Conformation of Alkylene Segments of Poly(ester amides) in Their Crystalline and Mesomorphic States

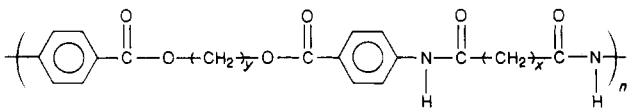
S. M. Aharoni,* S. T. Correale, W. B. Hammond, G. R. Hatfield, and N. S. Murthy

Allied-Signal Inc., Morristown, New Jersey 07960. *Received June 6, 1988; Revised Manuscript Received September 9, 1988*

ABSTRACT: Several X-ray techniques and solid-state carbon-13 NMR spectroscopy were combined to elucidate the conformational nature along the x- and y-alkylene segments in the crystalline and mesomorphic states of highly regular, hydrogen-bonded poly(ester amides). In general, the X-ray data for poly(ester amides) with $y = 3$, $y = 4$, $y = 5$, and $y = 9$ *and* $x \geq 5$ indicate that in the high-temperature mesomorphic state as well as in the quick-quenched corresponding samples, the polymers exhibit a smectic liquid crystalline order. In the stable crystalline modification, the repeat distance along the draw direction is essentially the same as for the liquid crystalline state. In addition, the results indicate that (1) the conformations in the x-alkylene segments are exclusively trans, while the conformations in the y-alkylene segments include both trans and gauche states; (2) the presence of the gauche conformers in the y-segments is associated with the liquid crystallinity of the poly(ester amides) and allows the chains in the crystalline and mesomorphic states to adopt an overall zigzag configuration; and (3) the conformation of y-segments involving the α-CH_2–CH_2 bond in crystalline poly(ester amides) is only trans for $y = 2$, exists as a distribution of, or rapidly interconverts between, trans and gauche for $y = 3$, and is only gauche for $y = 4$, $y = 5$, and $y = 9$. The above results appear to be congruent with existing literature data on comparable polyesters.

Introduction

A family of highly regular strictly alternating hydrogen-bonded poly(ester amides)



was recently synthesized and characterized.[1] By techniques such as hot-stage cross-polarized light microscopy, differential scanning calorimetry (DSC), and variable-temperature X-ray diffractometry, it was found that when $y = 2$ the poly(ester amides) change from the crystalline solid to the isotropic melt in a single step. Subsequent determination[2] of the heats of transition indicates the phase transition to be a normal melting point. When $y \geq 3$, the poly(ester amides) were found to change from the crystalline phase to the isotropic melt in several steps, whose number and magnitude depend on the sizes of y and x. A temperature interval, associated with the multiple transitions, was found in which these polymers exhibited thermotropic liquid crystallinity.[1] Calorimetric studies[2] indicate the multiple transitions to be involved with at least one mesomorphic state. Infrared studies[1] indicate the amide groups of the poly(ester amides) to be hydrogen bonded in the crystalline, glassy, and mesomorphic states. X-ray studies suggest that these hydrogen bonds exist between chains and are not intrachain bonds. Thus, a novel family of interchain hydrogen-bonded highly regular liquid-crystalline poly(ester amides) with $y \geq 3$ was obtained.[1]

The wide-angle X-ray diffraction (XRD) patterns of poly(ester amides) with $y \geq 3$, obtained from the high-temperature thermotropic samples and from their quick-quenched room temperature analogues, are characterized by a very small number of reflections.[1] The number of reflections for polymers with $x \geq 5$ is smaller than for polymers with $x < 5$. The flat plate camera patterns of highly oriented polymers with $y \geq 3$ *and* $5 \leq x \leq 14$ each contains only a single intense and diffuse reflection perpendicular to the draw direction, i.e., equatorial, and several sharp streaks in the draw direction, i.e., meridional. These streaks can be indexed as increasing orders of a single repeat distance in the draw direction (fiber axis). Except for the equatorial and meridional reflections, no other reflections were visible in the XRD patterns of poly(ester amides) with $y \geq 3$ and $5 < x \leq 14$. The diffuse equatorial reflection and the multiple sharp meridional streaks indicate that these poly(ester amides) have fluidlike disorder in the equatorial plane but possess a high degree of long-range order along the draw direction. This pattern is typical of smectic liquid crystalline substances and we, therefore, conclude that these poly(ester amides) have a smectic liquid crystalline order. In the stable crystalline state, several additional X-ray reflections are present. Infrared spectroscopy revealed[1] that practically all of the amide groups in the poly(ester amides) are associated with one another by interchain hydrogen bonds (H-bonds). These H-bonds were found to persist into the mobile mesomorphic state at high temperature.[1] In order to maximize the number of interchain H-bonds, the chains are forced into axial register which, in turn, is responsible for the multiple meridional (00l) reflections from which the smectic layer repeat distance can be calculated. This repeat distance was found to be essentially the same for each poly(ester amide) in the crystalline state and in the high-temperature mesomorphic, mobile, and birefringent, phase.[1]

