Stereochemistry Driven Cocrystallisation Phenomena in Partially Cycloaliphatic Polyamides

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Summary: Two series of isomeric copolyamides were synthesised, *viz.* polyamides 12.6 for which the adipic acid residues were partially replaced by *cis/trans*-1,4-cyclohexanedicarboxylic acid (1,4-CHDA), and polyamides 4.14 for which the 1,4-diaminobutane residues were partially replaced by *cis/trans*-1,4-diaminocyclohexane (1,4-DACH). A careful DSC and WAXS analysis learned that only the trans isomers of both 1,4-DACH and 1,4-CHDA are incorporated into the crystalline phase. During DSC analysis, an intitial high trans content is preserved in the case of the non-isomerising 1,4-DACH, whereas the 1,4-CHDA residues gradually isomerise from a high initial trans content to a significanly lower trans content. Since these cis residues are not incorporated into the crystalline domains, the lower second heating melting points of the 1,4-CHDA-based copolyamides in comparison with 1,4-DACH-based copolyamides, having similar cycloaliphatic monomer contents, can be understood.

Keywords: copolymerisation, crystallisation, differential scanning calorimetry (DSC), polyamides, WAXS

Introduction

Although the incorporation of cyclohexyl moieties into the backbone of polyamides and polyesters, and its influence on crystallisation, have been studied quite extensively,[1-10] a question which still remains to be answered is, whether or not both the cis and the trans isomers of either 1,4-cyclohexanedicarboxylic acid (1,4-CHDA) or 1,4-diaminocyclohexane (1,4-DACH) are participating in the formation of crystalline domains in the resulting step-growth

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polymers. On forehand one might expect that stable crystals prefer the more 'stretched' trans configuration over the 'kinky' cis configuration, but no scientific evidence is available for such a preference. In our efforts to find this evidence, we decided to study the relation between the stereochemistry of cycloaliphatic residues, and thermal transitions as well as X-ray structures of two series of isomeric copolyamides. In the series based on polyamides 12.6, the adipic acid (AA) residues were partially replaced by *cis/trans*-1,4-cyclohexanedicarboxylic acid (1,4-CHDA), and in the series based on polyamides 4.14, the 1,4-diaminobutane (1,4-DAB) residues were partially replaced by *cis/trans*-1,4-diaminocyclohexane (1,4-DACH). The four types of repeating units, occurring in both isomeric copolyamides 12.6/12.1,4-CHDA and 4.14/1,4-DACH.14 are given in Figure 1.

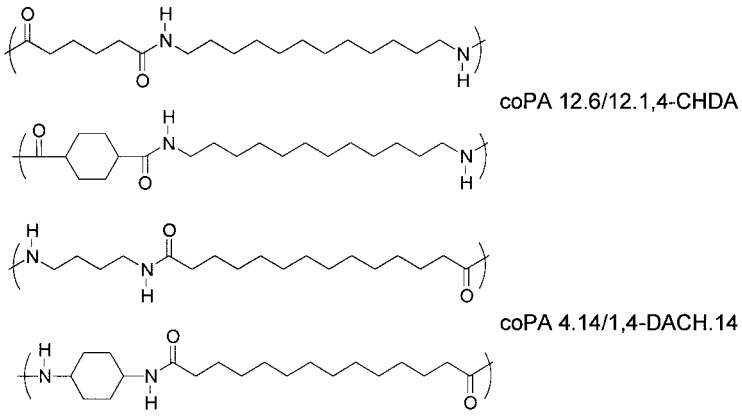

Fig. 1. Chemical structures of repeating units occurring in copolyamides 12.6/12.1,4-CHDA and 4.14/1,4-DACH.14.

Preliminary DSC results have been reported earlier by us,[11,12] which however did not allow the drawing of hard conclusions regarding the problem we were eager to solve. In the current paper, fine-tuned DSC results are combined with new WAXS data collected at room temperature, after which we were able to get an indisputable answer to the question raised above.

