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Arthur James Tipton
University of Massachusetts Amherst

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PREPARATION OF LIQUID CRYSTALLINE POLYMERS WITH CYCLOHEXANE MESOGENS

A Dissertation Presented
by
ARTHUR JAMES TIPTON

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirement for the degree of

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Polymer Science and Engineering

PREPARATION OF LIQUID CRYSTALLINE POLYMERS WITH CYCLOHEXANE MESOGENS

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ARTHUR JAMES TIPTON

Approved as to style and content by:

Simon W. Kantor

Simon W. Kantor, Co-chairperson of Committee

Robert W. Lenz

Robert W. Lenz, Co-chairperson of Committee

Stephen S. Hixson

Stephen S. Hixson, Member

William J. MacKnight

William J. McKnight, Acting Department Head
Polymer Science and Engineering

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The act of writing and finishing a dissertation provides a convenient avenue for expressing thanks, primarily because it so clearly delineates between two of life's stages.

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To Tom St. Pierre, the man who first introduced me to Polymer Science---like many others, I wished I had had more time to spend with you. You were, beyond all other teachers I have known, an inspiration.

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In the future, when I remember the time that I spent in the Pioneer Valley I will remember the friends I made who were an inspiration and at times a crutch for me, most especially Doreen and Rob. Special thanks also to all the 18 Red Gate crew, most especially Marty, and to Rick and Paul and the other members of the all too occasional Thursday Night Poker Gang.

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Finally to Katie---what can I say? You helped me through the "dissertation blues", but more than that you have helped me through the most difficult times of my life, remaining always a source of inspiration and strength. For the past decade, for the past two years, I thank you.

ABSTRACT

PREPARATION OF LIQUID CRYSTALLINE POLYMERS WITH CYCLOHEXANE MESOGENS

SEPTEMBER 1988
ARTHUR JAMES TIPTON
B.S., SPRING HILL COLLEGE
PhD., UNIVERSITY OF MASSACHUSETTS AT AMHERST
Directed by: Simon W. Kantor and Robert W. Lenz

Because of their outstanding mechanical properties, liquid crystalline polymers have become commercially important in the past decade. However, the molecular rigidity and linearity of these materials makes processing difficult. Specifically, the low solubility and high melting point of these materials necessitate the use of a strongly acidic solvent or a high processing temperature. A great deal of research has been directed at easing processing of liquid crystalline polymers. Most of this research has involved copolymerization of flexible units within the polymer backbone, and although this method leads to a lower-melting polymer, it also decreases mechanical performance. The research described in this dissertation was begun to examine possibilities for preparing liquid crystalline polymers that would melt below 300 °C without an inherent decrease in mechanical strength.

For liquid crystallinity the overriding necessities are rigidity and high axial ratio. Aromatic mesogens, used in all commercial liquid crystalline polymers and most research examples, possess both these requirements. However, aromatic mesogens also have a relatively high intermolecular attraction (high ΔH) and no mechanism for becoming less flexible on melting (low ΔS). A great advantage would be rigid, high-axial materials with a low intermolecular attractive force and a degree of flexibility available on melting. Cyclohexane in a *trans*-1,4-linkage has a higher axial ratio than a *para*-linked benzene ring. Polarizability is less because there is no aromaticity, leading to a decrease in melting point, viscosity and dielectric anisotropy in low molecular weight liquid crystals. However, little work has been done in examining cyclohexane mesogens in polymers, and no well-characterized, all-cyclohexane-based polymer has been described. The goal of this research was to examine a number of polymeric systems based solely on cyclohexane.

The desired linear cyclohexane monomers were separated from isomer mixtures by recrystallization and other methods. Configurational purity was monitored by nuclear magnetic resonance and high performance liquid chromatography. With these monomers, polyesters, polyamides and polyesteramides were synthesized. Examples from all classes displayed liquid crystalline phases. Copolymerization was used to lower the melting points of the polymers, and several series of copolymers were synthesized. In most cases, cocrystallinity occurred, leading to a linear decrease in melting point. Linear, aliphatic monomers were also incorporated in polymers. In these copolymers, linear decreases in melting point were also observed, indicating that the linear, flexible monomer cocrystallized with the cyclohexane monomer by adopting the same conformation.

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BD	1,4-butanediol
BP	4,4'-bipiperidine
1,3-CHD	*cis*-1,3-cyclohexanediol
1,4-CHD	*trans*-1,4-cyclohexanediol
CHDAA	*trans*-1,4-cyclohexanediacetic acid
CHDC	*trans*-1,4-cyclohexanedicarboxylic acid dichloride
CHDI	*trans*-1,4-cyclohexane diisocyanate
CHDM	*trans*-1,4-cyclohexanedimethanol
DMF	*N, N*-dimethylformamide
DSC	differential scanning calorimetry
GC/MS	gas chromatography/mass spectrometry
HBA	4-hydroxybenzoic acid
HD	1,6-hexanediol
HFIP	hexafluoroisopropanol
HMPA	hexamethylphosphoramide
4-HP	4-hydroxypiperidine
INPA	isonipecotic acid
IV	inherent viscosity
M_n	number average molecular weight
M_w	weight average molecular weight
$\vec{n}$	order parameter
n_2	mole fraction, component 2
NMR	nuclear magnetic resonance

PET	poly(ethylene terephthalate)
POM	polarized optical microscopy
R	gas constant
S	quadrapole
S_N2	nucleophilic substitution, bimolecular
T	temperature
T_m	melting temperature
TGA	thermogravimetric analysis
TMP	4,4'-trimethylenedipiperidine
WAXS	wide angle X-ray scattering
V_1	volume fraction, component 1
ΔH	enthalpy change
ΔS	entropy change
θ	angle between order parameter and individual mesogens
λ	wavelength
χ	polymer solvent interaction parameter

CHAPTER 1

INTRODUCTION

Liquid crystals: a historical perspective

The assumption that all physical matter exists in three physical states was contradicted at the end of the last century by experiments with certain organic compounds (1). In the first well-documented study, one hundred years ago, Friedrich Reitnitzer, an Australian botanist, discovered that cholesterol derivatives do not melt as ordinary organic compounds do. To his surprise, cholesterol benzoate formed a colorful, turbid liquid at 145 °C, and only after continued heating (and an interesting color change) did it form a conventional liquid melt above 179 °C (2, 3).

