57/10.31	12.51/7.07	18.52/4.79	23.73/3.75	32.13/2.78
P87-Cu <sup>e</sup>	4.31/20.50	8.57/10.31	12.51/7.07	18.52/4.79	23.93/3.72	32.13/2.78
P100-Cu <sup>e</sup>	4.31/20.50	8.57/10.31	12.97/6.82	18.73/4.73	23.53/3.78	32.13/2.78
P'100-Cu <sup>e</sup>	5.26/16.79	10.21/8.66	13.42/6.59	18.52/4.79	23.53/3.78	32.13/2.78

<sup>a</sup> As a fiber, annealed at 100 °C for 1 h.<sup>b</sup> Four spots on the first layer.<sup>c</sup> Strongly equatorially polarized halo.<sup>d</sup> Strongly polarized line.<sup>e</sup> Cold pressed powder, annealed at 220 °C for 1 h.

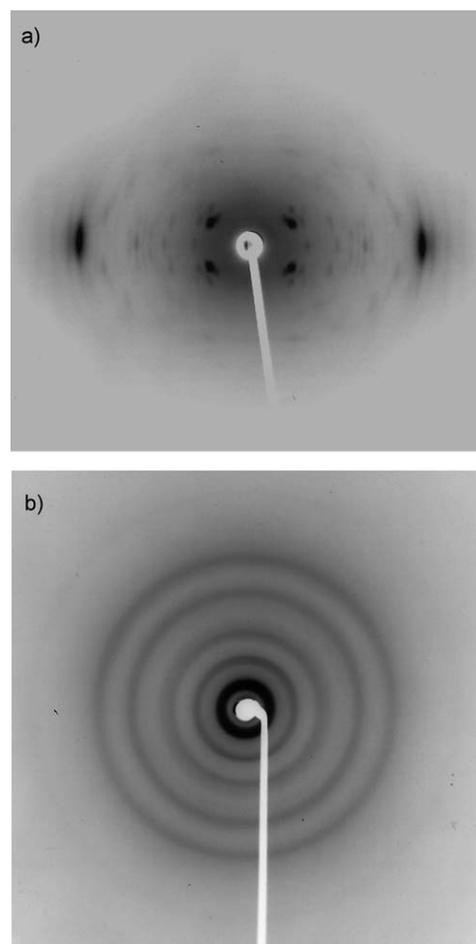
observed instead the exothermic phenomenon typical of P100-Cu and associable to recrystallization of rigid units rich amorphous zones (this phenomenon was actually already observed for P40-Cu, just after the isotropization) and it is shown in Figure 3(c). The recrystallization temperature depends upon the composition and is lower for lower content of rigid units. This is expected, because copolymers with higher content of flexible units experience a higher mobility at a given temperature and thus structuration processes are favored.

The simultaneous DSC-optical microscope analysis suggests that the synthesized copolymers have a partial block character in their constitution: phase behavior typical of P0-Cu are in fact observed for copolymers containing higher amount of flexible units (up to 40%). This constitutional feature could arise from the different reactivity of the two bis-imines used in the synthesis: in P12-8N the two hydroxylimine chelating moieties sit well separated from each other while in DHTI these chelating functionalities are on the same ring resulting in a totally different electronic environment giving rise to a different reactivity.

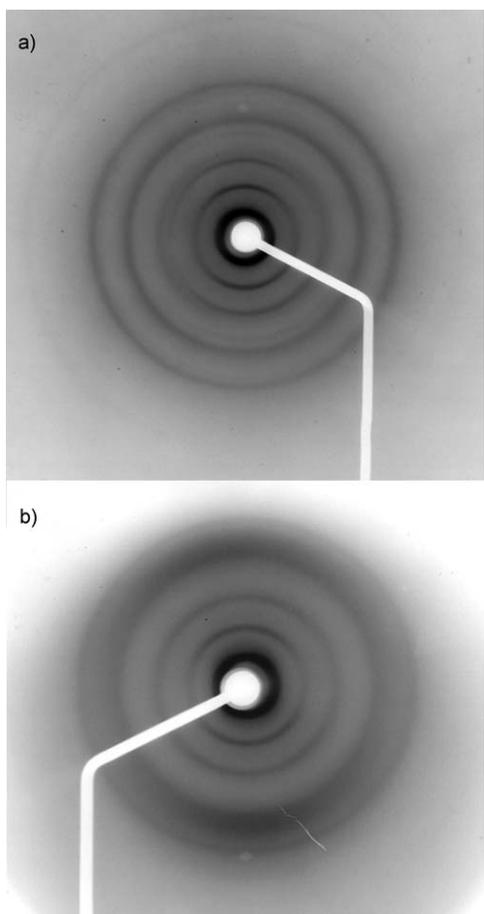
XRD spectra of the synthesized polymers were recorded to better investigate their structural features; in Table 2 these features are summarized. In Figure 5, the diffraction spectrum of a fiber of P0-Cu and of P100-Cu are reported. The spectrum in Figure 5(a) is referred to an annealed fiber of P0-Cu. The four spots observed in the low angle region of the spectrum ( $2\theta = 4.79$  Å) are indicative of the cybotactic nature of this phase. The diffraction images of an annealed P100-Cu sample, reported in Figure 5(b), features six different reflections, corresponding to interplanar spacings of 20.50 Å ( $d_1$ ), 10.31 Å ( $d_2$ ), 6.82 Å ( $d_3$ ), 4.73 Å ( $d_4$ ), 3.78 Å ( $d_5$ ), and 2.78 Å ( $d_6$ ), the latter being very weak. Following the experimental evidences arisen from the DSC analysis [see Fig. 3(a)], the chosen annealing temperature was 220 °C.