The repeat distance of the smectic layers in the draw direction is consistently shorter than the length of a chemical repeat unit of the fully extended poly(ester amide) chain. Thus, the polymer chain has to be inclined with respect to the draw direction. As will be shown below, the tilt angle in our case was found to be about 30°. Because the meridional reflections of the poly(ester amides) are strictly perpendicular to the equatorial plane, and because the meridional repeat distance is shorter than the molecular repeat distance, we know[3] that the chains are not merely tilted relative to the draw direction but that the tilt alternates in the direction producing an overall zigzag configuration in the crystalline and mesomorphic states. The XRD results strongly suggest the mesomorphic phase to be a smectic C or a twisted smectic C state. The above observations were found to hold true for the poly(ester amides) with $y \geq 3$ and $5 < x \leq 14$ which could be oriented. Poly(ester amides) with $y = 2$ could not be sufficiently oriented for flat-plate XRD patterns to be obtained and directly compared with those of $y \geq 3$.

0024-9297/89/2222-1137$01.50/0

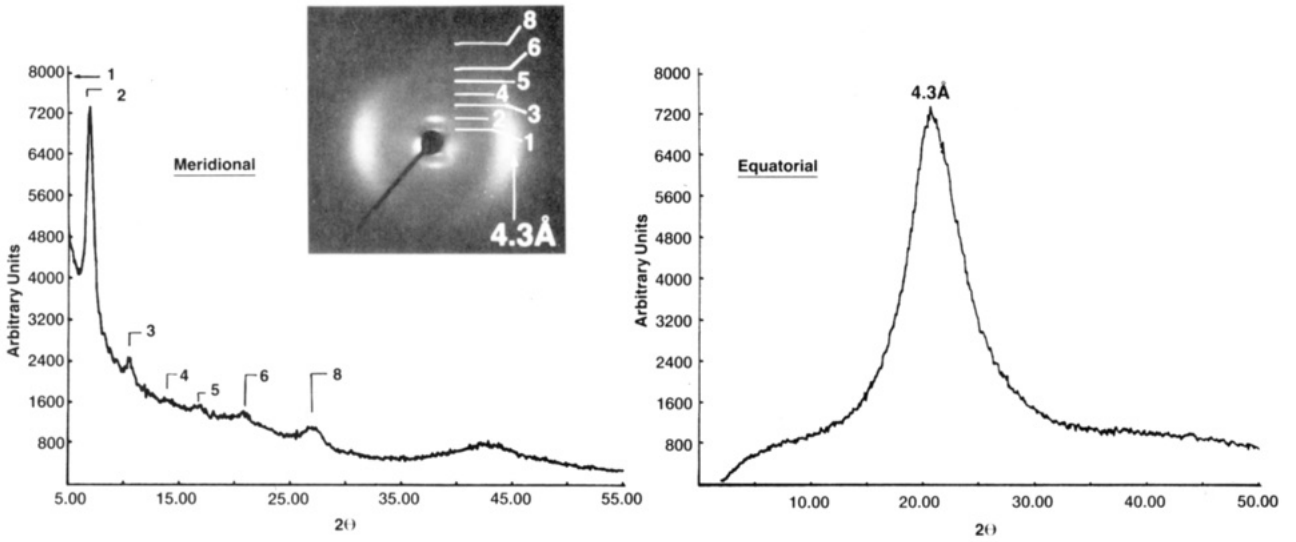


Figure 1. Meridional (left) and equatorial (right) patterns of poly(ester amide) $y = 3$, $x = 7$. The corresponding flat-plate camera photograph is shown in the insert.

