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Hydrogen-Bonded Liquid-Crystalline Poly(ester amides): Morphology and Kinetics of Structurization upon Cooling from the Isotropic Melt

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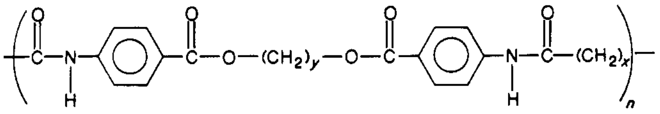
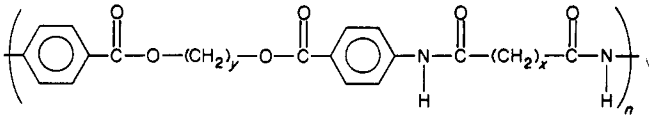
ABSTRACT: The morphologies and growth kinetics of particles growing out of isothermally annealed poly(ester amides) cooled from the isotropic melt were observed in the case of several typical polymers, with the following conclusions: (1) The shape of the developing ordered particles depends on the anneal temperature relative to T_{uje}, the uppermost major endotherm in the heating cycle. When the temperature, T_s, where spontaneous growth starts is higher than T_{uje} the structures appear as loosely packed spherulites originating from rather large batonnets or brushlike entities in instances where $y = 5$ and x is large or from small nuclei when $y = 5$ and x is small. For $y = 3$, small nuclei prevail for all x. When $T_s < T_{uje}$ the growing structures appear as densely packed spherulites. (2) The growth kinetics of the ordered particles appear to conform with the common kinetics of polymer crystallization, even though the ordered structures appear at temperatures far higher than the transition to the stable crystalline state.



Introduction

Recently, a large family of strictly alternating highly regular poly(ester amides) was synthesized,[1] in which the number of methylene groups between two ester residues is denoted by y and the number of methylenes between two amide groups is denoted by x. Most of these polymers are highly crystalline at room temperature with essentially all amide groups forming interchain hydrogen bonds with one another.[1] Upon heating, all poly(ester amides) with $y = 2$ and several others change to isotropic melts in a single step, but most other poly(ester amides) with $y = 3$, $y = 4$, $y = 5$, and $y = 9$ convert from the crystalline solid to the isotropic melt in several steps, in which the mobile or fluid polymers exhibit optical birefringence. The cases of poly(ester amides) with $y = 3$ or $y = 5$ and $8 \leqslant x \leqslant 14$ are most dramatic, with some of them undergoing up to five reproducible phase transitions observable in DSC heating scans and by hot-stage cross-polarized light microscopy.[1] Subsequently,[2] the heats of these transitions were estimated from DSC heating scans and crystallinity indices determined from X-ray powder patterns. The heats of transition, $\Delta H°$, fall in the range 9.7–99 kJ/mol for the major transitions and less than 2.4 kJ/mol for the minor ones. The minor transitions exist mostly in poly(ester amides) from the $y = 3$ and $y = 5$ families having $10 \leqslant x \leqslant 14$. They always appear above the uppermost major endotherm, T_{uje}, and below the isotropization temperature, T_i. The magnitudes of the minor transitions indicate that they involve at least one mesomorphic phase.[2] In the case of polymers exhibiting multiple major transitions but no minor ones, the uppermost transitions appears also to involve a mesomorphic phase. The observations above were corroborated by variable-temperature X-ray diffractometry[1] and by room temperature wide-angle X-ray diffraction patterns obtained from samples quick-quenched (at a rate not slower than −1200 K/min) from the isotropic melt and the mesomorphic state.



When heated to the liquid crystalline state, the poly(ester amides) exhibit a featureless, grainy birefringent texture. In general, when the polymer is soft and mobile its birefringence is intense. At higher temperatures many of the polymers abruptly turn spontaneously fluid, the nature of the light scattering is apparently altered, and the birefringence turns dull. If during the heating cycle a liquid-crystalline poly(ester amide) is isothermally annealed at the mesomorphic state for up to 90 min, no visible changes occur. If, however, the very same polymer is heated to the isotropic melt and then cooled to the same isothermal temperature, ordered structures start growing from the melt, often within seconds. In the case of the liquid-crystalline poly(ester amides) with $y = 3$ or $y = 5$ and $10 \leqslant x \leqslant 14$, these structures appear at temperatures up to 45 K above the uppermost major endotherm in the respective DSC heating cycle. In most cases the DSC cooling trace remains completely smooth in the region of interest, leaving no sign, exothermic or endothermic, associated with the development of structures above T_{uje}. At lower temperatures, there appear major exotherms in the cooling cycles. Microscopy and X-ray studies indicated[1] these exotherms to be associated with major structurization, most often crystallization into a stable C_2 crystalline modification.