It is now known that Reitnitzer was observing the *mesophase*, or middle phase, of a liquid crystalline compound. This type of liquid crystal has different thermal properties in three orthogonal directions and does not melt to an isotropic fluid. The simplest case of a molecule displaying this anisotropy of melting is a rigid and anisotropic covalently-bonded molecule. The cholesterol benzoate is a good example as seen in Figure 1.1, with a much greater dimension in the X direction than in the Y or Z directions.

Although cholesterol benzoate forms a liquid crystalline melt, cholesterol does not. Two important changes occur on preparation of the benzoyl ester from the hydroxy compound, cholesterol. One is an increase in length of the molecule. The second is the replacement of a strong intermolecular interacting group, the hydroxy, with a less powerful one, the phenyl ester. These two changes are central to the formation of a liquid crystal and are illustrative of trends repeated throughout the field of liquid crystals.

Research into liquid crystals waned in the first half of this century, but active research has resumed, particularly in the last quarter-century (3). In that time a wide range of low molecular weight liquid crystals have been synthesized, and commercial applications for these have abounded, particularly in optical display devices (4-7).

Polymers may be obvious candidates for liquid crystallinity due to the long polymer chains. However, from the viewpoint of obtaining a liquid crystalline state, most polymers do not display phases indicative of this high axial ratio. The key reason is chain folding, which causes a length decrease of approximately two orders of magnitude between the extended chain structure and the random coil adopted by most polymers (8). For a polymer to possess a liquid crystalline state, either the polymer must be composed entirely of rigid linear units which inhibit chain folding (such that the entire polymer backbone is a rigid rod), or the polymer must contain rigid units which are liquid crystalline, and are connected by nonrigid structures which may or may not chain fold.