A ribbon like crystal structure can be assumed for this polymer. The reflection occurring at interplanar spacing of

20.5 Å,  $d_1$ , can be associated to the aliphatic side chain of the polymer backbone (and hence, to the width of the ribbon), admitting their intercalation or a tilting respect to the



**FIGURE 5** (a) X-rays diffraction spectrum of P0-Cu fiber annealed 1 h at 100 °C; (b) X-rays diffraction spectra of P100-Cu cold pressed and annealed 1 h at 220 °C.



**FIGURE 6** X-rays diffraction spectra of: (a) P87-Cu cold pressed and annealed at 220 °C 1 h; (b) P50-Cu, in fiber shape, annealed at 100 °C.

backbone direction, or both these effects. The interplanar spacings  $d_2$  and  $d_3$  can be considered as second and third order reflections of  $d_1$ . The fourth reflection ( $d_4 = 4.73 \text{ \AA}$ ), for its position and intensity, should indicate a tight packing of the aliphatic side chain. The fifth reflection ( $d_5 = 3.78 \text{ \AA}$ ) can be associated to  $\pi$ - $\pi$  stacking of the macromolecules backbone, characterized by high planarity because of the square planar coordination of the rigid aromatic groups around the metal center. The sixth reflection cannot find an easy assignment.

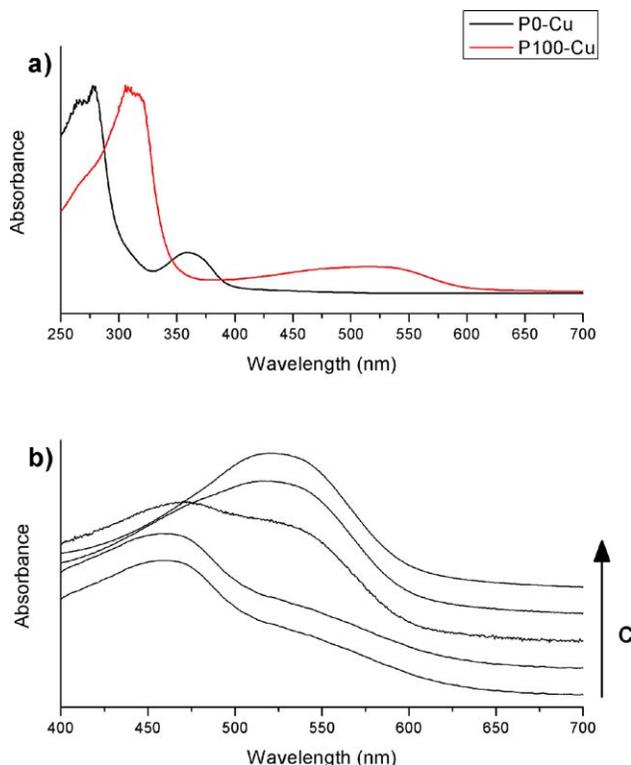
To obtain a further confirmation of the proposed model, the homopolymer P'100-Cu, characterized by shorter aliphatic side chain respect to P100-Cu, was synthesized (in particular, in the synthesis octylamine and 3-ethoxypropylamine were used instead of undecylamine and 3-butoxypropylamine). As expected, for P'100-Cu the spacing corresponding to ribbon width,  $16.8 \text{ \AA}$ , was lower than that found for P100-Cu ( $20.8 \text{ \AA}$ , see Table 2).