In general, for $y = 3$ and $y = 5$, the ability to grow ordered structures in the cooling cycle rapidly deteriorated as the length of x decreased. Such structures developed above the uppermost major endotherm when $8 \leqslant x \leqslant 14$. In the interval $5 \leqslant x \leqslant 8$, the structures formed at some supercooling below T_{uje}, and for $x \leqslant 4$ only occasional crystallization occurred at very large supercooling. In the last case very fine crystals formed with no apparent spherulitic growth. Some supercooling was required to induce crystallization in poly(ester amides) with $y = 4$ and $y = 9$, but in these cases rather well-organized spherulites developed in all instances where $x + y \gtrsim 10$.

In this paper, some morphological features of the structures of typical poly(ester amides) growing from the cooled isotropic melt, and the kinetics of their formation, will be described and briefly discussed.

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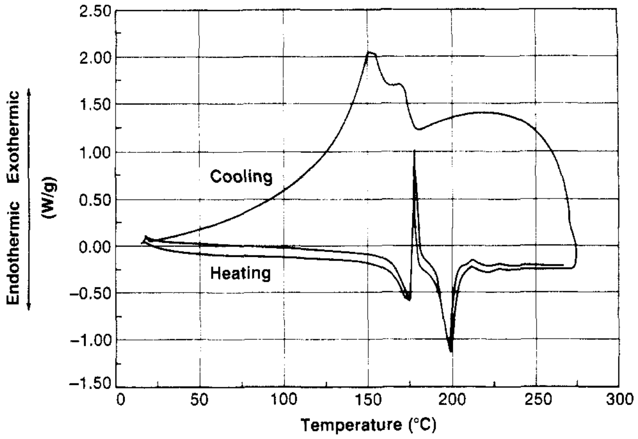

Figure 1. Heating and cooling cycles of poly(ester amide) $y = 3$, $x = 14$. Note reproducible minor transitions in the upper part of the heating cycle and absence of transitions in the corresponding part of the cooling cycle.

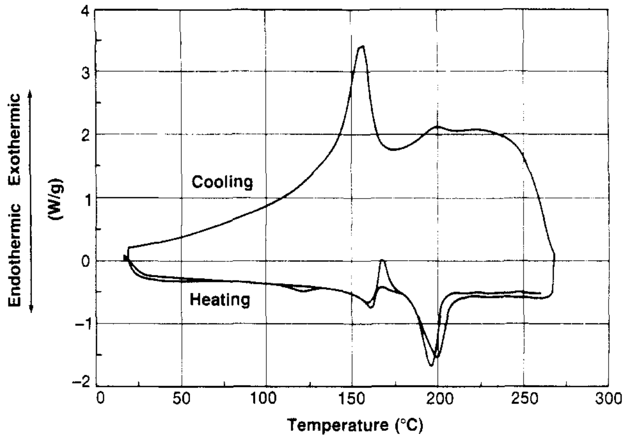

Figure 2. Heating and cooling cycles of poly(ester amide) $y = 5$, $x = 14$. Note reproducible minor transitions above the uppermost major endotherm and a rare, minor transition in the cooling cycle.