Experimental

Synthesis of the Copolyamides

Equimolar amounts of the desired dicarbonyl dichlorides (a mixture of adipoyl chloride and 1,4-cyclohexanedicarbonyl dichloride with the desired cis/trans ratio for the series 12.6/12.1,4-CHDA, and 1,12-dodecanedicarbonyl dichloride for the series 4.14/1,4-DACH.14) and the desired diamines (1,12-diaminododecane for the series 12.6/12.1,4-CHDA and a mixture of 1,4-diaminobutane and 1,4-DACH with the desired cis/trans ratio for the series 4.14/1,4-DACH.14) were polymerised with stirring in $CHCl_3$ under a nitrogen atmosphere. After polymerisation the solvent was evaporated, the polymers were dissolved in formic acid, followed by two successive precipitations in water, after which they were washed and dried. Details concerning the low temperature polymerisation, during which the initial cis/trans ratio of the cycloaliphatic monomers proved to be preserved, can be found elsewhere.[11,12]

Characterisation of the Copolyamides

Solution ^{1}H-decoupled ^{13}C NMR spectra of the copolyamides dissolved in deuterated trifluoroacetic acid (TFA-d) were obtained in the inverse-gated Fourier transform mode on a Bruker Avance DRX250 instrument equipped with a Quattro probe tuned to 62.93 and 250.13 MHz for ^{13}C NMR and ^{1}H NMR nuclei (details can be found elsewhere[11,12]). Determination of the copolyamide composition and the cis/trans ratio of the cycloaliphatic residues in the polymer main chain was performed from integrated signal areas as obtained by line deconvolution of ^{13}C NMR resonances using the PERCH TLS (Total Line Shape) software.[13]

Polymer solutions (1.0 g/dL in *m*-cresol) were used to determine intrinsic viscosities at 25 °C using a Cannon-Ubbelohde viscometer.

DSC curves were recorded under nitrogen on a Perkin Elmer DSC 7 using a scanning speed of 10 °C/min, both for cooling and heating. After first heating the polyamides were kept at 300 °C for 30 min in order to remove all residual crystallites, capable of acting as nucleating agents during cooling. The T_ms, taken from the first and second heating curves, were defined as the endsets of the endotherms.

WAXS measurements were performed at room temperature using a horizontal Geigerflex diffractometer on a Rigaku Rotaflex RU-200B rotating Cu-anode at a power of 4 kW. Cu K_α

radiation with a wavelength of 1.542 Å was used. Measurements were of the transmission type, and were performed in the diffraction angle range $2 < 2\theta < 60°$. Data were accumulated in steps of $2\theta = 0.05°$, each for a period of 6s.

Results and Discussion

All copolyamides, either belonging to the series 12.6/12.1,4-CHDA or to its isomeric series 4.14/1,4-DACH.14, were synthesised following a recipe during which the initial cis/trans ratio of the cycloaliphatic moieties is totally preserved. This was proven using solution ^{1}H-decoupled ^{13}C NMR spectroscopy, a technique giving both the incorporated comonomer ratio as well as the desired information on the stereochemistry of the built-in 1,4-CHDA and 1,4-DACH residues. The compositions of the copolyamides, as well as their intrinsic viscosities (which are sufficiently high to exclude any possible influence of molar mass on thermal transitions) are given in Tables 1 and 2.

Table 1. Chemical compositions and intrinsic viscosities of synthesized copolyamides 12.6/12.1,4-CHDA.

Entry	Initial molar monomer feed ratio		Molar ratio in final copolyamide		[η](dL/g)
	AA/1,4-CHDA	cis/trans	AA/1,4-CHDA	cis/trans	
1	100/0	-	100/0	-	0.55
2	90/10	2/98	91/9	2/98	0.86
3	85/15	80/20	86/14	80/20	0.75
4	85/15	3/97	84/16	6/94	0.67
5	80/20	80/20	79/21	80/20	0.57
6	75/25	80/20	75/25	80/20	0.54
7	80/20	0/100	74/26	0/100	0.54