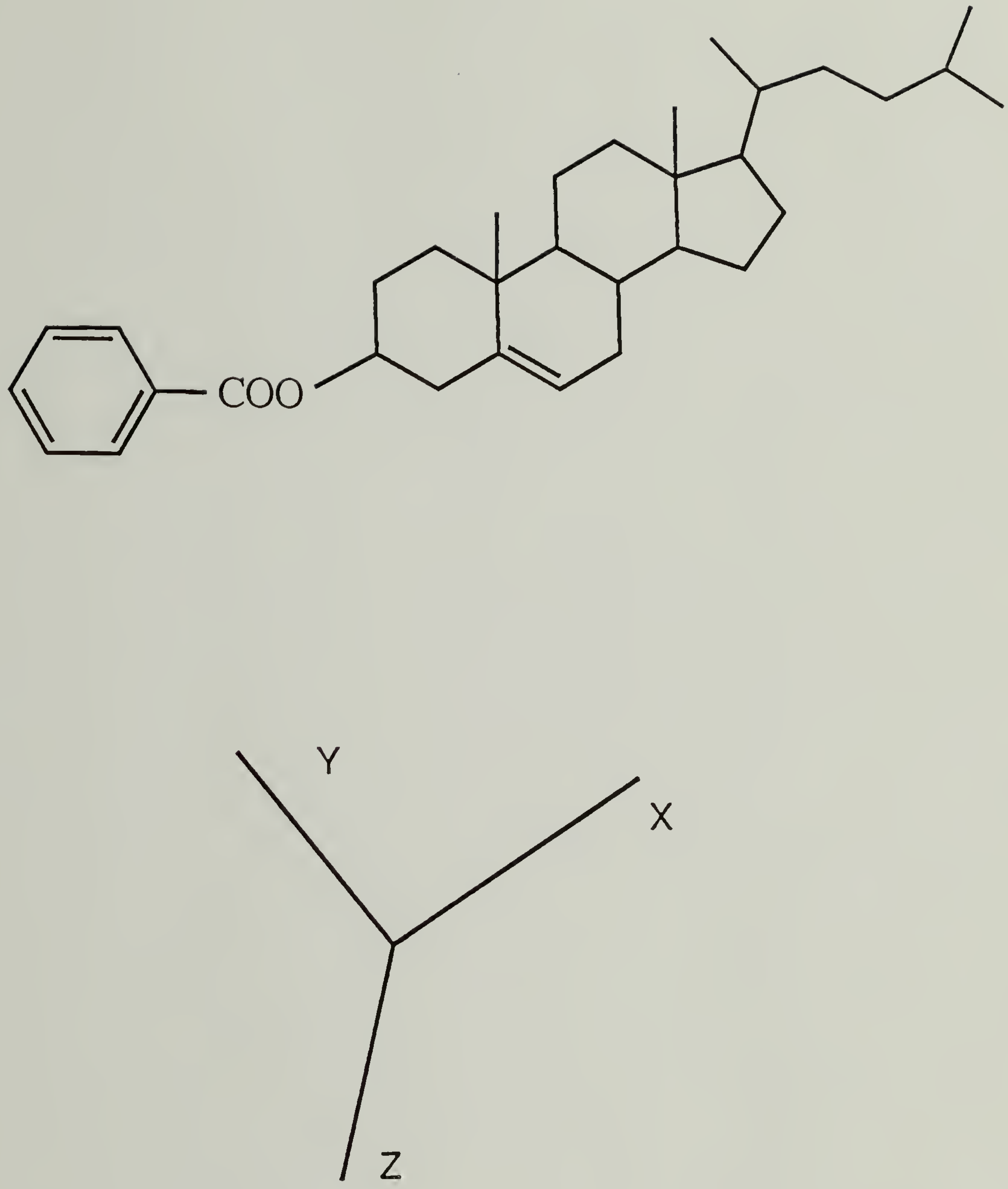


Figure 1.1 The structure of cholesterol benzoate

The first polymeric liquid crystals discovered were in biological systems. Bawden and Pirie noted that a tobacco mosaic virus solution separated into an isotropic and an anisotropic phase at relatively low concentrations (9). In 1950 Elliot and Ambrose described anisotropic properties of poly(α-benzyl-L-glutamate) in chloroform and described orientation as "... [arising] from a process akin to crystallization in the solution"(10). Paul Flory developed his much-cited theory of lyotropic liquid crystals in 1956 (11), suggesting lyotropic behavior in synthetic polymer systems. This behavior was subsequently confirmed with several examples of lyotropic, all-aromatic polyamides by DuPont researchers (12-15).

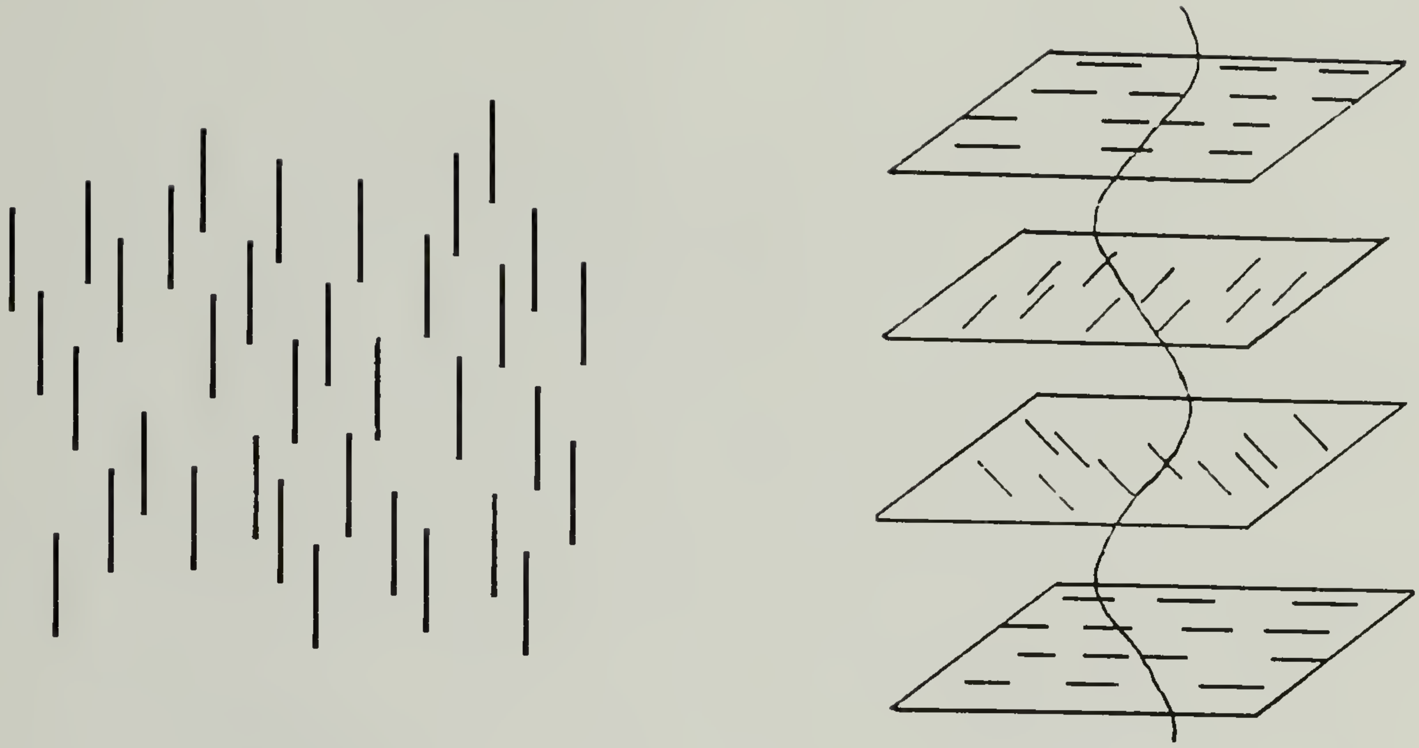
The existence of thermotropic liquid crystalline polymers, implied though not directly stated in Flory's theory, was suggested by DeGennes in 1975 (16). He theorized that rigid mesogens linked into a polymer backbone by a flexible spacer would be thermotropic. This suggestion was confirmed in the next few years by several workers (17-19). In these early cases the polymers were all polyesters. These claims were predated by a 1965 report of an anisotropic melt intermediate formed in the graphitization of bituminous material and other pre-graphite materials (20). These materials were of relatively low molecular weight (~1700), but the molecular order was high and the material displayed optical anisotropy that had "...obvious affinity with liquid crystals" (20).