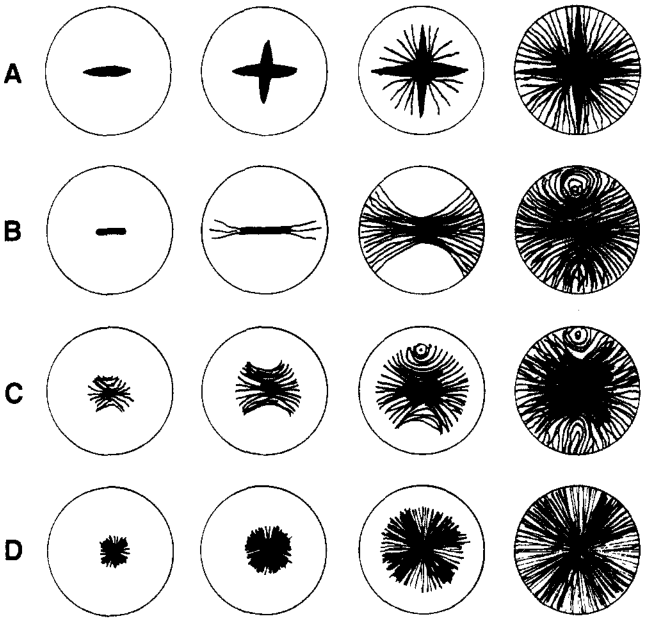

Figure 3. Isothermal growth types observed in poly(ester amides) cooled from the isotropic melt. Each type presented at four different stages during its growth.

Experimental Section

All microscopic observations were conducted with a cross-polarized light microscope (Olympus BHS) equipped with an automatically controlled Polaroid camera and a Mettler FP-82 hot stage controlled by a Mettler FP-80 central processor capable of maintaining temperatures to within ±0.1 K. In addition to constant visual observations and record keeping, there were taken at intervals photomicrographs with 100× magnification showing the growth of structures with time and their morphologies. From measurements of several such structures in sequences of micrographs, the average growth rates were easily determined. All heatings and coolings were at 10 K/min, the same rate used in DSC studies. Prior to the microscopy studies, each poly(ester amide) was subjected to several heating and cooling cycles in a Du Pont differential scanning calorimeter (DSC) Model 910 controlled by a Du Pont Model 9900 computer/thermal analyzer. All runs were performed under nitrogen atmosphere. Transition temperatures were defined by the positions of the peaks in the DSC scans. Details of the polymer synthesis and other characterization procedures were given in ref 1.

Wide-angle X-ray diffraction (WAXD) patterns were obtained from the powdered samples at ambient temperature. The indices of crystallinity were abstracted from the WAXD patterns by measuring the areas under the crystalline reflections only and dividing them by the total areas of the WAXD patterns above the background noise. Each such index determination was repeated at least twice for better statistics.

Results and Discussion

Morphology. In Figures 1 and 2 DSC traces of heating and cooling cycles for the poly(ester amides) $y = 3$, $x = 14$ and $y = 5$, $x = 14$ are, respectively, reproduced. These are typical of poly(ester amides) with large x and $y = 3$ or $y = 5$. The lack of any ordering exotherm in the cooling cycle in Figure 1, down to the major structurization exotherms corresponding to the major endotherms in the heating cycle, is far more commonplace than the small and broad exotherm in the high-temperature interval in the cooling cycle in Figure 2. As indicated in the Introduction, intense featureless birefringence accompanied by slow mobility or dull grainy birefringence together with spontaneous flow is typical of most poly(ester amides) at or above the uppermost major endotherm, T_{uje}, in their heating cycles. For polymers with $y = 3$ or $y = 5$ and $8 \leq x \leq 14$, the dull birefringence and spontaneous flow cover the whole range of minor transitions above T_{uje}. Annealing of such polymers for up to 90 min during the heating cycle at or around any minor transition temperature failed to produce morphological changes or growth of ordered structures. Conversely, when cooled from the isotropic melt to the same anneal temperature, large organized structures rapidly grew from the melt, within minutes or often within seconds. We have followed by microscopy the growth of structures of several representative poly(ester amides) while being annealed isothermally during the cooling cycles. The results are tabulated in Table I and schematically represented in Figure 3.

Several general observations concerning overall growth characteristics of structures sufficiently large to be followed by microscopy are presented in the following.

(1) Upon cooling from the isotropic melt, a point T_s is reached where growth spontaneously starts. Above this point no growth occurs even after prolonged annealing. Usually, growth becomes more rapid as the temperature decreases below T_s.