Figure 2 shows the first heating melting points of the 12.6/12.1,4-CHDA copolyamides with an initially incorporated 1,4-CHDA cis/trans ratio of either close to 0/100 (◊) or 80/20 (◆). In the same figure, the second heating melting points are shown for both series of copolyamides (■), both obtained after cooling down the melt after storage for 30 min at 300 °C. It is obvious that the incorporation of the cycloaliphatic monomer into the polyamide main chain raises the first

heating $T_{m,end}$ significantly with respect to the reference polyamide 12.6, provided that *trans*-1,4-CHDA units are present in the copolyamide. On the other hand, the first heating melting points of copolyamides initially rich in cis moieties correspond remarkably well with the melting point of the homopolyamide 12.6. However, after exposure of both *cis*- and *trans*-1,4-CHDA-rich copolyamides to a temperature of 300 °C for 30 min, the subsequent cooling and reheating yields melting points which show a linear dependency of the mole % 1,4-CHDA, irrespective of the initial cis/trans ratio. It is obvious that the thermal treatment of the initially trans-rich copolyamides results in a significant decrease of the T_m in the second melting. On the other hand, a similar treatment of cis-rich copolyamides results in a significant raise of the T_m in the second melting. It is known that the 1,4-CHDA residues are susceptible to cis/trans isomerisation, for which a mechanism was proposed by Kricheldorf and Schwarz.[1] Solution ^{13}C NMR experiments revealed that, during the thermal treatment for 30 min at 300 °C, isomerisation of the 1,4-CHDA moieties, incorporated in the polyamide main chain, had occurred indeed. As illustrated in Figure 3, for copolyamides based on initially high *trans*-1,4-CHDA contents significant amounts of the trans isomer have been converted into the cis isomer, whereas for copolyamides based on initially high *cis*-1,4-CHDA contents significant amounts of the cis isomer have been converted into the trans isomer. For both copolyamides, after thermal treatment the cis/trans ratio is very similar, indicating that isomerisation equilibrium has been reached, which is in agreement with the straight line in Figure 2 (■).

Table 2. Chemical compositions and intrinsic viscosities of synthesized copolyamides 4.14/1,4-DACH.14.

Entry	Molar monomer ratio in feed		Molar ratio in final copolyamide		[η](dL/g)
	1,4-DAB/1,4-DACH	cis/trans	1,4-DAB/1,4-DACH	cis/trans	
8	100/0	-	100/0	-	0.53
9	95/5	0/100	93/7	0/100	0.59
10	90/10	0/100	86/14	0/100	0.57
11	90/10	0/100	80/20	0/100	0.57
12	90/10	66/34	79/21	57/43	0.48
13	85/15	83/17	80/20	75/25	0.44

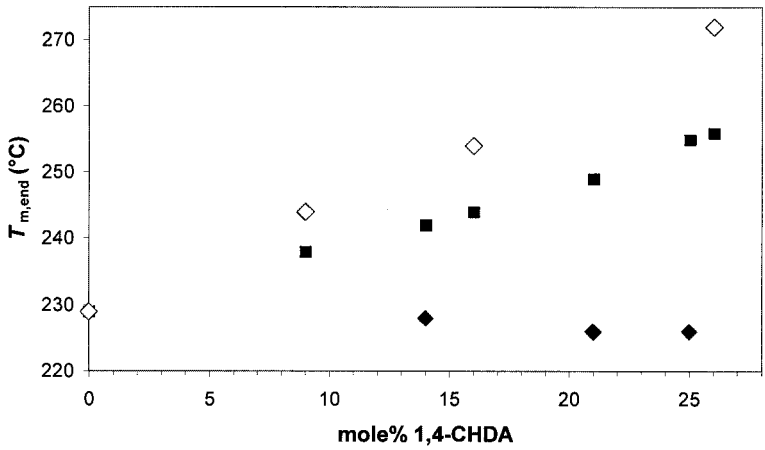

Fig. 2. Comparison of melting points obtained from 1st and 2nd heating of copolyamides 12.6/12.1,4-CHDA with different initial cis/trans ratios. Legend: melting point of originally cis-rich (◆) or trans-rich (◊) copolyamides obtained from 1st heating; (■) melting point after annealing for 30 min at 300 °C.

Combining the results presented in Figure 2 and Figure 3, it is obvious that the melting point only increases with respect to the reference polyamide 12.6 if detectable amounts of the 'stretched' and rigid *trans*-1,4-CHDA isomer are available for cocrystallisation with the adipic acid residues. So, based on the DSC experiments, we are bound to conclude that the *trans*-1,4-CHDA residues are capable of cocrystallising in a common crystal lattice with adipic acid residues. In view of the similar first heating melting points for polyamide 12.6 and the copolyamides rich in *cis*-1,4-CHDA moieties, it is tempting to conclude that the *cis*-1,4-CHDA moieties are excluded from the crystalline phase. However, WAXS diffractograms of both polyamide 12.6 and the copolyamides are required to draw this conclusion, since a possible melting point raising effect of the incorporated rigid *cis*-1,4-CHDA moieties might just be compensated by the inferior quality of the generated crystals, caused by the 'kinky' structure of the cis isomer.

