

Poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate): Influence of Stereochemistry of 1,4-Cyclohexylene Units on the Thermal Properties

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ABSTRACT: A series of poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate) (PCCD) samples, characterized by different *cis/trans* ratio of the 1,4-cyclohexanedicarbonyl unit, have been synthesized and analyzed by thermogravimetry (TGA), calorimetry (DSC), and X-ray diffraction (WAXD). The thermal stability results are good and are not affected by the stereochemistry of the 1,4-cyclohexylene units. On the other hand, the thermal transitions are notably influenced by the *cis/trans* content. With the increment of the *trans* content the polymer changes from completely amorphous to semicrystalline material. T_g , T_m , and crystallinity increase. These results suggest that the *trans* configuration induces a better chain packing and higher symmetry, improving the crystallizability of the samples. The effect of the molecular structure on the thermal properties is analyzed by using a statistical approach. From the effective correlations found between stereochemistry of the C₆ rings and transition temperatures it is possible to extrapolate that the configuration of 1,4-cyclohexylene ring deriving from 1,4-cyclohexanedicarboxylic acid or dimethyl 1,4-cyclohexanedicarboxylate results to be the main element responsible for the thermal properties. This is due to the high rigidity of the 1,4-cyclohexanedicarbonyl unit with respect to 1,4-cyclohexanedimethylenedioxy unit, deriving from the diol. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 46: 619–630, 2008

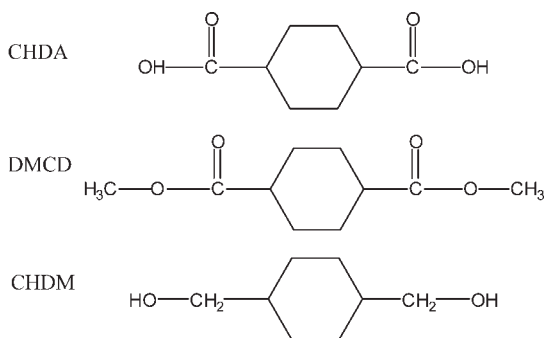
Keywords: aliphatic polyester; *cis-trans* isomerization; isomer/isomerization; polyesters; thermal characterization; thermal properties

INTRODUCTION

Poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate)s (PCCD) are completely aliphatic polyesters, characterized by good thermal and mechanical properties, and resistance to

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Scheme 1. Chemical structure of monomers used to synthesize PCCD.

weather, heat, light, and humidity. They are materials with a large potential field of applications, especially after the recent improvements in their preparation procedure.^{1–3} The synthesis starts from 1,4-cyclohexanedicarboxylic acid (CHDA) or dimethyl 1,4-cyclohexanedicarboxylate (DMCD) and 1,4-cyclohexanedimethanol (CHDM) (see Scheme 1), which are monomers characterized by the presence of 1,4-cyclohexylene moieties. The 1,4-cyclohexylene rings adopt a chair conformation which produces considerable rigidity in the polymer backbone. Indeed, glass transition (T_g) and melting (T_m) temperatures of polymers containing 1,4-cyclohexylene moieties are found to be higher with respect to those of the corresponding aromatic polymers.^{4,5} Therefore, PCCD polymers are expected to have good thermal properties, that is, high T_g and T_m values.

Furthermore, it is noteworthy that the 1,4-cyclohexylene rings can exist in two isomeric forms, *cis* and *trans*. Particular attention has been paid in literature to the thermal *cis/trans* isomerization of the 1,4-cyclohexylene rings incorporated into the backbone of polyamides and polyesters,^{6–8} because it appears that the *cis/trans* ratio present depends on the chemical-physical properties of the polymers. For example, crystalline or liquid-crystalline phases are characterized by the presence of the *trans* isomer, whereas in isotropic phases a thermodynamically stable *cis/trans* ratio of 34/66 is found.^{6,9–11} Moreover, a considerable influence of the *cis/trans* ratio on thermal behavior has also been observed.^{12–18}

In this work, a series of PCCD samples with different *cis/trans* isomeric ratio have been prepared. The samples can be divided into two families: (i) samples obtained from CHDM containing 66% *trans* isomer and CHDA with

various *trans* isomer content; (ii) samples deriving from CHDM containing 66% *trans* isomer and DMCD with various *trans* isomer content.

The *cis/trans* isomeric ratio equal to 34/66 is commercially available for CHDM and does not vary during the synthesis and characterization, because CHDM is unable to isomerize.^{1,2} On the other hand, the 1,4-cyclohexylene rings in CHDA and DMCD can isomerize, for example, during the polymer synthesis or during thermal treatments carried out at temperatures higher than 260 °C and for longer than 1 h. Therefore, the initial *cis/trans* ratio of the cycloaliphatic units in the CHDA or DMCD monomers can notably vary in the final PCCD polymers. Thus, it appears very important to analyze the corresponding possible changes in the thermal properties of the materials, and to find a relationship between *cis/trans* ratio and properties.

For this reason, we have prepared PCCD polymers with *trans* content of the C₆ rings derived from CHDA and DMCD varying from about 25 to 100%, and we have managed to prevent the *cis/trans* isomerization of these cycloaliphatic units under the conditions used in PCCD characterization. The final aim of this work is to try to distinguish the role of the configuration of the 1,4-cyclohexylene ring deriving from CHDA or DMCD from that of the ring deriving from CHDM on the PCCD thermal properties.

As the characterization of the PCCD polymers presents a notably complexity, mainly from a structural point of view, in this article we report only the first results obtained by TGA, DSC, and WAXD analyses.