(2) In all cases where batonnets and/or loosely packed spherulites were formed, these structures appeared at or higher than the uppermost major endotherm: $T_s \geqslant T_{\mathrm{uje}}$. In the cases where densely packed spherulites appeared, they started growing at temperatures substantially lower than the uppermost major endotherm: $T_s \ll T_{\mathrm{uje}}$.

(3) In general, no additional nucleation was observed during isothermal growth. In some cases, a small number of very small nuclei started growing later than others,

Table I
Microscopic Observations of Growth of Ordered Structures of Poly(ester amides) upon Cooling from the Isotropic Melt at a Constant Temperature and Approximate Avrami Exponents

poly(ester amide)	T_{uje}, K	T_s, K	n	type in Figure 3	crystal type	microscopic observations
$y = 5, x = 11$	455	483	1.58	A	branching fibrillar	initially batonnets; then develop into very loose structures; constant number of nuclei; upon cooling, no decoration of structures, fine growth in between them
$y = 5, x = 14$	472	519.9, 523	3.17, 3.17	B, B	spherical, spherical	initially long brushes, then grows into very loosely packed spherulites; spherulites reach a constant size and then their number increases with time; upon cooling, additional spherulites appear; with further cooling, finer morphology appears
$y = 5, x = 7$	463	463.2	2.90	C	spherical	start as loose spherulites; constant number of nuclei; continues the same; upon prolonged anneal, spherulites grow with fine texture in between them; upon cooling, no decoration; fine texture with time
$y = 3, x = 14$	473.1	488.0	3.09	C	spherical	starts as loosely packed, well-formed spherulites; constant number of nuclei; grow as same spherulites; upon cooling, no decoration, no different texture
$y = 9, x = 3$	503	463	3.13	D	spherical	start as well-formed densely packed spherulites; constant number of nuclei; upon cooling, no decoration; new finer texture in between spherulites
$y = 4, x = 11$	474	458	2.9	D	spherical	start as well-formed densely packed spherulites; constant number of nuclei; upon cooling, both decoration of spherulites and new finer texture

producing the same morphology, but these small nuclei were generally discernible by careful microscopic scans with higher magnification at the beginning of overall growth. The isothermal growth of the rather constant number of structures continued until they either impinged upon one another or, in quite a few cases, growth simply stopped or enormously slowed even though amorphous material was clearly visible around the ordered structures.

(4) When the temperature was further reduced after some growth was present, the following were observed: (a) In the case of densely packed spherulitic growth, an exterior layer of different morphology started growing on and decorating the surface of the existing spherulites. (b) New, fine structures nucleated and started growing in the amorphous phase in between the existing spherulites. (c) Both the above morphologies appeared concurrently.

(5) When batonnets isothermally grew from the melt, they often had fine fringes at their growing tips, giving the appearance of branching fibrillar growth. In many instances during isothermal growth, the batonnets started developing into flat crosslike structures, type A in Figure 3. The arms of each crosslike structure appeared to be morphologically the same. After the crosslike structures were fully formed, a new, fine-fibril growth started emanating from the centers of the crosses and gradually filled the areas between their arms. If maintained isothermally, the growing entities attained spherulitic shape and continued to grow as spherulites at a slow rate, often stopping to grow without impinging on one another. When cooled, a new and very fine morphology, salt-and-pepper with occasional minuscule needles, appeared and filled the volume in between the spherulites and between the finer fibrillar growth within the loosely packed spherulites.

(6) Oftentimes growth started as rodlike or elongated straight fibrillar entities which, after being kept isothermally, matured into sheafs which later developed into spherulites. These spherulites were not densely packed but were rather loose with lots of voids and empty space between the branches, filled with amorphous polymer. When maintained isothermally, the loosely packed spherulites grew until they either impinged upon each other or growth became so slow that it could not be estimated conveniently. Upon cooling, finer new growth, usually of salt-and-pepper texture, developed in between the spherulites and between the branches within them.