Nevertheless, the repeat distances of poly(ester amides) with $y = 2$ indicate their chains to be tilted relative to the draw direction.

The directional changes indicated above are associated with bends in the chain brought about by replacing one or more trans conformations in the alkylene segments by gauche conformers. From XRD patterns of several poly(ester amides) in which either x or y were held constant while the other was systematically changed, the contribution to the repeat distance in the draw direction due to incremental addition of methylene units can be assessed. A trans conformation of bonds along an alkylene chain contributes 1 Å or more to its projected length in the draw direction, while a gauche conformation of bonds, causing a bend in the chain, produces a far smaller contribution. Thus, the existence of trans or gauche conformations in the x or y segment can be determined from careful evaluation of the incremental contribution of additional methylene groups to the repeat distance in the draw direction.

Many polymer studies in the literature infer that that solid-state carbon-13 NMR lacks sufficient resolution to clearly differentiate between trans and gauche conformations of the bonds about an ester "α-CH_2" group. By our convention, the α-CH_2 is the methylene connected on one side to the ester oxygen and on the other side to another methylene group. However, a few reports indicate that several polymers do produce resonances for trans and gauche conformations about α-CH_2 with chemical shifts that are sufficiently resolved to permit assignment. Among such polymers are polypivalolactone,[4] which is highly crystalline, and the somewhat less crystalline poly(ethylene terephthalate).[5] We have found that similar resolution of trans and gauche conformations about the α-CH_2 is possible in the case of poly(ester amides).

In this work both X-ray and solid-state carbon-13 NMR techniques were combined to detect where the bends are located in the poly(ester amide) chains in the crystalline and mesomorphic states.

Experimental Section

Wide-angle X-ray diffraction (XRD) patterns were obtained at ambient temperature from powdered samples, unoriented molded films, and heat-treated quick-quenched films by using a Philips APD 3600 automated diffractometer operating in parafocus mode and using monochromatized copper Kα radiation. The same procedure was used to obtain the equatorial reflections from oriented samples. Transmission scans were obtained on a Huber two-circle diffractometer to record the meridional data. Flat-plate photographs were obtained from all oriented samples by using a Unicam X-ray camera. To obtain oriented films, the poly(ester amides) were molded above their clearing points to produce films 0.25 mm thick. These films were quick-quenched and XRD patterns indicated them to be amorphous. Strips were cut from the films, heated to the point where intense birefringence appeared when observed by a cross-polarized light microscope, stretched by hand at this temperature to draw ratio of 3–5, and then rapidly quenched in ice/water mixture. Highly crystalline strips and those for $y = 2$ polymers could not be significantly drawn and tore in the process.

Solid-state carbon-13 NMR spectra were obtained by using cross-polarization (CP) and magic angle spinning (MAS) techniques[6-8] at 50.3 MHz on a Varian XL-200 spectrometer equipped with Doty Scientific solids accessories. Powdered samples were spun at 3.5–4.5 kHz. The magic angle was adjusted to within 0.1° by using the ^{79}Br spectrum of KBr.[9] Spectra were acquired with a 2-ms contact time and a 2-s repetition time. Solution NMR spectra were also obtained at 50.3 MHz by using the same Varian XL-200 spectrometer. All carbon-13 spectra were referenced externally to tetramethylsilane at 0.0 ppm.

Results and Discussion

X-ray Diffraction. The repeat distances in the draw direction were obtained from the first and higher order d-spacings in the meridional direction (00l) of patterns obtained from appropriately oriented specimens. These were either semicrystalline or quick-quenched from the mesomorphic state. The results of flat-plate photographs were in agreement with the meridional scans in transmission mode on oriented specimens and with the diffractometer scans in parafocus mode from powdered samples. Figure 1, for the poly(ester amide) $y = 3$, $x = 7$, is typical. The 00l diffraction spacings correspond to the repeat distances along the draw direction (fiber axis) and are listed in Table I. Quite a few of the reported repeat distances are averages of several results obtained in different scans of single batches or several batches of each polymer. Also listed in Table I are the lengths of the fully extended chemical repeat units (all alkylene bonds between the ester oxygens and amide carbonyls in the trans conformation) calculated from data of Flory[10] and Manzini et al.[11] and the tilt angle between the chain and the draw direction. The increments per added methylene group, calculated from the differences in the (00l) diffraction spacings, are listed in the last column of Table I. The d-spacings do not display any odd–even effect and mon-