Research in the last decade has continued with the trend of lyotropic polyamides and thermotropic polyesters. These polymers have been based almost solely on aromatic mesogens. Examples of both classes display excellent mechanical properties, and as a result have obtained a wide range of commercial applications (21, 22). It is worth noting that much of the research on liquid crystals originated in searches for polymers for high temperature applications. In these studies, many liquid crystals were made, but never examined as such (23-25).

Definition of terms

Liquid crystals can be classified by several methods, three of which will be described here. The first is on the basis of structural phase as shown in Figure 1.2, which illustrates the three main phase types of liquid crystals. The *nematic* phase has orientational order, but loses positional order (26); there is no correlation between the centers of gravity of the molecules. This combination results in individual oriented mesogens, which can move relatively independently of each other, giving rise to a low viscosity fluid.

A *cholesteric* liquid crystal, such as the cholesterol benzoate that Reitnitzer examined, is very similar to a nematic phase, with the added structural feature of a pitch developing perpendicular to the orientational order. This helical stacking of nematic layers forms in many liquid crystalline compounds with a chiral center, and in mixtures of a nematic liquid crystal dissolved in a chiral, non-liquid-crystalline solvent (27). The helical pitch is proportional to the wavelength of light. The pitch is sensitive to the temperature and electromagnetic fields, and can be changed instantly and reversibly by either, with a resulting color change. This behavior is what Reitnitzer noted (2) and is used in a range of commercial applications (3, 28, 29).



Nematic

Cholesteric

Smectic A

Smectic C

Figure 1.2 Classification of liquid crystals based on structural phase

The *smectic* liquid crystal phase is more ordered, as shown by two examples in Figure 1.2, in that the orientational order is supplemented by a layer spacing. Within a layer, there may be no positional order as in smectic A and smectic C structures. There may also be well-defined order in the layers, seen in increasing amounts in going from B (hexagonal) to D (body center cubic) to E (orthorhombic), and in F through I, which are higher order smectics (primarily tilt versions of B, D and E) (26, 30, 31). The lettering reflects only the order of discovery.

The second classification of liquid crystalline polymers is based on the method of obtaining the liquid crystalline state. *Lyotropic* liquid crystals require the action of a solvent. *Thermotropic* liquid crystals form a liquid crystalline phase on heating. It must be understood that in both cases the same intermolecular forces are overcome. In fact, some polymers show both types of behavior (32-34). A common problem for rigid rod polymers which are likely candidates for liquid crystallinity is that the transition temperature needed to obtain a thermotropic liquid crystalline state may be above a degradation temperature, or the polymer may not be soluble enough to obtain the necessary concentration needed for a lyotropic liquid crystalline phase (~10%). Both factors may be operative and a polymer structure that is thought to be ideal for possessing a liquid crystalline phase may not allow observation of that phase. This research contains numerous examples of such behavior.

Lyotropic materials are, of course, lyotropic over a certain temperature range. Heating (or cooling) may lead to an isotropic phase and cooling (or heating) may lead to a condensed phase. Little work has been done on solution properties of lyotropics over a temperature range or, more importantly, on solution studies of non-liquid crystalline rigid rod polymers over a temperature range. In many polymer structures the analysis is made more complicated by the morphology of blockiness in copolymers or the possibility of phase separation. For example, a structure that is thought to be a side chain polymeric mesogen may actually be either a crystal or a liquid crystal in the main chain solvent (35).

A third classification of polymeric liquid crystals is based on the placement of the mesogen. As seen in Figure 1.3, the mesogen may either be located in the backbone or connected to the backbone. These two types are known as *main chain* and *side chain*, respectively.

The research described in this dissertation involves main chain liquid crystalline polymers only, and an in-depth description of types and uses of main chain polymers will be presented later in this chapter. Side chain liquid crystalline polymers will be described only briefly here. The interested reader is referred to several reviews (36-38).

Side chain liquid crystalline polymers have been based on polyacrylate (39, 40), polymethacrylate (41, 42), siloxane (43, 44) and other polymers (45). Interesting properties are seen with the absence or presence of a spacer and a tail, and on changing the length of the spacer and the number of bonds (odd or even) in the spacer (36-38, 46). Interesting recent developments include polymers with both side chain and main chain mesogens (47) and polymers where the side chain mesogen is connected to the polymer backbone at the midpoint of the mesogen (48). Such a core/clad arrangement leads to a mesogen orientation in the same direction as the polymer chain orientation.

The applications of side chain liquid crystalline polymers are very different from the high strength uses of main chain liquid crystalline polymers. The uses of