EXPERIMENTAL

Materials

The PCCDs were synthesized in our laboratories in a two-stage process, starting from CHDA or DMCD and CHDM, as described in literature.^{2,3} The monomers were purchased from Aldrich with a defined *cis/trans* ratio. The CHDM used is characterized by 66% of *trans* isomer content. CHDA is a sample containing 99% of *trans* isomer: during the synthesis this percentage notably decreases because the isomerization process is catalyzed by acids. For this reason, it is possible to obtain the PCCD polymers from CHDA with a lower degree of *trans* content with respect to the starting 99% *trans* content. Two commercial

Table 1. Description of the PCCD Samples: *trans* Isomer Percentage in the Polymers, Calculated on the Cyclohexylene Rings Derived from CHDM, CHDA, and DMCD; Molecular Weight and Molecular Weight Distribution

Sample	<i>trans</i> % in the Polymers ^a			M_w $\times 10^{-3}$ (g/mol) ^b	M_w/M_n (g/mol) ^b
	CHDM	CHDA	DMCD		
D66-A79	66	79	—	20.8	2.3
D66-A91	66	91	—	39.1	2.0
D66-E24	66	—	24	43.3	2.2
D66-E52	66	—	52	83.7	2.7
D66-E66	66	—	66	56.3	2.9
D66-E81	66	—	81	60.4	2.4
D66-E90	66	—	90	45.6	2.4
D66-E97	66	—	97	55.1	2.2

^a Calculated by ¹H NMR.^b Measured by GPC in CHCl₃.

DMCD samples have been used, characterized by 22 and 100% of *trans* isomer content, respectively. The different percentages of *trans* isomer in the C₆ rings of polymers have been obtained by starting of a convenient mechanical mixture of the two DMCD monomers. The PCCD synthesis has been carried out in the presence of titanium tetrabut-oxide (TBT) as catalyst.

Characterization

The ¹H NMR spectra were recorded at room temperature on samples dissolved in CDCl₃ using a Varian Mercury 400 spectrometer, the proton frequency being 400 MHz. In Table 1 the samples are coded as Dxx-A(or E)yy, where xx indicates the percentage of C₆ rings deriving from CHDM (D) in *trans* configuration, and yy the percentage of C₆ rings deriving from CHDA (A) or DMCD (E) in *trans* configuration. The *trans* percentages reported are calculated by ¹H NMR on the polymer by using the ratio of the signals centered at 2.3 (*trans* isomer) and 2.5 (*cis* isomer) ppm for the A or E units, and by using the ratio of the signals centered at 3.9 (*trans* isomer) and 4.0 (*cis* isomer) ppm for the D units. Molecular weights (expressed in equivalent polystyrene) were determined by gel permeation chromatography (GPC), using a Hewlett Packard Series 1100 liquid chromatography instrument equipped with a PL gel 5μ Mixed-C column. Chloroform was used as eluent, and a

calibration plot was constructed with polystyrene standards.

The thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA7 thermobalance under nitrogen atmosphere (gas flow 40 mL/min) at 10 °C/min heating rate from 40 to 900 °C. The temperature of the maximum degradation rate (T_D), corresponding to the maximum of the differential thermogravimetric curve, was calculated.

The calorimetric analysis was performed by means of a Perkin-Elmer DSC6, calibrated with high-purity standards at the heating rates used during the measurements. The measurements were performed under nitrogen flow. To cancel the previous thermal history, the samples were initially heated to 250 °C (260 °C for D66-E97), kept at this temperature for 1 min and then cooled to 10 °C at 20 °C/min. After this thermal treatment, the samples were analyzed by heating from 10 to 250 °C (260 °C for D66-E97) at 20 °C/min (2nd scan). During the cooling scan the crystallization temperature (T_{CC}) and the enthalpy of crystallization (ΔH_{CC}) were measured. During the 2nd scan the T_g , the T_m , and the enthalpy of fusion (ΔH_m) were measured. Other peculiar thermal treatments are described in the Results and Discussion part.

The wide-angle X-ray scattering (WAXD) data were collected with a X'PertPro diffractometer, equipped with a copper anode (K_α radiation, $\lambda = 1.5418$ Å). The data were collected in the 2θ range 5°–60° by means of a X'Celerator detector. *In situ* high-temperature X-ray diffraction was performed by an Anton Paar TTK450 camera.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

The PCCD samples are materials with high thermal stability. Under nitrogen flow the degradation process begins above 380–400 °C and occurs in a single step up to a complete weight loss, as shown in Figure 1. The temperatures of the maximum degradation rate (T_D), reported in Table 2, evidence that all the samples behave in a very similar way, independently of the configuration of the C₆ rings. This result excludes an influence of the *cis/trans* ratio of the 1,4-cyclohexylene units deriving from CHDA or DMCD on the PCCD thermal stability.

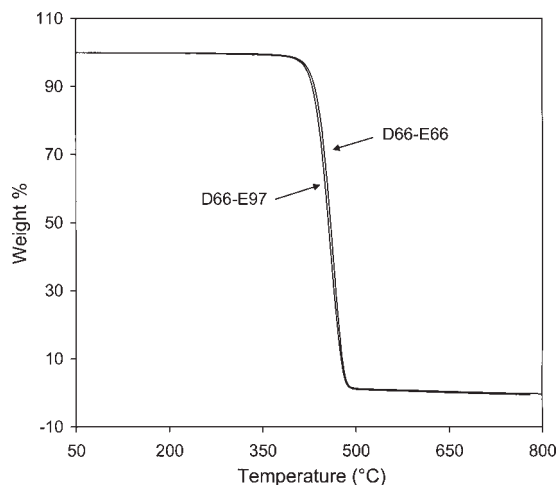


Figure 1. TGA thermograms for D66-E66 and D66-E97 PCCD samples, obtained under nitrogen flow at 10 °C/min.

DSC Analysis

Table 2 shows the DSC results obtained after a first heating scan at 250–260 °C (depending on the melting process of the samples) and 1 min of isotherm at the melting temperature, treatment carried out to cancel the thermal history.