Table I
Analysis of X-ray Diffraction Patterns of Poly(ester amides)

polymer		calcd chain-axis, Å[a]	obsd fiber-axis repeat, Å	tilt angle btwn chain- and fiber-axes, deg	obsd increment along fiber-axis per CH_2, Å
y	x				
3	1	22.9	18.5	36	
3	3	25.4	21.3	33	1.4
3	4	26.7	22.6	32	1.3
3	7	30.5	26.4	30	1.3
3	8	31.8	27.8	29	1.4
3	11	35.6	31.7	27	1.3
3	14	39.4	35.0	27	1.1
5	11	38.1	32.0	33	
5	14	41.9	35.6	32	1.2
9	3	33.0	29.8	25	
9	4	34.3	31.0	25	1.2
9	7	38.1	33.3	29	0.8
9	8	39.4	34.3	29	1.0
9	11	43.2	37.5	30	1.1
9	12	44.5	38.6	30	1.1
9	14	47.0	41.0	29	1.2
2	14	38.1	34.6	25	
3	14	39.4	35.0	27	0.4
4	14	40.6	35.2	30	0.2
5	14	41.9	35.6	32	0.4
9	14	47.0	41.0	29	1.4
2	7	29.2	26.3	26	
3	7	30.5	26.4	30	0.1
4	7	31.8	26.6	33	0.2

[a] Calculated from data in ref 10 and 11. The chain-axis projection of a trans CH_2–CH_2 bond is 1.27 Å.

otonically increase with increased x. These facts together with the rather constant tilt angle imply that the overall nature and symmetry of chain packing in the crystalline unit cell is about the same for all poly(ester amides) with $x > 4$.

It can be seen in Table I that whenever y was held constant and x incrementally increased, the corresponding increase in d-spacing was in the range of 1.0–1.4 Å per CH_2 group, except for one sample for which the increment was 0.8 Å per methylene unit. On the other hand, when x was held constant and y changed from 2 to 3 to 4 and on to 5, the incremental additions to the d-spacings were in the range 0.1–0.4 Å. Only upon changing from $y = 5$ to $y = 9$ did the incremental change of the d-spacings increase to 1.35 Å for the bonds above and beyond those counted for $y \leq 5$. The addition of 1.0–1.4 Å indicates that a trans conformation was added to the alkylene chain, while an addition of only 0.1–0.4 Å indicates that a gauche conformation is associated with the newly added methylene. Thus, our data indicate that in the crystalline state the x-alkylene segments are fully extended and all the C—C and C—C=O bonds are in the trans conformation.

The XRD data alone are insufficient to determine the conformations in the y-segments when $y = 2$. However, the XRD data do tell us that the additions to obtain $y = 3$, 4, and 5 are all associated with the presence of gauche conformers. It can be stated, therefore, that the introduction of gauche conformations into the chain, and the associated chain-bend, is limited to the y-segments, i.e., in between the ester groups. The addition of methylenes to $y = 5$ in order to form polymers with $y = 9$ is associated with incremental addition of only trans conformers. One may speculate that the number of gauche conformations needed for bending the chain is already satisfied when $y = 5$ and there is no geometrical or energetic need to add more gauche conformations.

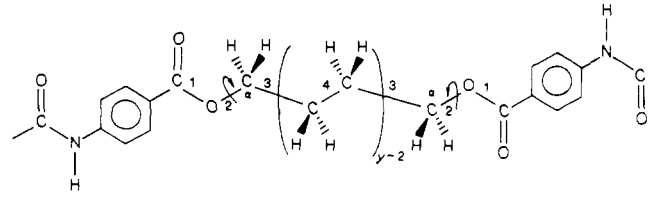
Table II
Carbon-13 NMR Chemical Shifts of α-Methylenes in Solid Poly(ester amides)

polymer		chem shift,[a] ppm	polymer		chem shift,[a] ppm
y	x		y	x	
2	4	60.9	4	4	65.5
2	14	61.1	4	14	65.2
3	4	61.0	5	4	64.9
3	6	63 (br)	5	14	65.0
3	8	63 (br)	9	4	65.4
3	14	63 (br)	9	14	65.7

[a] Unless indicated otherwise, all resonances are sharp.