As can be seen from Table 2, XRD spectra of copolymers present close similarity to P100-Cu spectrum when content of the rigid units is  $\geq 30\%$ ; all copolymers from P30-Cu to P87-Cu feature in fact the five characteristic reflections of P100-Cu. In Figure 6, the spectra of P87-Cu and P50-Cu are

reported. Both the spectra present a slight equatorial polarization of the second and third reflections (hence confirming that these reflections belong to the same family of planes, being the second and third order reflection of that at  $20.5 \text{ \AA}$ ). The main difference between the two spectra is that in P50-Cu spectrum the reflection corresponding to  $d_3$  is somehow broader because of the contribution of the dodecamethylene chain in the polymer backbone coming from 50% of flexible units. With higher content in flexible units, this signal becomes even broader and turns actually in to a halo.

XRD analysis, consistently with the results of the calorimetric analysis, suggests that large blocks made up of rigid units characterize the series of copolymers, affording eventually structural features typical of P100-Cu. The optical properties of all the synthesized polymers were investigated through UV-Vis spectroscopic analysis, both in solution and in film phase. In Figure 7, the spectra of the homopolymers in chloroform solution are reported. P0-Cu is characterized by two main absorption regions, centered at 278 and at 360 nm, respectively. The first could be associated to the aromatic part of the polymer while the second involves ligands-metal interaction (LMCT band).

For what concerns P100-Cu, the spectrum is once again characterized by two main absorptions, red shifted as compared to P0-Cu [see Fig. 7(a)]. The first absorption peak is centered at around 311 nm while the second absorption



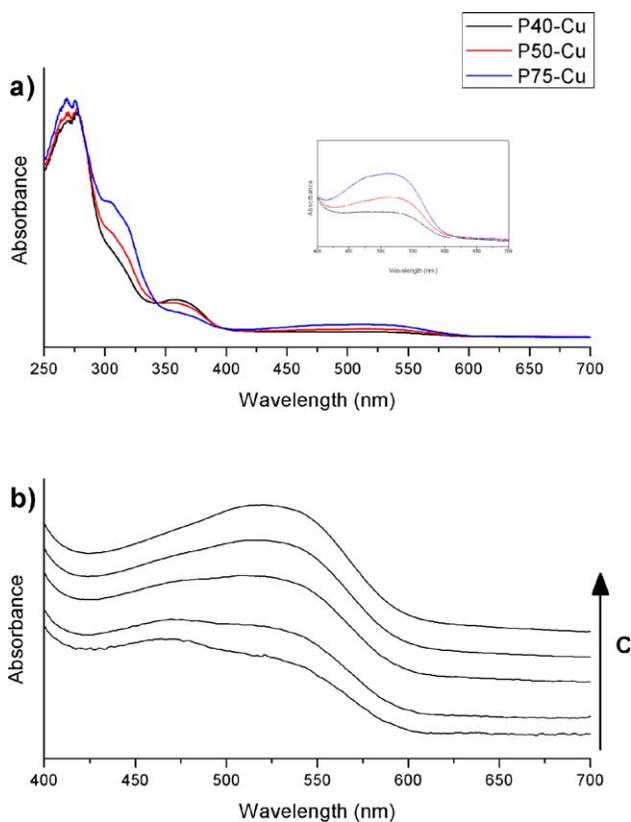
**FIGURE 7** UV-Vis spectra in chloroform solution of P0-Cu and P100-Cu (a); concentration dependence of LMCT band position and shape for P100-Cu (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

band position is strongly related to the solution concentration. In particular, as shown in Figure 7(b), as the concentration increases, the maximum of this second absorption shifts from  $\sim 479$  to  $530$  nm. This phenomenon is related to the establishing of aggregates that, because of strong  $\pi$ - $\pi$  interactions between the highly planar strands of polymers, occurs even in very diluted solution as already observed in the previously discussed SEC experiments (see Table 1).