From the data of Table 2, it is noteworthy that during the cooling scan from the melt at 20 °C/min only certain samples crystallize. In particular only D66-A79, D66-A91, D66-E81, D66-E90, D66-E97 samples—in other words, only those samples with the highest *trans* content—crystallize. Figure 2 shows the cooling scans of these samples. It may be observed that in general the exothermal peaks become more and more intense and narrow as the *trans* content increases, in particular by comparing the samples belonging to one of the two series (D66-

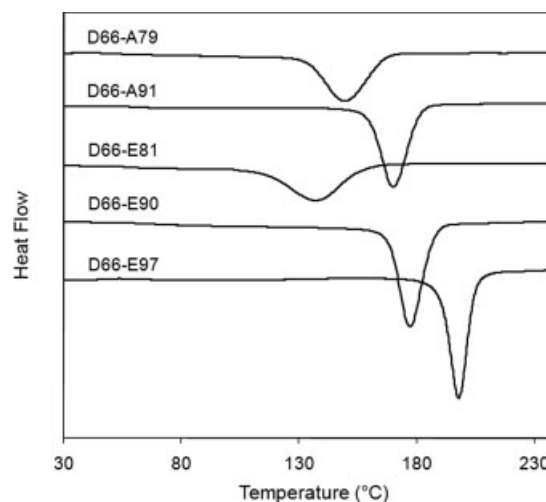


Figure 2. DSC traces obtained during the cooling from the melt at 20 °C/min.

A79 and D66-A91; D66-E81, D66-E90, and D66-E97). Accordingly, the temperature at which crystallization from the melt occurs (T_{CC}) and enthalpy (ΔH_{CC}) tend to increase, as shown in Table 2. For example, for the D66-Eyy series, the D66-E81 sample shows a crystallization process very wide and with relatively low intensity, whereas the D66-E97 sample shows a crystallization temperature higher than 60 °C and the capacity to reach a relatively higher degree of crystallinity, as suggested by the ΔH_{CC} value. Therefore, the *trans* configuration of the C₆ rings along the chain notably influence the capacity of the samples to crystallize and the crystallinity. It is significant that the other samples, with a percentage of *trans* stereoisomer equal or lower than 66%, are totally unable to rearrange toward an ordered state, in the experimental conditions used.

Table 2. TGA and DSC Data

Sample	T_D (°C) ^a	T_{CC} (°C) ^b	ΔH_{CC} (J/g) ^b	T_g (°C) ^c	T_m (°C) ^c	ΔH_m (J/g) ^c
D66-A79	464	149	25	60	187–201	30
D66-A91	458	170	28	68	209–218	30
D66-E24	462	—	—	41	—	—
D66-E52	462	—	—	52	—	—
D66-E66	465	—	—	56	—	—
D66-E81	461	138	22	64	195–205	22
D66-E90	459	177	31	70	219–226	27
D66-E97	458	198	31	—	233	30

^a Temperature of the maximum degradation rate, measured in TGA under N₂ flow at 10 °C/min.

^b Measured in DSC during the cooling scan at 20 °C/min.

^c Measured in DSC during the 2nd heating scan at 20 °C/min.

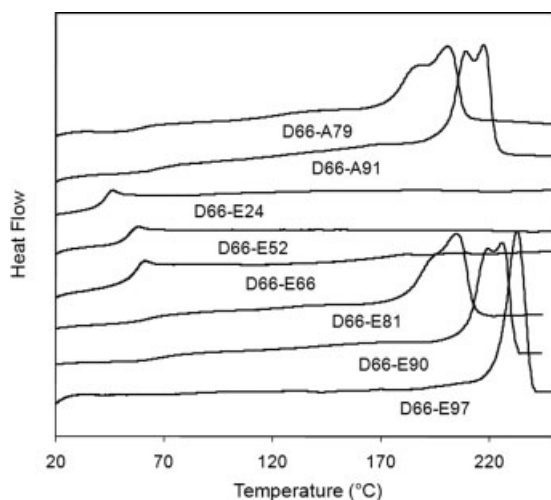


Figure 3. DSC traces recorded during the heating scan at 20 °C/min.

It is notable that D66-A79 and D66-E81 samples have the same *trans* composition but differ in T_{CC} by about 11 °C (149 °C for D66-A79 and 138 °C for D66-E81). This behavior can be justified by considering the low-molecular weight of the D66-A79 sample, with respect to the other PCCDs.

Figure 3 shows the second heating scans of all the samples, carried out at 20 °C/min after the cooling scan at 20 °C/min. It is confirmed that for these scan rates some PCCD samples (D66-E24, D66-E52, D66-E66)—the samples containing 66% or less than 66% of the *trans* isomer of 1,4-cyclohexanedicarbonyl units—do not show the capacity to crystallize, and thus have the characteristics of completely amorphous materials. On the other hand, for *trans* content equal or higher than 79% the PCCD are semicrystalline, with T_m s increasing notably, up to 233 °C for the highest *trans* content. Correspondingly, ΔH_m also reaches a high value (30 J/g). Therefore, the stereochemistry of the 1,4-cyclohexylene rings plays a fundamental role in determining the thermal behavior of PCCD.

The tendency of the *trans* C₆ rings, deriving both from CHDA (or DMCD) and CHDM, to crystallize can be explained by considering that in this configuration the chain assumes a more “stretched” form and a higher symmetry, and thus has a better packing capacity. On the other hand, compared with the *trans* isomer, the *cis* 1,4-cyclohexylene rings introduce “kinks” into the main chain, which may hinder the formation of stable crystals. This observation is in agree-

ment with the literature studies. For example, in liquid-crystalline polyesters only the *trans* isomer is compatible with melt anisotropy.¹³ The *cis* units represent “kinks” which disrupt the rigid-rod main-chain structure, leading to nonordered polymers.^{9,14} Moreover, in partially cycloaliphatic polyamides, characterized by the insertion of 1,4-cyclohexylene rings along the chains, only the *trans* isomer was found to be present inside the crystals, whereas the *cis* units are located in the amorphous phase.^{10,11,17} Again, Kricheldorf and Schwarz,⁶ who studied the thermodynamically controlled *cis/trans* ratio of polyesters deriving from CHDA, observed that the favored *trans* content of the crystalline material is 100%. Moreover, the formation of stable crystals of *trans* isomer seems to be the driving force for the observed *cis*→*trans* isomerization in various polyesters.^{6,8}