X-ray diffraction patterns of the mesomorphic phases of the poly(ester amides) were obtained at elevated temperatures and also at room temperature from samples quick-quenched from the mobile mesomorphic phases.[1] Mesomorphicity was observed in polymers only when $y \geq 3$ and never when $y = 2$. The d-spacings and repeat distances along the overall chain direction in the mesomorphic state were remarkably similar to the corresponding ones obtained from the crystalline and oriented solids listed in Table I. Because of the great similarity in repeat distances, we believe that the above description of extended x-segments and twisted y-segments when $3 \leq y \leq 5$, and partly twisted $y = 9$ segments, is valid for at least the first mesomorphic phase above the crystalline state.

Solid-State Carbon-13 NMR. Solid-state carbon-13 NMR was pivotal in determining the conformational nature of the $y = 2$ segments and the location of the gauche conformers in the y-segments of the other poly(ester amides). The assignment of solid-state ^{13}C NMR peaks was based on literature data[4,5] and model compounds such as 1,3-propanediol bis(p-aminobenzoate) and 1,3-propanediol bis(N-n-nonyl-p-amidobenzoate). Solution spectra were also obtained from these model systems as well as the poly(ester amides) $y = 3$, $x = 6$ and $y = 3$, $x = 8$. All the poly(ester amides) give resonances between 60 and 70 ppm that can be assigned to the α-CH_2 groups of y, attached to oxygen:



The chemical shifts obtained by solid-state ^{13}C NMR from several poly(ester amides) are listed in Table II. The shifts for $y = 2$ and $y = 4$ are easily understood. Only $y = 3$ presents special problems. In poly(ethylene terephthalate) (PET), a good model for $y = 2$, a sharp resonance at 61.5 ppm and a broad resonance at 64.5 ppm can be assigned respectively to the crystalline and amorphous fractions of the polymer.[5] X-ray diffraction analysis[12] of crystalline PET shows a trans-trans-trans conformation of the glycol O–CH_2–CH_2–O bonds. Infrared, Raman, and ^1H NMR spectroscopy show these bonds to be predominantly trans-gauche-trans in amorphous PET in the melt, glass, and solution.[13-18] Therefore, peaks around 61.0 ppm can be assigned to a trans-trans-trans conformation of the ethylene glycol sequence in the y-segments of the $y = 2$ poly(ester amides).

The α-CH_2 resonance appears at 65 ppm for both samples with $y = 4$. This is a typical chemical shift for α-CH_2 groups of linear alkyl esters with over four carbon atoms in the chain and is observed in both solution and solid-state spectra. This resonance is expected to shift to higher field

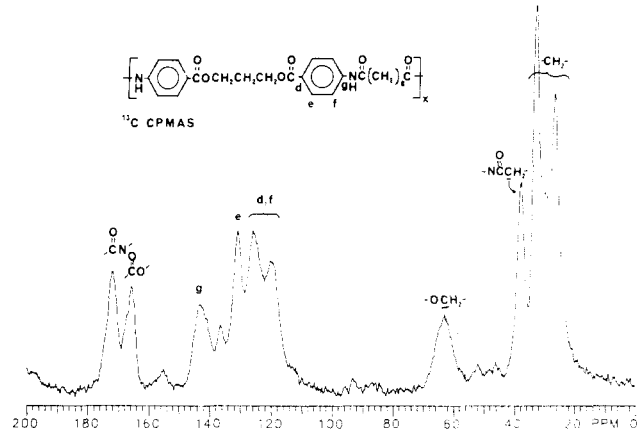


Figure 2. Carbon-13 NMR spectrum of poly(ester amide) $y = 3$, $x = 8$ obtained by using cross-polarization and magic angle spinning techniques. The broad peak centered at 63 ppm is for the α-CH_2 carbon. In the cases of $y = 2$ and $y \geq 4$, sharp resonances for α-CH_2 appear at 61 and 65 ppm, respectively. Secondary peaks in the scan are spinning side bands.