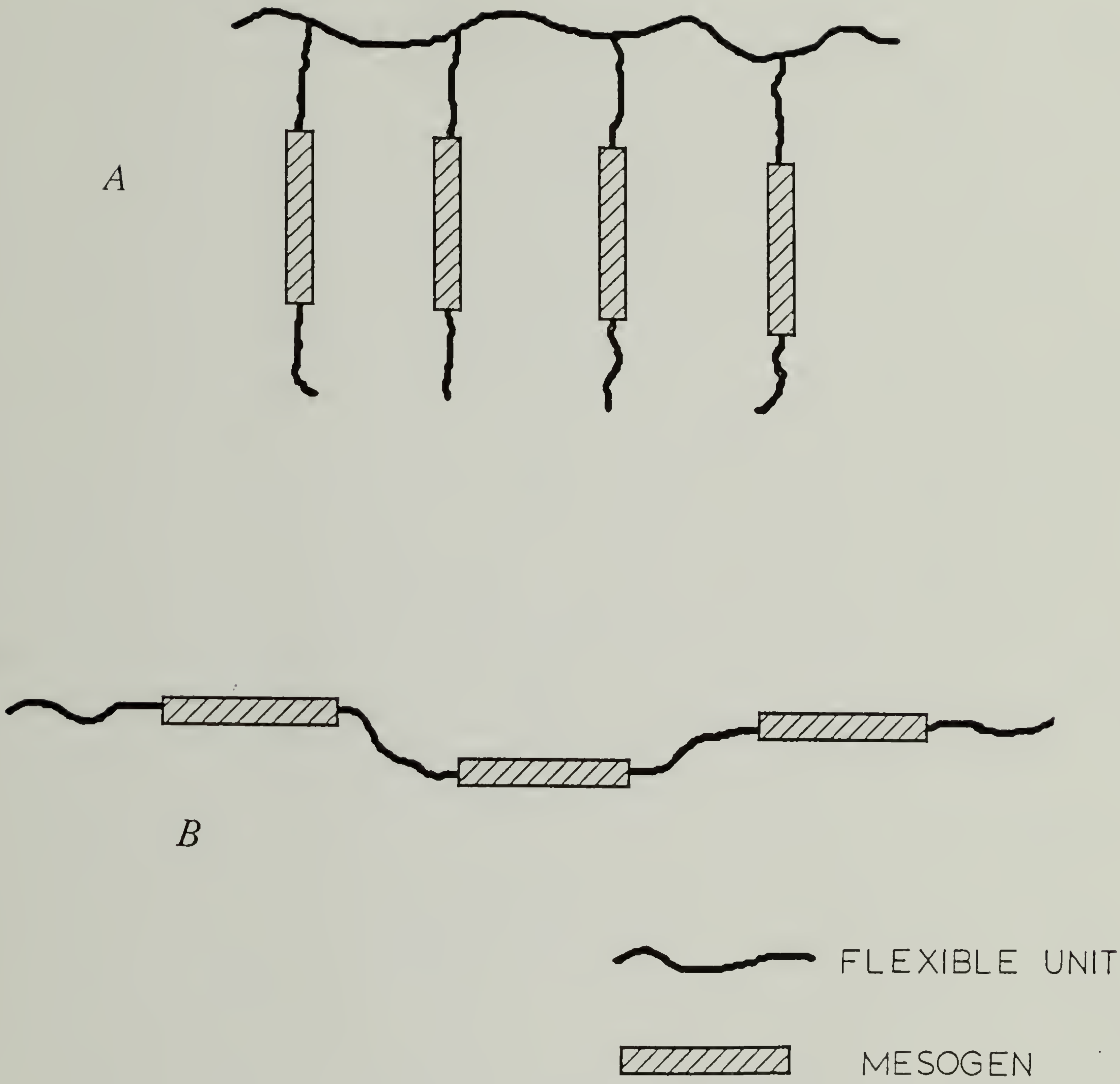


Figure 1.3 The structure of side chain (*A*) and main chain (*B*) liquid crystalline polymers

side chain liquid crystalline polymers are extensions of the uses of low molecular weight liquid crystals (49), in optical display devices, optical memory devices, light filters (49, 50) and gas chromatography column packings (51). In these applications, advantages of the side chain liquid crystalline polymers over low molecular weight liquid crystals are low volatility and ease of processing.

Theory and characterization of liquid crystalline polymers

Flory extended his lattice theory for polymer solvation to solutions of rigid rod polymers separating into two phases---an isotropic and anisotropic---in an early paper (11). He later published reviews and further extended his theory to include energetic interactions (52-60). Earlier theories, considering tobacco mosaic virus as the prime example, were based on the second virial coefficient. These continuum theories (61-63) are applicable only in dilute solutions whereas Flory's theory is more accurate in more concentrated polymer solutions.

As Flory pointed out, the overriding necessity for liquid crystallinity is a high axial ratio (54). His calculations give a minimum axial ratio of 6.7 (60) without mesogenic interactions. This packing into a liquid crystalline phase results from a maximizing of entropy (26). For liquid crystals, translational entropy is maximized at the expense of orientational entropy, or in simpler terms, rod alignment results in more freedom of movement.

Flory's theory is best understood in light of the much-cited phase diagram seen in Figure 1.4 for a rigid rod of axial ratio of 100 (54). The χ parameter, defined as:

$$\chi = \frac{\Delta H_m}{RTn_2V_1} \tag{1.1}$$

where n_2 is the mole fraction of component *2* and V_1 is the volume fraction of component *1*, is seen to be key in the existence of a liquid crystalline phase. For a favorable polymer/solvent interaction, the separation into two phases is seen with a narrow biphasic region. As the polymer/solvent interaction becomes less favorable, the heterogeneous region broadens. On a practical level this broadening means the lyotropic state is difficult to form, unless there is a negative or just slightly positive χ. The theory also predicts that if two phases form, the anisotropic phase is the more concentrated one.

That the lattice and continuum theories are derived for systems of non-interacting rods is a basis for inaccuracy in a real world system of organic molecules. (The χ parameter measures only energetic considerations between the polymer and solvent, not between polymeric mesogens.) Anisotropic energetic terms alone were considered in Maier-Saupe theory (64, 65). Since the time of Maier-Saupe, a number of theories have considered both energetic and geometric terms (66-70) including Flory's refinement of the lattice theory (71, 72). (For a good review of current theories, the interested reader is referred to Reference 69 and the references therein.)