By observing the curves reported in Figure 3, it is also evident that all the semicrystalline samples, with exception of D66-E97, present a double melting peak. As far as the melting process is concerned, it is worth remembering that the multiple behavior of semicrystalline polymers has been intensely studied in the past and can give rise to controversial interpretations. The main hypotheses invoked to explain the multiple behavior are (i) a melting-recrystallization-remelting process occurring during the calorimetric scan,^{19–26} (ii) existence of different crystal structures.^{27,28} For numerous polymers, and for polyesters in particular, the multiple behavior is generally explained in terms of a melting-recrystallization-remelting process. The low endotherm is because of the superimposition of the melting endotherm of the pre-existing crystals and the recrystallization exotherm of the just molten material. The high endotherm, located at temperatures where the recrystallization cannot occur more, is due to the melting of the crystals formed during the heating scan as dominant process.

A multiple melting behavior arising from melting-recrystallization-remelting during heating generally exhibits a strong dependence on the heating rate. Figure 4 shows the effect of the heating rate on the melting peak of the D66-A91 sample crystallized from the melt at 20 °C/min. It is evident that the separation of the melting process into two well-separated peaks is more significant at low-heating rates (curves c–e), suggesting that in these cases a recrystallization of the crystalline phase can be promoted. However, there is not a clear evidence of the

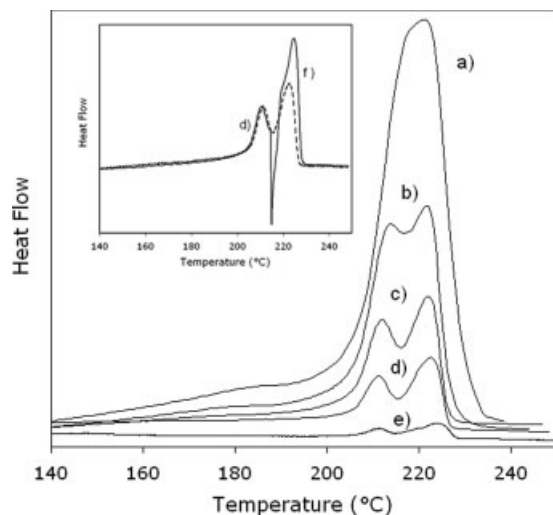


Figure 4. DSC heating curves performed on D66-A91 sample after crystallization from the melt at 20 °C/min: (a) scan at 40 °C/min; (b) scan at 20 °C/min; (c) scan at 10 °C/min; (d) scan at 5 °C/min; (e) scan at 1 °C/min; (f) scan at 5 °C/min from 10 to 215 °C, isotherm for 30 min at 215 °C and scan from 215 to 250 at 5 °C/min. The curves have not been corrected for changes in the thermal lag with the heating rate.

expected shift of the high endotherm to major temperatures and the expected increment of its intensity with the decrement of the heating rate. Moreover, to improve the recrystallization process at high temperature, the sample, crystallized at 20 °C/min, was heated to 215 °C (the end of the 1st peak) at 5 °C/min, held at this temperature for 30 min and then heated to 250 °C at 5 °C/min (curve f in the insert). It is evident that the high-melting peak notably increases of intensity. Therefore, the result suggests that the sample shows the melting-recrystallization process well known for polyesters,^{20,23–26,29} but other possibilities, as for example the presence of two different crystalline structures, cannot be excluded. For this reason the X-ray diffraction analysis becomes a very powerful technique to understand the thermal behavior of the samples. In any case, it is notable that the sample with the highest *trans* content shows only a melting peak, suggesting the presence of more perfect and stable crystals. Moreover, as the melting-recrystallization process during the fusion is really probable in the PCCD samples, the melting enthalpy values reported in Table 2 are only indicative data, because they do not refer to a simple melting phenomenon, but to a more complex process. This could be a reason why there is not a perfect

coincidence between the crystallization and melting enthalpies in Table 2.

As regards the T_g , Table 2 shows the experimental data. The table is not complete because the sample D66-E97, with the highest crystallinity, does not show any endothermal shift of baseline, indicating that in this case the percentage of amorphous phase is not detectable by DSC in the experimental conditions used in this work. It is notable that the T_g values increase as the *trans* percentage increases. For example, in the series D66-Eyy, from D66-E24 to D66-E90, T_g increases by about 30 °C (from 41 to 70). This increment is highly significant. Similar effects of the *cis/trans* ratio on T_g have been observed, for example, in polyamides obtained from CHDA and various diamines: from 23 to 100% *trans* content of the 1,4-cyclohexylene moieties T_g increases up to about 17 °C.¹⁵

Considerable information exists in literature on the influence of the structure upon the T_g . The most important factors influencing the value of T_g were found to be the chain flexibility, symmetry, and the steric hindrance and bulkiness of the side groups attached to the back-bone chain. In amorphous polymers it has been observed that an increment in symmetry can induce an increment in T_g , as seen for example in 1,4-ring substituted nylon 66 copolyamides which have higher T_g values with respect to 1,2- and 1,3-ring substituted copolyamides.⁴ One explanation for this behavior is that in 1,4-ring polymers a better molecular fit is achieved in the polymer backbone, resulting in a better chain packing and improved orientation, which would restrict the movement of the chains upon heating. The same consideration can be made for analyzed polymers, where the *trans* isomer is more symmetrical than the *cis* isomer. Moreover, in the presence of high *trans* % the high T_g values observed can be traced to the notable level of crystallinity, which creates numerous impediments to chain mobility in the amorphous state.

WAXD Analysis

Before WAXD measurements, the samples were submitted to the same thermal treatments (heating at 20 °C/min to fusion, isotherm for 1 min, cooling at 20 °C/min) as the samples showed in Figure 3. Figure 5 shows the X-ray powder diffraction patterns of some PCCD samples which resulted semicrystalline.