Figure 4 shows WAXS diffractograms of homopolyamide 12.6, of a copolyamide containing some 1,4-CHDA with a high trans content (entry 4 in Table 1), and of a copolyamide containing a similar amount of 1,4-CHDA with a high cis content (entry 3 in Table 1), all recorded at room temperature.

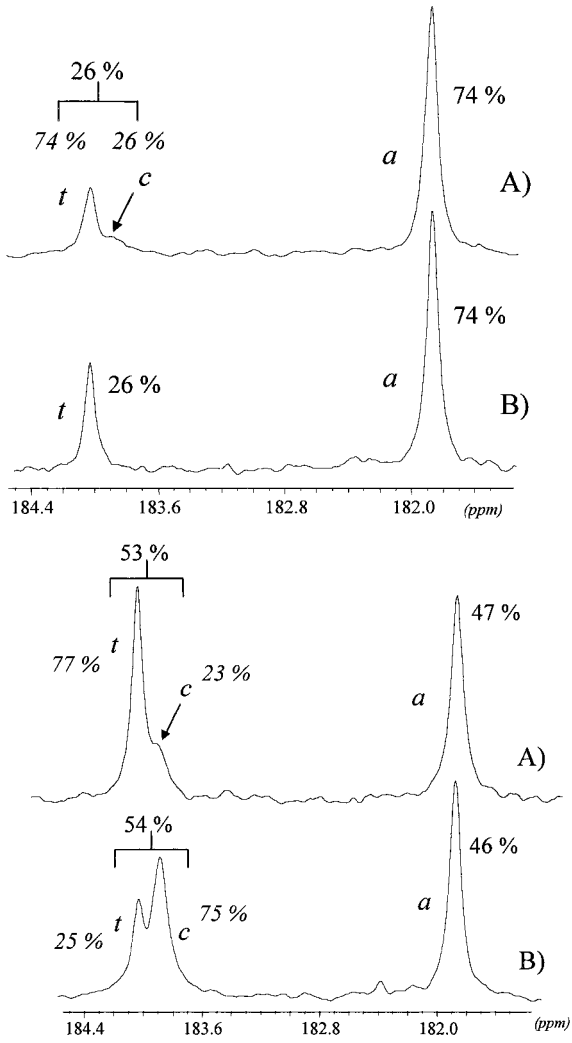

Fig. 3. Solution ^{13}C NMR analysis (TFA-d) of copolyamides 12.6/12.1,4-CHDA, A) after and B) before submission of the samples to 300 °C for 30 min. The partial isomerisation of the 1,4-CHDA residues of an initially trans-rich (top) or cis-rich (bottom) copolyamide, resulting in equilibrium cis/trans ratios of the cycloaliphatic residues, is shown. Legend: a: AA residues; c: *cis*-1,4-CHDA residues; t: *trans*-1,4-CHDA residues.

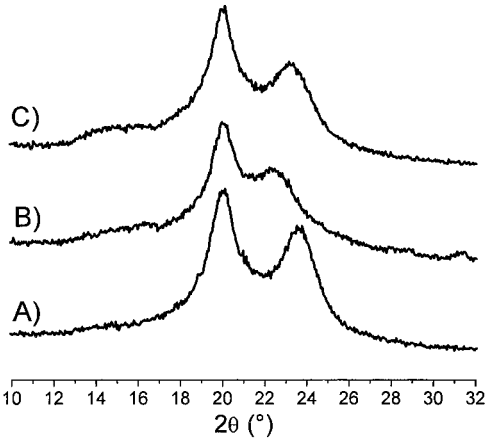

Fig. 4. Room temperature diffraction patterns obtained by WAXS analysis of copolyamides 12.6/12.1,4-CHDA as a function of composition (λ = 1.542 Å). Legend: (A) polyamide 12.6; (B) 16 mole% 1,4-CHDA (cis/trans: 6/94) and (C) 14 mole% 1,4-CHDA (cis/trans: 80/20).