by 3–4 ppm if bond 4 were in a gauche conformation, due to the γ-gauche effect,[19] but it is unaffected by the conformations of bond 3. In fact, there is considerable evidence that there is little difference in energy between the gauche and trans conformations around bond 3.[20-25] A system comparable to $y = 4$ is poly(butylene terephthalate) (PBT). Here, both X-ray and infrared studies indicate that in its relaxed crystalline state the $CH_2CH_2CH_2CH_2$ segment is present in a gauche(+)-trans-gauche(−) conformation,[20-23] although a recent solid-state NMR study[26] questions this interpretation. However, this study does point out that a gauche conformation about the 3 bond in esters of butylene glycol ($y = 4$) produces an upfield shift of the internal methylene groups but does not alter the chemical shift of the α-CH_2's. In our poly(ester amides) the resonances for the internal methylenes of the diesters are not resolved from the internal methylenes of the diamide segments. We conclude that solid-state NMR alone cannot distinguish between trans and gauche conformations about bond 3 for $y \geq 4$.

It can be stated, however, that bond 4 must be in a trans conformation since a gauche conformation would shift the α-CH_2 resonance upfield and this is not observed. Since the incremental d-spacing changes observed by XRD require the introduction of gauche conformations into the y-segment as y increases from 2 to 3 to 4, it is likely that the gauche conformations are localized on bond 3.

The esters of trimethylene glycol in the $y = 3$ poly(ester amides) represent a unique case. Here bond 4 and bond 3 are symmetrically equivalent. We propose that in the $y = 3$, $x = 4$ poly(ester amide), the $CH_2CH_2CH_2$ group in the y-segment exists in a gauche-gauche conformation so that both α-methylenes experience shielding by a γ-gauche interaction and shift to 61.0 ppm as a sharp singlet. This is in agreement with literature data on poly(trimethylene terephthalate) (PTMT),[25] a polyester analogue of $y = 3$. Accordingly, the conformations of the $CH_2CH_2CH_2$ segment of crystalline PTMT are gauche-gauche, with identical conformations present in two trimethylene glycol dibenzoate model compounds. Figure 2 is typical of poly(ester amides) with $y = 3$ and $x = 6$, 8, and 14, where a broad resonance centered at about 63 ppm is observed. This is consistent with either a distribution of conformers or a rapid interconversion of trans and gauche bonds, so that an average shift is observed.

Literature data on polyesters with pentamethylene and nonamethylene sequences in their chains are not available to serve as analogues for our $y = 5$ and $y = 9$ poly(ester amides). However, the excellent agreement between our observations of the conformations involving the α-CH_2 groups in poly(ester amides) with $y = 2$, 3, and 4 allows us to proceed one step further. By extension, and from the combined X-ray and solid-state NMR results, we conclude that in the poly(ester amides) with $y = 5$ and $y = 9$, the OCH_2CH_2 groups each contains a gauche conformation.

To evaluate the effects of crystallinity on the solid-state carbon-13 NMR results, three samples of the poly(ester amide) $y = 3$, $x = 14$ were prepared. One was quick-quenched from the isotropic melt with no crystallinity detectable by X-ray techniques, the second was annealed for several hours upon cooling from the melt to obtain a sample with about 60% crystallinity, and the third sample was in the "as-prepared" state with about 35% crystallinity. The solid-state carbon-13 NMR spectra of the three samples in the range of interest (60–70 ppm) were essentially identical. In the course of this work a few additional spectra were obtained from different batches of the same $y = 3$ or $y = 5$ poly(ester amides). In no case were differences in the 60–70 ppm range observed which could be attributed to differences in degrees of crystallinity between the different batches. The above indicates that the solid-state carbon-13 NMR techniques is insensitive to the crystallinity of the poly(ester amides) with $y \geq 3$. We believe the reason for this is that the α-CH_2 groups in the y-segments of $y \geq 3$ are already in the gauche state in the crystalline phase and this conformation does not change when the poly(ester amide) turns mesomorphic or amorphous.