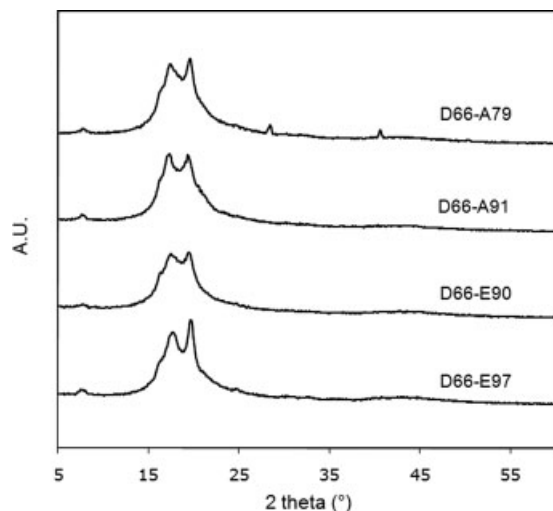


Figure 5. X-ray diffraction patterns of the semicrystalline PCCD samples.

The WAXD patterns of D66-A79, D66-A91, D66-E90, and D66-E97 samples are characterized by the presence of peaks positioned essentially at the same angular values: this evidence suggests that the ordered fraction is arranged in the same crystalline phase. By comparing the WAXD data and the T_m s (Fig. 3 and Table 2), it is surprising that the D66-A79, D66-A91, D66-E90, and D66-E97 samples have very similar X-ray diffraction patterns (and thus same crystalline structure, crystallinity degree, and crystal perfection) and T_m varying from 187–201 °C to 233 °C, that is, in a very wide range, of about 40–50 °C. To better understand this behavior, the *in situ* WAXD analysis has been carried out as a function of the temperature, and the results for the D66-A91 sample are reported in Figure 6 as an example. It is evident that during the heating scan a change in the X-ray diffraction pattern takes place starting at about 90 °C: the number of peaks increases and the crystallinity degree becomes higher. This modification results to be reversible, that is, it also occurs during the cooling scan from high to low temperatures. It is notable that the correspondent thermal transitions are not clearly evident in the DSC traces, at least in the experimental conditions used in this work. Moreover, these crystal rearrangements take place also in the other PCCD samples, but at different temperatures depending on the material characteristics.

Therefore, at room temperature the PCCD crystals are characterized by a low degree of perfection, whereas at high temperatures they

tend to acquire more perfection or to assume a different, more ordered crystalline structure. For this reason, there is not a strict correlation between the diffraction patterns of Figure 5, which refers to the sample at room temperature, and the T_m data of Table 2, which are the T_m s of crystals rearranged during the heating scan. Anyway, to better understand this process a more detailed study is necessary, which will be the object of a following study together with specific thermal treatments to improve the polymer crystallinity.

Molecular Structure Analysis

As the thermal behavior of the PCCD samples is very complex, a first attempt to correlate the structure of the samples with their thermal properties has been made. In this section the chemical structure of the polymer has been analyzed by considering that the two units characteristic of the PCCD are the 1,4-cyclohexanedicarbonyl unit (called A/E), deriving from CHDA or DMCD, and the 1,4-cyclohexanedimethylenoxy unit (called D), deriving from CHDM. Attention has been focused on a sequence of three 1,4-cyclohexylene rings: D-A/E-D and A/E-D-A/E, represented in Scheme 2.

Considering that each ring can be in *trans* (*t*) or *cis* (*c*) configuration, eight different triads are possible (*ttt*, *ctt*, *tct*, *ttc*, *cct*, *tcc*, *ctc*, *ccc*) for each D-A/E-D or A/E-D-A/E sequence. As the polymer chain is very long, it can be considered as formed by a high number of triads and each triad can assume one of the eight configurations

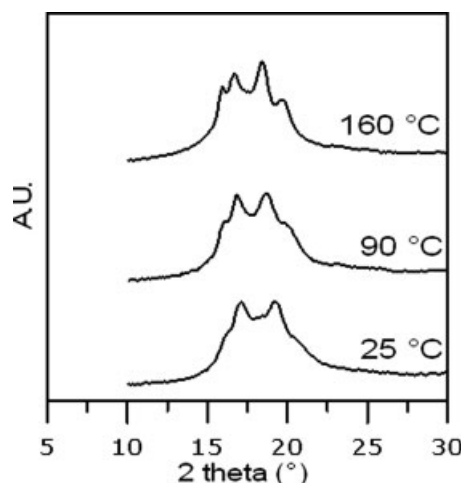
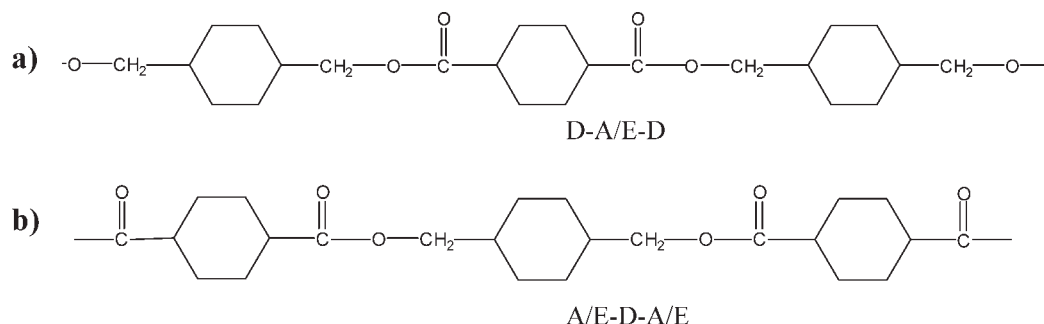


Figure 6. *In situ* high-temperature WAXD for D66-A91 sample.