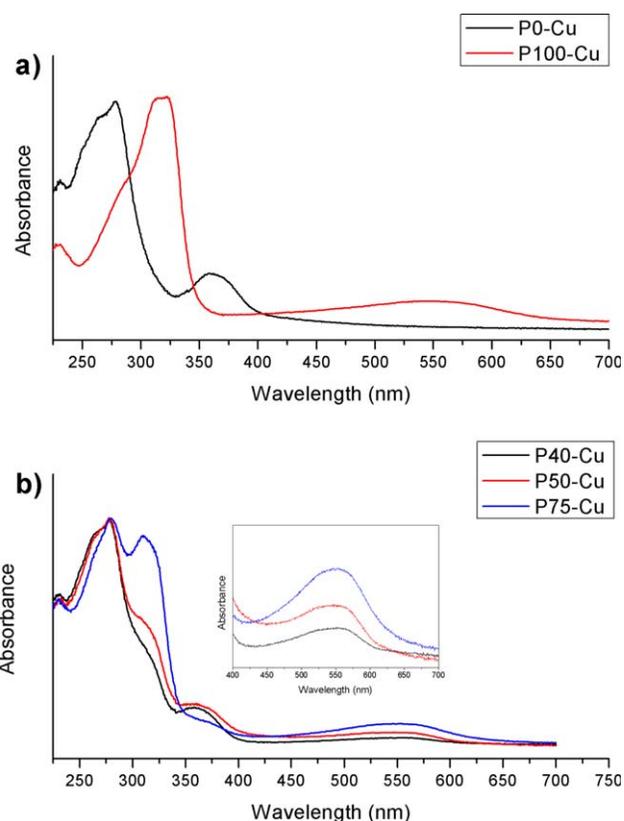
In Figure 8, the spectra of some of the synthesized copolymers are shown: in these spectra, the signals typical of the parent homopolymers to which they are related are clearly visible, in ratios depending upon the composition of the copolymers.

Also for copolymers rich in rigid units, a strong dependence of the absorption involving metal-ligand interaction upon concentration was observed, as for P100-Cu. In Figure 7(b), the spectrum of P50-Cu, at different solution concentrations, is presented. Once again, this behavior is consistent with the results of SEC experiments (see Table 1).

All the prepared materials were moreover processed as thin film by spin coating of a chloroform solution. The UV-Vis spectra of these films are presented in Figure 9. The optical behavior of P0-Cu film closely resembles that of P0 in



**FIGURE 8** UV-Vis spectra in chloroform solution of P40-Cu, P50-Cu, and P75-Cu (a); concentration dependence of LMCT band position and shape for P50-Cu (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**FIGURE 9** Normalized UV-Vis spectra of thin film of (a) P0-Cu and P100-Cu; (b) P40-Cu, P50-Cu, and P75-Cu. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

solution; for what concerns instead P100-Cu, the film spectrum is similar to that of a concentrated solution with the difference that the lower energy electronic transition is largely red shifted ( $\sim 30$  nm). This red shift is clearly related to the film structuration, which results in a well ordered stacking of the planar macromolecular strands. Also in film phase, copolymers present the same peaks shown by the related homopolymers: it is worth noting that the presence of an absorption band at  $\sim 550$  nm in copolymer films is indicative of long sequences of rigid units that can pack together leading to absorption in the same range of the P100-Cu film. The copolymer film optical behavior is in line with the previous analysis that indicate a partial block arrangement of copolymer constitution.

## CONCLUSIONS

In conclusion, we prepared a novel set of metallopolymers in which repeating units are connected through metal centers. The repeating units were endowed with two salicylaldiminate end groups that work as bischelating groups in the polymer assembling. Two kinds of repeating units were used: one flexible, in which the chelating groups were separated by a long and flexible chain and the other rigid, where the chelating groups sit on the same phenyl ring. Several copolymers with rigid units contents in the range 0–100% were synthesized and characterized. All the polymers show a

good processability and solubility in chlorinated solvents. A combined molecular, thermal, structural and optical analysis revealed a peculiar and very interesting feature for the synthesized copolymers: a partial block character in their constitution seems to emerge, with long sequences of rigid units alternating to sequences of flexible units. Copolymers with content in rigid units  $\geq$  than 50% presented in fact XRD spectra very similar to that of the polymer P100-Cu, based exclusively on rigid units. This behavior has been associated to the existence of long sequences of rigid repeating units in these copolymers that can interact forming crystalline domains. The analysis of the XRD reflections is consistent with a ribbon-like arrangement in which highly planar strands of polymer stack thanks to  $\pi$ - $\pi$  interactions. UV-Vis absorption measurement in solid phase showed for the more rigid copolymers optical features common to P100-Cu: once again, this occurrence has been interpreted by assuming the existence of long sequences of rigid units and to their packing. The synthesized class of copolymers can be thus considered extremely appealing: the possibility of enhancing the processability of P100-Cu, by inserting in its main chain flexible units, while preserving its ability of giving highly planar and well structured packing, make these materials interesting for applications in different field, like for instance, organic electronics and spintronics.

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