It is important to recognize that all the poly(ester amides) with $y \geq 3$ and $x > 5$ are characterized by smectic-type XRD patterns. They all contain gauche conformers in their y-segments. Importantly, they all exhibit thermotropic liquid crystalline behavior.[1] On the other hand, none of the $y = 2$ poly(ester amides) showed any propensity toward mesomorphic behavior.[1] Their y-segments are only trans in the crystalline state and, at present, we do not know whether the chains are merely tilted with respect to the draw direction or are in a zigzag configuration. Either way, the existence of the y-segments of $y = 2$ polymers exclusively in trans conformation appears to be related to the inability of these poly(ester amides) to pass through a mesomorphic state. Conversely, the presence of gauche conformers in the y-segments of $y \geq 3$ poly(ester amides) allows for thermotropic liquid crystallinity.

Conclusions

The X-ray data for poly(ester amides) with $y \geq 3$ *and* $x \geq 5$ indicate the existence of smectic liquid crystalline order. The repeat distance in the draw direction is essentially the same for the crystalline and mesomorphic polymers.

In our poly(ester amides) the conformations in the x-alkylene segments are exclusively trans, while the conformations in the y-alkylene segments include both trans and gauche states.

The presence of gauche conformers in the y-segments allows the chains in the crystalline and mesomorphic states to bend and adopt an overall zigzag configuration.

The conformation of the y-segments involving the α-CH_2 groups is solely trans for the crystalline poly(ester amides) with $y = 2$. In the crystalline and mesomorphic states of the poly(ester amides) with $y = 3$, the conformations about the α-CH_2 groups are less defined and appear to be present as a distribution of, and/or rapidly interconvert between,

trans and gauche conformers. For the polymers with y = 4, 5, and 9, the conformations of bond 3 have been shown to be gauche.

We speculate that in the mesomorphic state, the extended segments containing the aromatic and x-alkylene residues can rotate and delineate cones of rotation. In the crystalline state their rotational motion is inhibited. The repeat distance in the draw direction is essentially the same in both states. This is necessary in order to support the highest number of H-bonds. The ability to rotate is probably due to the presence of gauche conformers in the y-alkylene segments, explaining why no mesomorphicity was observed in the fully trans y = 2 polymers.

Acknowledgment. We thank Dr. C. E. Forbes, A. Kahn, and M. H. Cozine for their help in obtaining the solution NMR spectra and several solid-state spectra of the model compounds and of some of the poly(ester amides) and H. Minor for help with some X-ray scans.

Registry No. Poly(ester amide) y = 3, x = 1, 114677-86-0; poly(ester amide) y = 3, x = 3, 114677-88-2; poly(ester amide) y = 3, x = 4, 114677-89-3; poly(ester amide) y = 3, x = 7, 114677-92-8; poly(ester amide) y = 3, x = 8, 114677-93-9; poly(ester amide) y = 3, x = 11, 114677-95-1; poly(ester amide) y = 3, x = 14, 114677-97-3; poly(ester amide) y = 5, x = 11, 114678-16-9; poly(ester amide) y = 5, x = 14, 114678-18-1; poly(ester amide) y = 9, x = 3, 114678-20-5; poly(ester amide) y = 9, x = 4, 114678-21-6; poly(ester amide) y = 9, x = 7, 114678-22-7; poly(ester amide) y = 9, x = 8, 114678-23-8; poly(ester amide) y = 9, x = 11, 114678-24-9; poly(ester amide) y = 9, x = 12, 114691-78-0; poly(ester amide) y = 9, x = 14, 114678-25-0; poly(ester amide) y = 2, x = 14, 114677-84-8; poly(ester amide) y = 3, x = 14, 114677-97-3; poly(ester amide) y = 4, x = 14, 114678-08-9; poly(ester amide) y = 5, x = 14, 114678-18-1; poly(ester amide) y = 2, x = 7, 114677-82-6; poly(ester amide) y = 4, x = 7, 114678-04-5; poly(ester amide) y = 2, x = 4, 114677-81-5; poly(ester amide) y = 3, x = 6, 114677-91-7; poly(ester amide) y = 4, x = 4, 114678-01-2; poly(ester amide) y = 5, x = 4, 114678-10-3.