Scheme 2. Representation of the different sequences of three 1,4-cyclohexylene rings considered for the determination of the probability of finding the triads reported in Tables 3 and 4.

described earlier, in a random distribution. Therefore, the probability (P) of finding a peculiar triad, for example the probability P_{tct} of finding the tct triad, within the chain is calculated from the product of the probability (f_c or f_t) of finding the *cis* or *trans* configuration for each ring:

$$P_{tct} = (f_t \cdot f_c \cdot f_t) \cdot 100$$

f_t and f_c are calculated by the *trans* and *cis* content of D and A/E units, reported in Table 1, divided by 100.

Firstly, the D-A/E-D sequence was analyzed. Table 3 shows the probabilities of finding the eight possible triads within the chains in the analyzed samples.

As regards the thermal transitions characteristic of the PCCD samples, the DSC data of Table 2 have been used, independently of the crystal modifications occurring during the heating scan (shown in Fig. 6). Indeed, these thermal transitions are those which characterize the thermal behavior and the practical applications of the samples.

A first correlation between molecular structure and thermal properties is described in Figure 7,

where the T_m values (Table 2) are reported as a function of the probability of finding the ttt , ctt , tct , ttc , cct , tcc , ctc , and ccc triads (Table 3). For the samples presenting a double melting peak, only the first peak is reported, due to the fact that, for the possible melting-recrystallization process, it corresponds to the melting of the crystals actually formed at T_{CC} during the cooling scan.

Firstly, it is noteworthy that linear trends, with good correlation coefficients, are obtained. Moreover, it is notable that T_m increases with the increment of the percentage of four triads (ttt , ctt , ttc , and ctc). For example, T_m varies from 190 to 230 °C when the percentage of the ttt triads changes from about 35 to 42%. The same trend is observed for the ctt and ttc triads, that is, for triads containing two consecutive rings in *trans* configuration. This result suggests that a high percentage of two or three *trans* sequences has a significant role in improving the crystalline perfection of PCCD. The observation is in perfect agreement with the previous discussion and with the literature results.

Moreover, by observing Figure 7, it may also be seen that the ctc triads, that is, the triads containing only the unit A/E in *trans* configura-

Table 3. Probability of Finding the ttt , ctt , tct , ttc , cct , tcc , ctc , and ccc Triads in the D-A/E-D Sequence

Sample	P_{ttt} (%)	P_{ctt} (%)	P_{tct} (%)	P_{ttc} (%)	P_{cct} (%)	P_{tcc} (%)	P_{ctc} (%)	P_{ccc} (%)
D66-A79	34.4	17.7	9.1	17.7	4.7	4.7	9.1	2.4
D66-A91	39.6	20.4	3.9	20.4	2.0	2.0	10.5	1.0
D66-E24	10.5	5.4	33.1	5.4	17.1	17.1	2.8	8.8
D66-E52	22.7	11.7	20.9	11.7	10.8	10.8	6.0	5.5
D66-E66	28.7	14.8	14.8	14.8	7.6	7.6	7.6	3.9
D66-E81	35.3	18.2	8.3	18.2	4.3	4.3	9.4	2.2
D66-E90	39.2	20.2	4.4	20.2	2.2	2.2	10.4	1.2
D66-E97	42.3	21.8	1.3	21.8	0.7	0.7	11.2	0.3

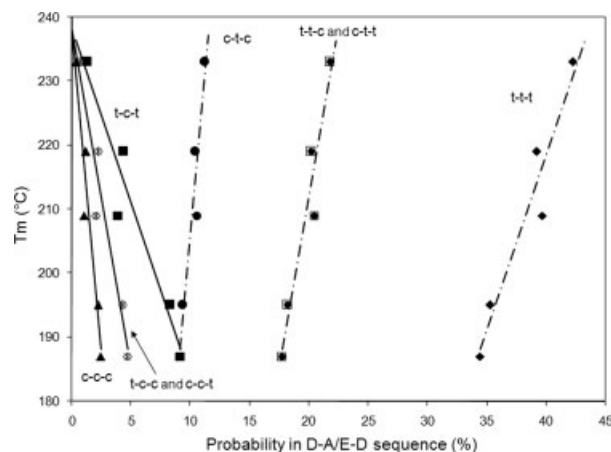


Figure 7. Trends of T_m versus the probabilities of finding the *ttt*, *ctt*, *tct*, *ttc*, *cct*, *tcc*, *ctc*, and *ccc* triads in the D-A/E-D sequence.

tion, improve T_m significantly, independently of the fact that the other two rings are in *cis* configuration. This result is important because it is a first indication of a different effect of the stereochemistry of the D and A/E units on thermal properties.

Analysis of the remaining curves shows that T_m decreases as the percentages of the *ccc*, *tcc*, *cct*, and *tct* triads increase. Also in this case, for the sequences of two or three rings in *cis* configuration, the result is expected: the presence of “kinks” along the macromolecular chains prevents a high-crystal perfection and high-melting peak. However, the decrement of T_m with the increment of the percentage of *tct* sequences is very interesting: in this case, if the A/E unit presents the ring in *cis* configuration, crystal perfection decreases. Instead, we observed that the *ctc* triads improve T_m . Therefore, it seems that the configuration of the A/E unit has a very important effect in influencing the trend of T_m .

Given these results, the effect of the percentage of triads on the crystallization temperature, measured in DSC during the cooling scan from the melt (Table 2), is also significant. In Figure 8 it is evident that the presence of the *ttt*, *ctt*, *ttc*, and *ctc* triads causes an increment of T_{CC} . The trends are the same with respect to those observed in Figure 7, indicating that a high-crystallization capacity and crystal perfection are improved by the presence of two and three sequences of rings in *trans* and, more significantly, by the presence of an isolated ring, belonging to A/E unit, in *trans* configuration. On

the contrary, two and three sequences of rings in *cis* and, more significantly, an isolated ring belonging to A/E unit, in *cis* configuration inhibit the crystallization process.