The diffraction pattern of the copolyamide containing 14 mole% 1,4-CHDA with a high cis content is similar to the pattern of the homopolyamide 12.6. This is a clear indication that the cis moieties are not incorporated into the crystals. On the contrary, the copolyamide containing 16 mole % 1,4-CHDA with a high trans content shows a pattern clearly deviating from that of polyamide 12.6, implying that the trans residues are cocrystallising with the adipic acid residues. These X-ray data are fully in agreement with the DSC data shown in Figure 2.

According to the isomerisation mechanism suggested bij Kricheldorf and Schwarz,[1] 1,4-DACH residues are not expected to isomerise. The ^{13}C NMR spectra shown in Figure 5 provide evidence for this. Before and after a 30 min stay at 300 °C, the stereochemistry of the 1,4-DACH-based copolyamides is, within experimental error, the same.

In view of their insensitivity towards isomerisation during thermal analysis, the 1,4-DACH-based partially cycloaliphatic copolyamides are the preferred polymers to study the influence of the stereochemistry of cyclic main chain parts on thermal transitions and crystallisation phenomena. Figure 6 shows that, in analogy with the 1,4-CHDA-based copolyamides, only the trans isomer residues are incorporated into the crystals. The diffraction pattern of the

copolyamide containing 20 mole% 1,4-DACH with a high cis content (entry 13 in Table 2) is very similar to the pattern of the homopolyamide 4.14. This once more is a clear indication that the cis moieties are not incorporated into the crystals. On the other hand, the copolyamide containing 20 mole % 1,4-DACH with a high trans content (entry 11 in Table 2) shows a pattern strongly deviating from that of polyamide 4.14, implying that the *trans*-1,4-DACH residues are cocrystallising with the 1,4-diaminobutane residues.

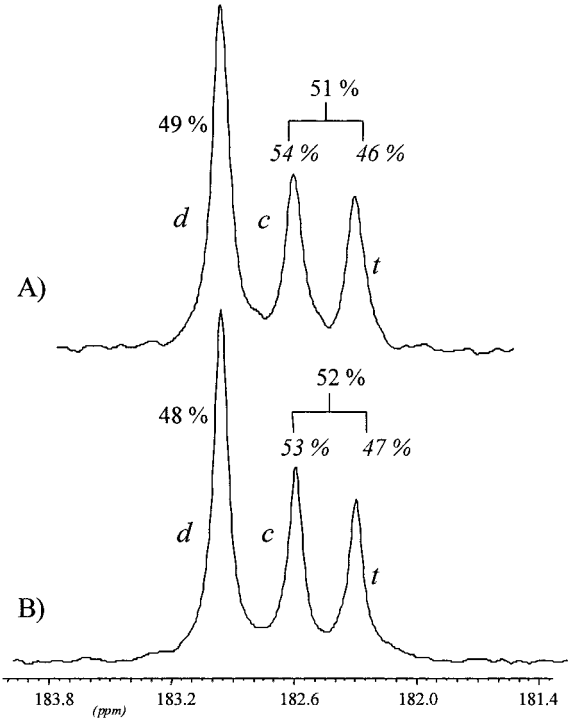

Fig. 5. Solution ^{13}C NMR analysis (TFA-d) of a copolyamide 4.14/1,4-DACH.14, A) after and B) before submission of the sample to 300 °C for 30 min, showing the absence of isomerisation. d: 1,4-DAB residues; c: *cis*-1,4-DACH residues; t: *trans*-1,4-DACH residues.

In view of the WAXS data on the 1,4-DACH based copolyamides, it is not surprising that the $T_{m,end}$ values of polyamide 4.14 and cis-rich 4.14/1,4-DACH.14 80/20 (entry 13, Table 2), all

obtained after cooling following a treatment of 30 min at 300 °C, are very similar, *viz.* 228 and 227 °C, respectively, whereas the $T_{m,end}$ of the trans-rich 4.14/1,4-DACH.14 80/20 (entry 11, Table 2) is significantly higher, *viz.* 270 °C. The $T_{m,end}$ of homopolyamide 4.14 corresponds remarkably well with that of its isomer 12.6, being 229 °C.