It is important to emphasize that when ordered structures grew out of the cooled melt above T_{uje}, no corresponding exotherms were observed in the DSC cooling cycles of most poly(ester amides). This lack of exotherms is only in part due to the slow growth rate of the ordered structures and is largely brought about by the very small heats of transition associated with this kind of structurization. This is supported by two facts: (1) The heats and entropies of the minor transitions above the uppermost major endotherm in the heating cycle are extremely small with $\Delta H°$ being smaller than 2.5 kJ/mol and $\Delta S°$ smaller than 5 J/(mol K). (2) The rate of cooling in the DSC instrument and on the microscope hot state was 10 K/min. Considering that many structures developed within seconds, a rapid growth rate relative to the cooling rate, one cannot explain the lack of exotherms by invoking only a very slow growth rate relative to the cooling rate.[3] Transitions from the isotropic state to a mesomorphic phase in which no exotherm appeared in the DSC cooling scans, as in our case, were reported in the literature.[4-7] This characteristic appears to occur in polymers having long flexible spacers along their main chain.

The morphologies of the well-developed spherulites schematically described in the two right-hand columns of rows B and C in Figure 3 are not unique and were previously observed during the crystallization of various polymers. However, the smallness of the heat of structurization of the poly(ester amides) indicates that only a small increment in order is gained at transitions above T_{uje} and that, most likely, the orientational order in the ordered structures growing above the uppermost major endotherm is quite imperfect.[8]

Kinetics. We are aware of only one study dealing with the kinetics of structurization of liquid crystalline polymers upon cooling from the isotropic melt.[9] Therefore, it was felt that a kinetic study of this process in the poly(ester amides) will be of interest. The structurization rates were followed by taking at time intervals photomicrographs of the structures as they isothermally grew from the melt and then measuring their sizes. Several structures in each sample were thus followed, their sizes recorded and then averaged, and the averages subsequently plotted as function of growth time. In the case of the poly(ester amide) $y = 5, x = 11$, conforming to type A in Figure 3, the length and thickness of the growing batonnets were measured.

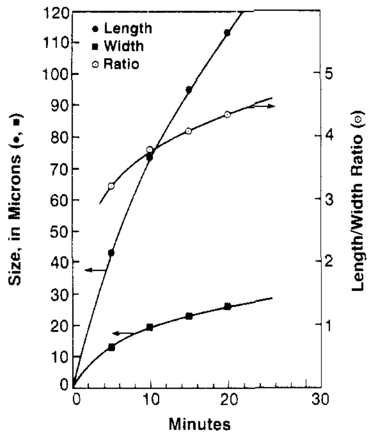

Figure 4. Batonnet growth of $y = 5$, $x = 11$ at 210 °C (cooled from 250 °C). Sizes in micrometers, times in minutes.

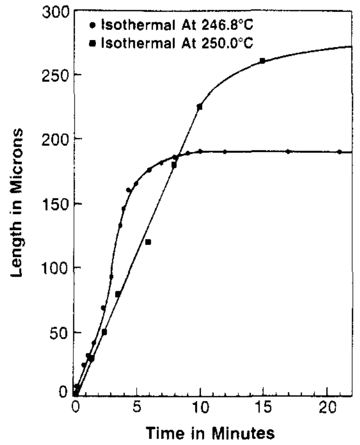

Figure 5. Growth of ordered structures of $y = 5$, $x = 14$, isothermally at 246.8 °C (●) and 250.0 °C (▪). Sizes in micrometers, times in minutes.

The results are shown in Figure 4. In Figure 5, the growth of elongated brushes of poly(ester amide) $y = 5$, $x = 14$ at two different temperatures was followed. In both cases the growth follows type B in Figure 3 and the measured length is the distance from the center to the growing tip of the averaged brushlike structure. As the loose spherulites evolve from such structures, the measured length corresponds to the radius of the developing spherulites. The spherulitic radii of two poly(ester amides), $y = 3$, $x = 14$ and $y = 5$, $x = 7$, are plotted against time in Figure 6. In both instances the growth is a type C growth and starts as loosely packed spherulites. The results for two poly(ester amides) exhibiting type D growth at temperatures below the corresponding T_{uje} are shown in Figure 7.