One important insight from these theories is the realization that liquid crystallinity results from a balance of a high axial ratio and energetic

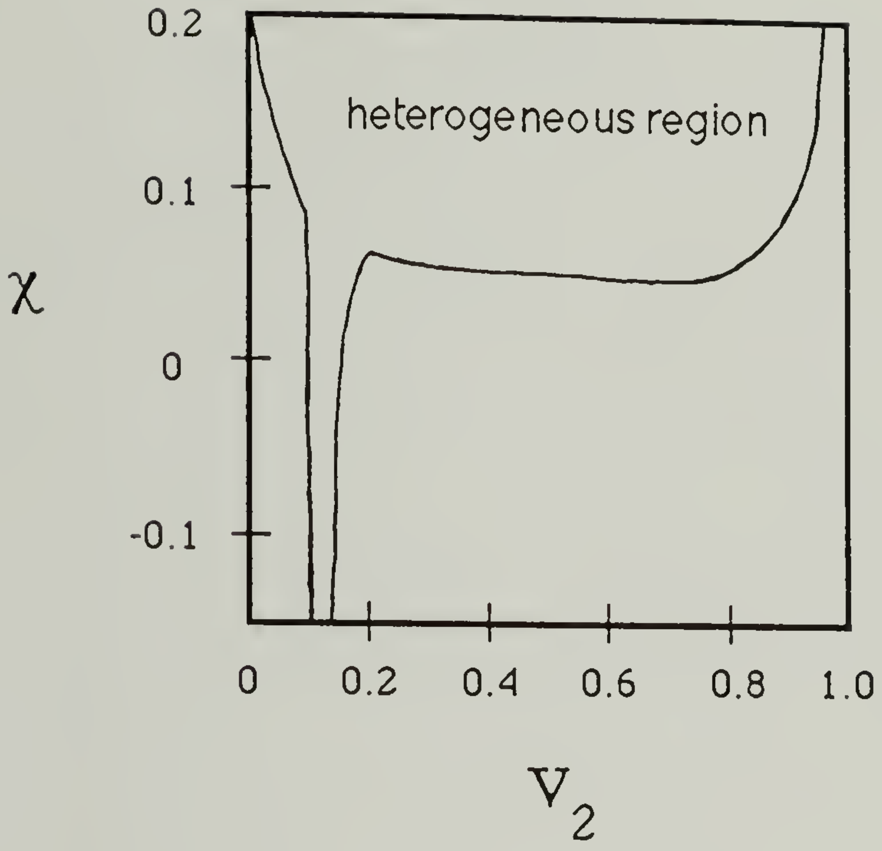


Figure 1.4 Flory's phase diagram for lyotropic liquid crystalline polymers (see text for description)

intermolecular interactions. Although a high axial ratio is the overriding requirement for liquid crystallinity, if intermolecular forces are too high the rods cannot separate into a liquid crystalline state and the product is an insoluble and infusible material. It is obvious that there is a relation between the high axial ratio, the packing and the intermolecular interactions, in that a large number of sites for interaction must be overcome before adjacent chain segments can separate by solvation or melting. A good analogy from non-liquid crystalline polymers is poly(ethylene), which has only weak dispersion forces as a connection between chains. This crystal packing and high crystallinity entail a large number of solvent molecules acting together and result in a polymer that is soluble in few solvents.

The early theories were concerned with lyotropic polymers and predicted axial ratios needed for liquid crystallinity and concentrations at which liquid crystalline phases would be observed. These theories apply to thermotropic polymers *in concept* (22) although they are not of a predictive nature. Although the forces that are overcome are identical, thermotropic theory is not as advanced as lyotropic theory due to complexities inherent in higher (100%) concentrations (66, 70, 71). As noted before, there are some polymers which show both lyotropic and thermotropic behavior (32-34).

The Figure 1.2 showed schematics of liquid crystalline phases, but was inaccurate in showing perfect alignment. In reality, the mesogens vary in orientation from the director, $\vec{n}$, as seen in Figure 1.5. A measurement of this fluctuation cannot be based on an average (which goes to zero) but is based on a higher-order measurement, the quadrapole (73), defined as:

$$S = 1/2\,(3\langle \cos^2\theta \rangle - 1) \qquad (1.2)$$

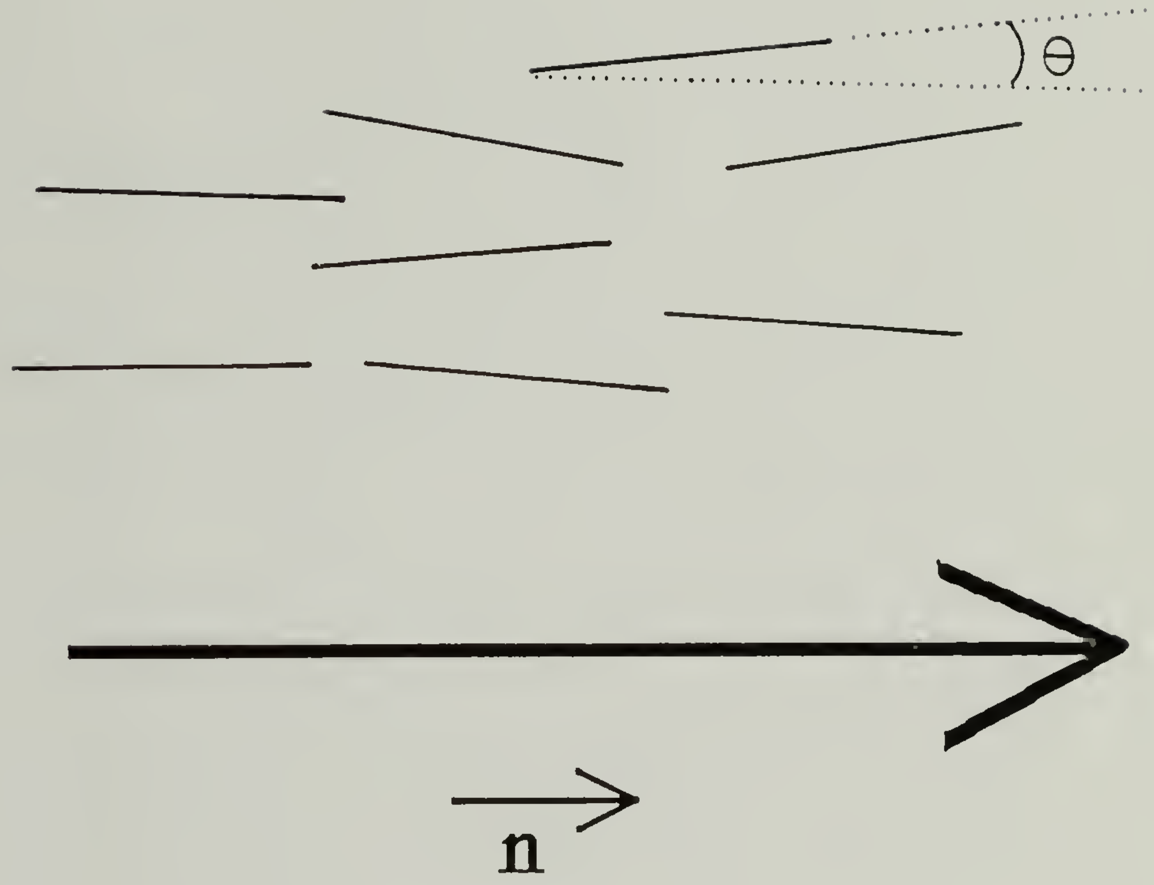


Figure 1.5 Schematic of the order parameter for liquid crystals

This measurement varies from 1 for perfect orientation to 0 for random orientation. The order parameter can be measured by X-ray diffraction or nuclear magnetic resonance, and in real polymeric liquid crystalline systems, order parameters from 0.3-0.8 are observed (74).

The transition from a crystal to a liquid crystal is a first-order transition that is seen as a peak in differential scanning calorimetry analysis. The transition from a liquid crystal to an isotropic melt is also a first-order transition. From the enthalpy measured by the differential scanning calorimetry, the entropy of the transition can be easily calculated, assuming equilibrium conditions, by the Gibb's free energy equation:

$$T_m = \Delta H / \Delta S \tag{1.3}$$

The type of liquid crystal phase formed details the relative magnitude of the two transitions. In a nematic liquid crystalline polymer, the entropy change for the transition from a liquid crystal to an isotropic melt is only 2-4% of the total entropy change observed in the transitions from a crystal to an isotropic melt (26). For smectic liquid crystalline polymers, the entropy change can vary a large amount depending on the type of smectic phase formed, but generally the entropy of the isotropization is larger than the entropy change from crystalline to liquid crystalline. Compounds can show multiple phases, and each transition is seen as a first-order transition, with the order from higher-order smectic (B, D-H) to lower-order smectic (C, A) to nematic to isotropic melt always being followed (26, 73).

Typical values for the isotropization transition enthalpy are 0.3-0.85 kcal/mol for nematics and 1.5-5.0 for smectics (75).

This use of thermal analysis is the most common method for analysis of liquid crystals. Because more than one transition is possible, multiple peaks can be observed by differential scanning calorimetry. Complications arise in polymeric systems where melting and/or isotropization temperatures may be above a degradation temperature. Other complications in polymers result from high viscosity and related effects such as slow crystallization or the slow development of a liquid crystalline phase. Liquid crystallinity may also be seen only on cooling in a non-equilibrium phase (monotropic) before the onset of crystallinity.

In most cases for thermotropic liquid crystalline polymers, evidence in addition to differential scanning calorimetry is needed to ascertain if a liquid crystalline phase is present, and to identify that phase. Of course, lyotropics cannot be characterized by differential scanning calorimetry.

The most common secondary technique is polarized optical microscopy (30, 76, 77). For the nematic phase, polarized optical microscopy shows the typical schlieren texture which results from the changing orientation within the sample. Disclination lines develop at the interface of the orientational domains (36). (The term disinclination was originally suggested by Sir Charles Frank, "...but the name was changed at the urging of a professor of English who was disinclined to grant a new meaning to that word.") (78) Black points also develop in sections of a sample oriented perpendicular to the plane of the polarizer (77). The smectic state shows a variety of textures by polarized optical microscopy, from mosaic to fan shape to schlieren, depending on both smectic type and sample treatment. (Details and excellent photographs are seen in References 3 and 36.)

Primarily because of viscosity in polymers, the textures are more difficult to observe as compared to low molecular weight liquid crystals. In fact the texture may not be distinguishable at all (77). Another common problem is that a certain texture may not be indicative of a unique phase. For example, a schlieren texture may indicate a nematic or smectic C structure.