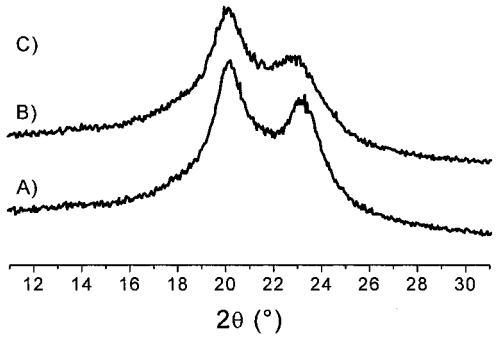

Fig. 6. Room temperature diffraction patterns obtained by WAXD analysis of copolyamides 4.14/1,4-DACH.14 as a function of composition (λ = 1.542 Å). Legend: (A) polyamide 4.14; (B) 20 mole% 1,4-DACH (cis/trans: 75/25) and (C) 20 mole% 1,4-DACH (cis/trans: 0/100).

Copolyamides 4.14 with *trans*-1,4-DACH incorporated show a higher T_m than the isomeric copolyamides 12.6/12.1,4-CHDA containing comparable amounts of initially *trans*-1,4-CHDA. This difference is visualised in a plot of the endset melting point versus composition of the two types of copolyamides (see Fig. 7).

The explanation for this difference is the isomerisation of the 1,4-CHDA residues: after the thermal treatment, part of the *trans*-1,4-CHDA residues has been converted into *cis*-1,4-CHDA residues. In this way, the final content of cocrystallising *trans*-1,4-CHDA units in the copolyamide 12.6/12.1,4-CHDA is lower than the initial content, and accordingly, after partial isomerisation from trans to cis residues, less cycloaliphatic residues are available for incorporation into the crystals, resulting in lower melting temperatures. As shown in Figure 5, the 1,4-DACH residues in copolyamides 4.14/1,4-DACH.14 do not isomerise under the applied

conditions. Thus, the content of *trans*-1,4-DACH residues remains constant during thermal analysis.

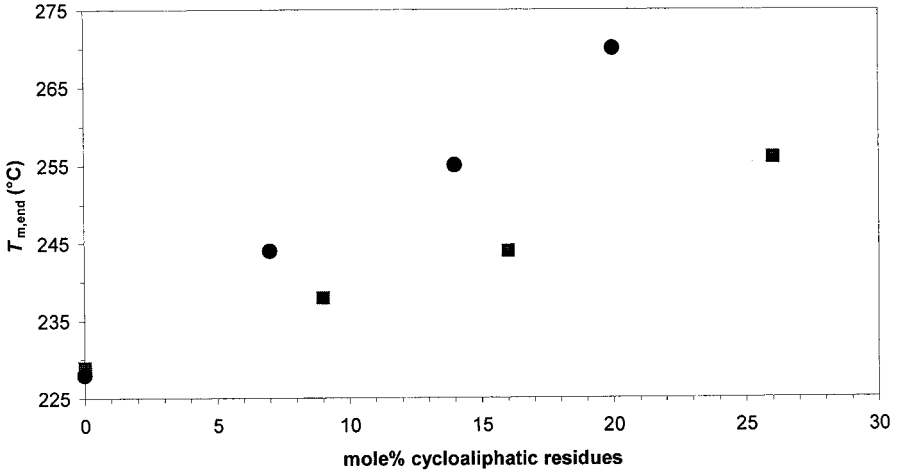

Fig. 7. Melting points of the copolyamides, after cooling following a treatment of 30 min at 300 °C, as a function of composition. Legend: (●) copolyamides 4.14/*trans*-1,4-DACH.14; (■) copolyamides 12.6/12.(initially) *trans*-1,4-CHDA.

Conclusions

A careful DSC and WAXS analysis on two series of isomeric copolyamides, *viz.* copolyamides 12.6/12.1,4-cyclohexanedicarboxylic acid (1,4-CHDA) and copolyamides 4.14/4.1,4-diaminocyclohexane (1,4-DACH), learned that only the trans isomers of both 1,4-DACH and 1,4-CHDA are incorporated into the crystalline phase. During heating, the intitial high trans content is preserved in the case of the non-isomerising 1,4-DACH, whereas during DSC analysis the 1,4-CHDA residues gradually isomerise from a high initial trans content to a significanly lower trans content, which in view of the non-cocrystallising cis residues can explain the lower thermal transition temperatures of the 1,4-CHDA-based copolyamides for similar cycloaliphatic monomer contents.

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