The volumes of batonnets were calculated from the size of the growing structures of polymer $y = 5$, $x = 11$ by the use of the relationship

$$v^0 = r^2h \tag{1}$$

where v^0 is the volume of the growing particle at time t, h is the length of the entity at that time, and r is its thickness. In the case of spherulitic growth, for all other polymers in Table I, the volumes of the spherulites were obtained from r, the measured radius at time t, by

$$v^0 = (4/3)\pi r^3 \tag{2}$$

The volumes of not less than six entities per sample were then averaged to minimize the measurement scatter and the averaged volumes plotted on log–log paper against time. Since in our case there were no impingements of the growing spherulites upon one another, the following variant of the Avrami equation was used[10] to obtain the Avrami exponent n:

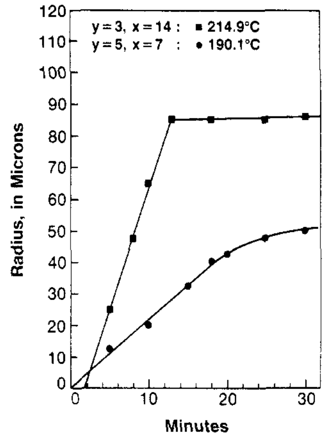

Figure 6. Spherulitic growth of poly(ester amides) from the cooled isotropic melt. $y = 3$, $x = 14$ at 214.9 °C (▪) and $y = 5$, $x = 7$ at 190.1 °C (●). Sizes in micrometers, times in minutes.

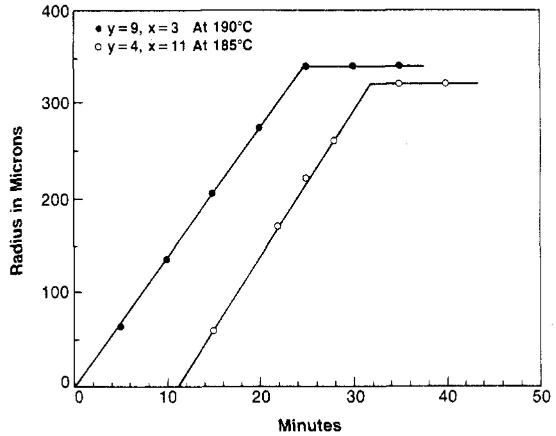

Figure 7. Spherulitic growth of poly(ester amides) from the cooled isotropic melt. $y = 9$, $x = 3$ at 190 °C (●) and $y = 4$, $x = 11$ at 185 °C (○). Radii in micrometers, times in minutes.

$$v^0 = Kt^n \tag{3}$$

describing the time dependence of the growth of individual particles. Here K is a constant which is not necessarily identical with the constant describing the development of crystallinity in bulk polymers. Under carefully defined conditions the exponent n is an integer, but very often this is not the case.[10] In agreement with expectation, the observed values of n, in Table I, were around 1.5 for the batonnets of the poly(ester amide) $y = 5$, $x = 11$ and around 3 for all other polymers. The results above are congruent with those in ref 9 with respect to the fact that, apparently, the growth of the mesomorphic phase out of the isotropic melt follows the same shape-dependent time exponents as the growth of a crystalline phase out of a less ordered one.

The reasons for the drastic decrease in the growth rate before all available amorphous polymer was consumed, in Figures 5–7, are not known at present. They may involve some segregation according to molecular weight and/or substantial temperature changes at the tips of the growing structures.

Conclusions

(1) The shape of ordered particles developing in mesomorphic poly(ester amides) isothermally annealed upon cooling from the isotropic melt depends on the anneal temperature relative to T_{uje}, the uppermost major endotherm in the heating cycle. When $T_{\mathrm{s}} > T_{\mathrm{uje}}$ the structures

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appear as loosely packed spherulites originating from rather large batonnets or brushlike entities in instances where $y = 5$ and x is large or from small nuclei when $y = 5$ and x is small, or when $y = 3$. On the other hand, when $T_s < T_{uje}$ the growing structures appear as densely packed spherulites originating from very small nuclei.

(2) The growth kinetics of ordered particles appear to conform with the common kinetics of polymer crystallization. The Avrami exponents describe athermal growth, as expected from microscopy observations on individual particles.