Therefore, to emphasize the different effect of the stereochemistry of the C_6 ring, depending on whether it belongs to A/E or D unit, we have analyzed the molecular structure of the PCCD samples focusing on the A/E-D-A/E sequences [Scheme 2(b)]. In this case, two A/E units and only one D unit have been considered. The probability of finding the eight possible triads (*ttt*, *ctt*, *tct*, *ttc*, *cct*, *tcc*, *ctc*, *ccc*) has been calculated and the results are reported in Table 4.

Figure 9 describes the trend of T_m as a function of the probability of finding the different triads in the A/E-D-A/E system. Now an important difference may be seen with respect to the trends reported in Figures 7 and 8: the increment of T_m occurs only for two kinds of sequences, that is, *ttt* and *tct*. All the other sequences (*ccc*, *cct*, *ctc*, *tcc*, *ttc*, and *ctt*) induce a decrement of T_m . It is notable that for T_{CC} the trend is exactly the same. Therefore, the *ccc*, *cct*, *ctc*, *tcc*, *ttc*, and *ctt* triads are responsible of lower crystal perfection and lower tendency to crystallize. Then, in this case the presence of two consecutive rings in *trans* configuration (triads *ttc* and *ctt*) is not determinant in improving crystallizability. Indeed, the configuration of the ring of A/E unit appears to be the most important factor influencing crystallization capacity: its *trans* configuration favors crystallization, whereas its *cis* configuration is unfavorable.

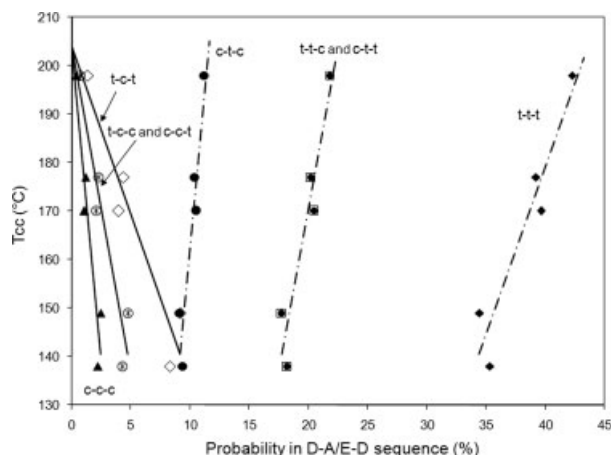


Figure 8. Trends of T_{CC} versus the probabilities of finding the *ttt*, *ctt*, *tct*, *ttc*, *cct*, *tcc*, *ctc*, and *ccc* triads in the D-A/E-D sequence.

Table 4. Probability of Finding the *t**t**t*, *ctt*, *tct*, *ttc*, *cct*, *tcc*, *ctc*, and *ccc* Triads in the A/E-D-A/E Sequence

Sample	P_{ttt} (%)	P_{ctt} (%)	P_{tct} (%)	P_{ttc} (%)	P_{cct} (%)	P_{tcc} (%)	P_{ctc} (%)	P_{ccc} (%)
D66-A79	41.2	10.9	21.2	10.9	5.6	5.6	2.9	1.5
D66-A91	54.7	5.4	28.2	5.4	2.8	2.8	0.5	0.3
D66-E24	3.8	12.0	2.0	12.0	6.2	6.2	38.1	19.6
D66-E52	17.8	16.5	9.1	16.5	8.4	8.4	15.2	7.8
D66-E66	28.7	14.8	14.8	14.8	7.6	7.6	7.6	3.9
D66-E81	43.3	10.2	22.3	10.2	5.2	5.2	2.4	1.2
D66-E90	53.5	5.9	27.5	5.9	3.1	3.1	0.7	0.3
D66-E97	62.1	1.9	32.0	1.9	1.0	1.0	0.1	0.03

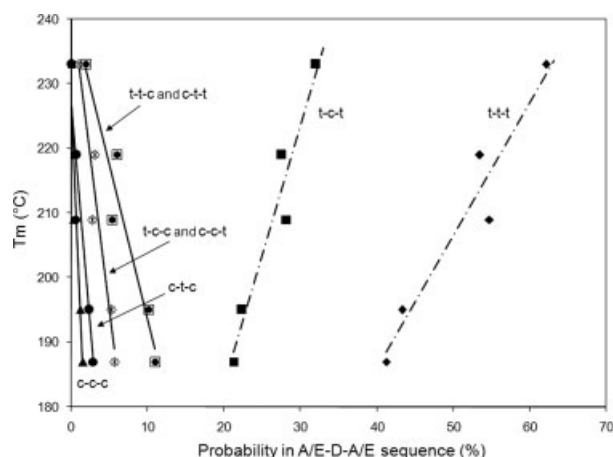
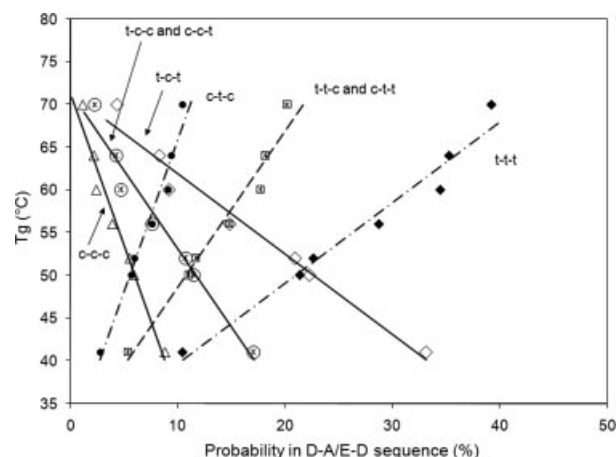
As regards the glass transition, Figure 10 describes the trend of T_g as a function of the probability of finding the different triads in the D-A/E-D sequences. It is notable that the same results discussed for T_m and T_{CC} (Figs. 7 and 8) are obtained. Analogously, for the A/E-D-A/E sequences the trend of T_g versus the probability of finding the different triads is exactly the same of that shown in Figure 9 for T_m and that obtained for T_{CC} . As a conclusion, T_g increases as the percentage of *t**t**t* triads increases and when the 1,4-cyclohexylene ring in A/E unit is in *trans* configuration.