References and Notes

(1) Aharoni, S. M. *Macromolecules* **1988**, *21*, 1941.
(2) Aharoni, S. M. *Macromolecules*, in press.
(3) Leadbetter, A. J.; Norris, E. K. *Mol. Phys.* **1979**, *38*, 669.
(4) Veregin, R. P.; Fyfe, C. A.; Marchessault, R. H. *Macromolecules* **1986**, *19*, 2379.
(5) Sefcik, M. D.; Schaefer, J.; Stejskal, E. O.; McKay, R. A. *Macromolecules* **1980**, *13*, 1132.
(6) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(7) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.
(8) Schaefer, J.; Stejskal, E. O. In *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; Wiley: New York, 1979; Vol. 3, pp 283–324.
(9) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.
(10) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley-Interscience: New York, 1969.
(11) Manzini, G.; Crescenzi, V.; Ciana, A.; Ciceri, L.; Della-Fortuna, G.; Zotteri, L. *Eur. Polym. J.* **1973**, *9*, 941.
(12) Daubeny, R.; Bunn, C. W.; Brown, C. J. *Proc. R. Soc. London* **1954**, *A226*, 531.
(13) Aharoni, S. M.; Sharma, R. K.; Szobota, J. S.; Vernick, D. A. *J. Appl. Polym. Sci.* **1983**, *28*, 2177.
(14) Lin, S. B.; Koenig, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2277.
(15) Schmidt, P. G. *J. Polym. Sci. A.* **1963**, *1*, 1271.
(16) Heffelfinger, C. J.; Schmidt, P. G. *J. Appl. Polym. Sci.* **1965**, *9*, 2661.
(17) Stokr, J.; Schneider, B.; Doskocilova, D.; Lövy, J.; Sedlacek, P. *Polymer* **1982**, *23*, 714.
(18) Konda, A.; Nose, K.; Ishikawa, H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1495.
(19) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.
(20) Mencik, Z. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2173.
(21) Hall, I. H.; Pass, M. G. *Polymer* **1976**, *17*, 807.
(22) Yokouchi, M.; Sakakibara, Y.; Chatani, Y.; Tadokoro, H.; Tanaka, T.; Yoda, K. *Macromolecules* **1976**, *9*, 266.
(23) Dobrovolny-Marand, E.; Hsu, S. L.; Shih, C. K. *Macromolecules* **1987**, *20*, 1022.
(24) Stokr, J.; Doskocilova, D.; Schneider, B.; Lovy, J. *Collect. Czech. Chem. Commun.* **1981**, *46*, 1658.
(25) Poulin-Dandurand, S.; Perez, S.; Revol, J.-F.; Brisse, F. *Polymer* **1979**, *20*, 419.
(26) Gomez, M. A.; Cozine, M. H.; Tonelli, A. E. *Macromolecules* **1988**, *21*, 388.

Dependence of the Packing Structure of Mesogenic Groups on the Flexible Spacer Length of Liquid Crystalline Side-Chain Polymers

Takanari Yamaguchi, Tadahiro Asada,* Hisao Hayashi, and Naotake Nakamura†

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan, and Department of Chemistry, Ritsumeikan University, Kyoto 603, Japan. *Received May 17, 1988; Revised Manuscript Received August 17, 1988*

ABSTRACT: Poly(cholesteryl ω-(methacryloyloxy)alkanoates) (pChMO-n, n = 1–5, 7, 9–11, 15, the carbon number of the alkyl chain), which are liquid crystalline side-chain polymers, were studied by differential scanning calorimetry and by small-angle X-ray scattering. The clearing point decreases with increasing n up to 7 and shows the even–odd effect, but it becomes almost constant with $n > 7$. The plot of transition entropy at the clearing point against n has a sharp negative inflection at n = 9. X-ray investigations show that the packing of mesogenic groups in pChMO-n with short spacers (n = 1–7) differs from that in pChMO-n with longer ones (n = 9–15). These two types of packing coexist in pChMO-n (n = 9–11) below their phase transition temperatures.

Introduction

Liquid crystalline side-chain polymers combine the properties of low molecular weight liquid crystals with those of polymers.[1-3] Investigations during this decade have shown that a flexible spacer linking the mesogenic group to the polymer main chain plays an important role in the realization of the liquid crystalline state.[4]

Finkelmann and Rehage have summarized the data on a number of liquid crystalline side-chain polymers and showed that the clearing point (T_{cl}) of these polymers generally decreases with increasing length of the flexible spacer.[5] Recently, however, Simon and Coles have reported on a side-chain polysiloxane in which T_{cl} increases

† Ritsumeikan University.

0024-9297/89/2222-1141$01.50/0