Registry No. (4,4'-$H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2$)($HO_2C(CH_2)_{11}CO_2H$) (copolymer), 114677-43-9; (4,4'-$H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2$)($HO_2C(CH_2)_{11}CO_2H$) (SRU), 114678-16-9; (4,4'-$H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2(HO_2C(CH_2)_{14}CO_2H)$ (copolymer), 114677-45-1; (4,4'-$H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2$)($HO_2C(CH_2)_{14}CO_2H$) (SRU), 114678-18-1; (4,4'-$H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2$)($HO_2C(CH_2)_7CO_2H$) (copolymer), 114677-40-6; (4,4'-$H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2$)($HO_2C(CH_2)_7CO_2H$) (SRU), 114678-13-6; (4,4'-$H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2$)($HO_2C(CH_2)_{14}CO_2H$) (copolymer), 114677-24-6; (4,4'-$H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2$)($HO_2C(CH_2)_{14}CO_2H$) (SRU), 114677-97-3; (4,4'-$H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2$)($HO_2C(CH_2)_3CO_2H$) (copolymer), 114677-48-4; (4,4'-$H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2$)($HO_2C(CH_2)_3CO_2H$) (SRU), 114678-20-5; (4,4'-$H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2$)($HO_2C(CH_2)_{11}CO_2H$) (copolymer), 114677-34-8; (4,4'-$H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2$)($HO_2C(CH_2)_{11}CO_2H$) (SRU), 114678-07-8.

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Geometric and Rotational Parameters for the Conformational Modeling of Liquid Crystalline Polyesters

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ABSTRACT: Geometric and rotational parameters appropriate for the molecular modeling of aromatic polyesters have been deduced by combining a study of published crystal, experimental and theoretical data, and quantum mechanical computations of our own. The central C–O bond of conjugated esters was estimated to be somewhat less rigid than generally imagined (barrier at 90° of about 7 kcal mol^{-1}), a finding of particular relevance to mesogenicity of aromatic polyesters. Further to this, a parameter set has been derived to enable the use of the MM2 program with aromatic esters and to infer the rotational energy profiles of the aromatic ester bonds more clearly. Differences in the geometry and rotational barriers of the variously substituted aromatic ester moieties commonly incorporated into polymers are discussed with reference to the chain mechanical properties that can be engineered by judicious formulation on the part of the polymer synthesist.

Introduction

A fundamental assumption underlying materials science is that properties are ultimately related to the interatomic correlations and forces within the material. In the case of thermotropic liquid crystalline polyesters, therefore, an understanding of important properties (e.g., phase transitions, moduli, coefficient of thermal expansion, permeability, electronic properties, etc.), and an enhanced power to predict these properties for the purposes of design, could be gained from a thorough description of these correlations and forces.

The problem is conventionally dealt with in two stages. The first is to understand the conformational behavior of isolated polymer chains. This is relatively accessible information, as techniques of intramolecular modeling of organic molecules have proved quite successful. The second is to understand how individual chains interact with their neighbors. It should be stressed that this approach is merely a convenience, made practicable by the observation that certain correlations within an organic material ("interatomic bonds") are much stronger and more permanent than some other correlations in the material ("intermolecular interactions").

This paper describes an investigation into the geometric and rotational parameters applicable to isolated chains of thermotropic liquid crystalline polyesters. A reasonable assessment of these parameters should lay a basis for modeling of interchain structure, of dynamics, and of polymer properties.

Main chain liquid crystalline polyesters synthesized to date typically consist of ester-linked mesogens (usually aromatic moieties), with or without the inclusion of flexible spacers (generally alkyl hydrocarbon). Aromatic rings are frequently taken to be rigid, flat entities in conformational modeling studies, and the validity of this approximation will not be assessed here. Conformational aspects of bi- and terphenyl aromatic moieties have been investigated by Meurisse et al.[1] Flexible spacer conformation has been the subject of an in-depth study by the same authors,[2] using the PCILO semiempirical quantum mechanical technique. The conformational energetics of alkyl hydrocarbon, in general, has been the subject of comprehensive studies and is well described by force fields such as MM2.[3] However, an ester group linking two aromatic rings (Figure 1) has received less thorough attention, and neither accurate nor sufficient force field parameters have been

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