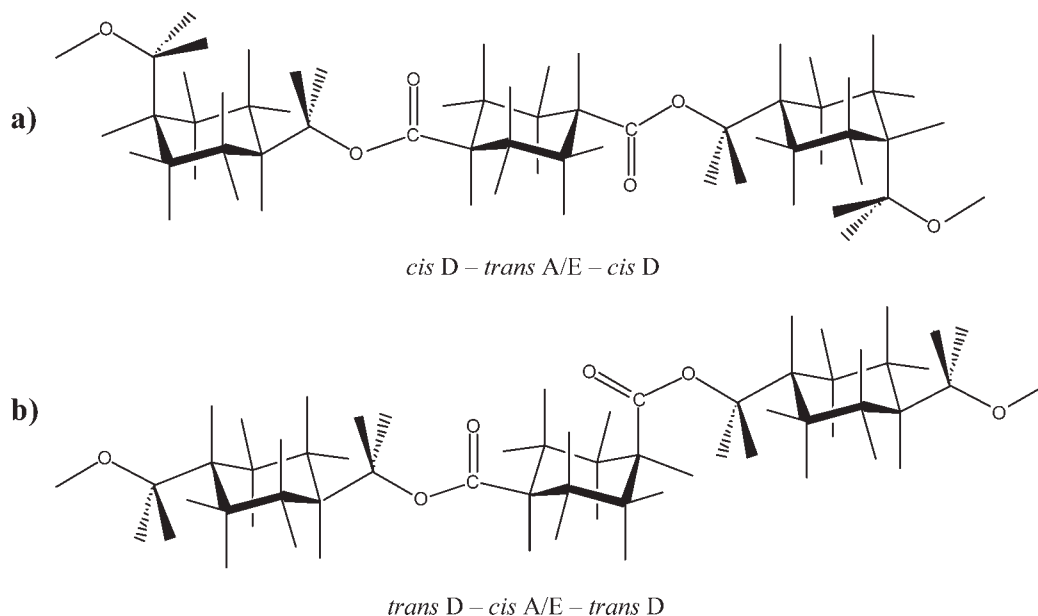
The results obtained can be discussed by observing the configurations of the two sequences D-A/E-D shown in Scheme 3: *ctc* and *tct*. The influence of these two sequences on the thermal transitions, previously discussed, is significant because the first sequence (a) causes an increment of T_g , T_{CC} , and T_m , whereas the second (b) induces a decrement of the T_g , T_{CC} , and T_m (see Figs. 7, 8, and 10). When the C₆ ring in

A/E unit is in *trans* configuration an improvement of the thermal properties occurs, whereas when the C₆ ring is in *cis* configuration the thermal properties are lower.

It is noteworthy that the central ring is linked to two ester groups, where the carbon atoms are characterized by sp^2 hybridization, with planar geometry and bond angles of 120°. This structure has a certain degree of rigidity. On the other hand, in unit D the rings are connected to two —CH₂— groups, which are characterized by carbon atoms with sp^3 hybridization, tetrahedral geometry, and bond angles of about 109°. In this case, each carbon atom possesses a higher mobility and can assume different but equivalent orientations in space. Therefore, the most rigid structure, the A/E unit, is found to have the highest influence in determining the thermal properties.

In particular, the rigidity of A/E unit in *trans* configuration [Scheme 3(a)] gives a high symmetry to *ctc* triad, improving chain packing, crystal-

**Figure 9.** Trends of T_m versus the probabilities of finding the *t**t**t*, *ctt*, *tct*, *ttc*, *cct*, *tcc*, *ctc*, and *ccc* triads in the A/E-D-A/E sequence.**Figure 10.** Trends of T_g versus the probabilities of finding the *t**t**t*, *ctt*, *tct*, *ttc*, *cct*, *tcc*, *ctc*, and *ccc* triads in the D-A/E-D sequence.



Scheme 3. Two configurations of D-A/E-D sequence.

line order, and also T_g . On the other hand, the *cis* configuration of A/E unit [Scheme 3(b)] is characterized by a high-steric hindrance of the two substituent groups. This leads to less probability of chain folding and crystallizability for *tct* than *ctc* triad.

CONCLUSIONS

The study of the thermal properties of PCCD has been performed on samples at different *cis/trans* ratio of the 1,4-cyclohexylene units deriving both from CHDA (A) or DMCD (E). It is notable that the *cis/trans* ratio is retained during thermal treatments, as isomerization between the two configurations does not take place. As a result, the thermal behavior of PCCD is highly dependent on the stereochemistry of the 1,4-cyclohexylene units. With the increment of the *trans* content, the polymer changes from completely amorphous to semicrystalline material. Correspondingly, T_g increases from about 40 to 70 °C and T_m varies from about 190 to 235 °C. This behavior has been attributed to the better chain packing which occurs in the presence of the more “stretched” *trans* configuration. Indeed, the rings in *cis* configuration cause “kinks” and a lower degree of symmetry.

Moreover, an analysis of the molecular structure shows that the stereochemistry of 1,4-cyclohexylene ring deriving from CHDA or DMCD is

the main element responsible for the thermal properties. This result is due to the higher rigidity of the 1,4-cyclohexanedicarbonyl unit with respect to 1,4-cyclohexanedimethyleneoxy unit, deriving from CHDM. Therefore, when the most rigid structure is in *trans* configuration T_g , T_m , and T_{CC} tend to increase, whereas the *cis* configuration of the 1,4-cyclohexanedicarbonyl unit tends to induce a decrement of T_g and crystallizability.

Some aspects about the crystalline phase and the crystal modifications occurring during the heating and cooling scans are now under investigation and will be the object of a future study.

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