X-ray analysis is the least ambiguous of any characterization technique (79, 80). With Figure 1.2 as a background, the periodicity seen in these diagrams is reflected in the X-ray diffraction. For a nematic the only periodicity is the side-to-side spacing of the molecule, typically around 5 Å. This is an average distance and this averaging is seen in a blurring of the diffraction band in the X-ray image. More blurring and a slight expansion of the bands is seen at higher temperatures, as expected. For a smectic A, the same periodicity is seen as for a nematic, but the additional periodicity of a layer spacing is also observed. This layering is a regular repeat distance with typical values from 15-50 Å depending on the size of the mesogen. This regular repeat distance is seen as a sharp band. For a powder sample, the diffraction pattern is averaged to a ring (or series of rings) due to the random orientation of the sample. Orienting the sample into a fiber allows additional information to be determined as equatorial and meridional reflections deconvolute. For example, the order parameter can be determined by the width of the equatorial reflectional arc (81).

Other methods for characterizing liquid crystal polymers, although less commonly used than the above methods, include miscibility studies (82, 83), melt viscosity (84-86), small angle light scattering (87) and solid nuclear magnetic resonance (73).

Applications of main chain liquid crystalline polymers

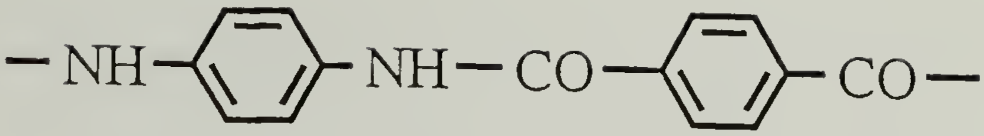
As noted before, the applications of main chain and side chain liquid crystal polymers are quite different. The uses of side chain liquid crystalline polymers are extensions of the uses of low molecular weight liquid crystals. Examples include optical memory devices, light filters, polarizers, and indicators for temperature, pressure or chemical environment (49, 50). In these uses advantages include low volatility and ease of processing.

The use of main chain liquid crystalline polymers is different, with the main applications resulting from the high strength and modulus of these materials. Keller has stated that "...if a high modulus fiber is to be achieved, an oriented extended chain type crystal structure relatively free from folds must be obtained" (88). Table 1.1 (21) shows the theoretical and actual values of several thermoplastics and of Kevlar®. The dramatic properties of the liquid crystalline polymer are seen quite clearly. The high strength is understood in light of Keller's comment as originating in an all-rigid, extended backbone, where deformation of the bulk material involves deformation of individual bonds and bond angles, and chain folding is impossible. The structures of Kevlar® and the commercial liquid crystalline polyesters are shown in Figure 1.6.

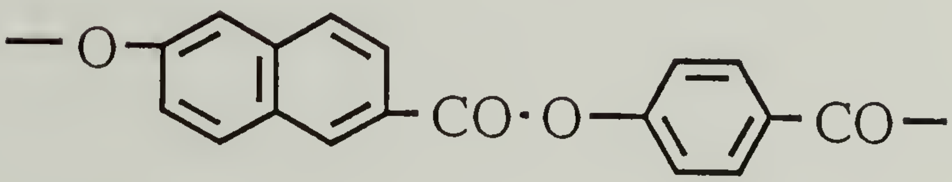
Any method for obtaining this alignment and structural rigidity, if translated into a finished product, will give a high-performance polymer. For example, poly(ethylene) and poly(ethylene terephthalate) have been processed by

Table 1.1 The theoretical and experimentally found modulus for several commercial polymers in 10^6 psi

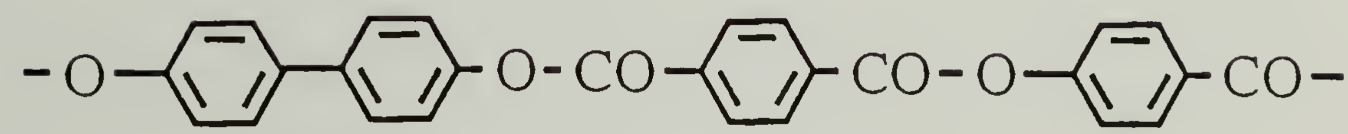
	THEORY	FOUND
Cellulose	12	1
Poly(ethylene)	51	1
Nylon	22	0.8
PET	18	1.5
Kevlar®	27	25



DuPont's Kevlar®



Celanese's Vectra®



Dartco's Xydar®

Figure 1.6 The structures of commercial liquid crystalline polymers nonconventional techniques, including slow crystal growth, gel spinning and orientation by high draw ratios, into fibers with exceptional properties (89-91). It must be realized that main chain liquid crystalline polymers are not used as liquid crystals. The liquid crystallinity is used only as a method for obtaining high orientation. The rigid rod structure necessary for liquid crystallinity gives superior mechanical properties on a molecular level; the orientation obtained translates into superior mechanical properties on a macroscopic level.

This ease of orientation that results from processing in the liquid crystalline state is seen clearly in an early paper (17), with the data reproduced in Figure 1.7. The first important fact about this data is the dramatic difference seen for flexural modulus along and across the processed flow direction. The second point is that at larger dimensions this orientational effect is diminished and tends to a limit of material properties independent of process direction. This data is understood as resulting from orientation developing in elongational flow, which is dependent on wall effects. Areas of the sample isolated from the walls show less orientation as a result of shear flow. From these trends it is seen that the ultimate in mechanical properties is in a processed fiber geometry (22). The solution-spun lyotropics are also limited to fiber geometry.

The flow behavior of nematic liquid crystalline polymers has been studied by Asada (92, 93) and others (94-96) and is most commonly understood as divided into a three-flow region, with the corresponding domain morphology as seen in Figure 1.8. The flow behavior of a conventional thermoplastic polymer is included for comparison and is seen to exhibit thixotropy at high shear rates. However, only liquid crystalline polymers exhibit Region I behavior, an observation explained by the orientational order shown in the Figure 1.8 schematic. Of prime importance is

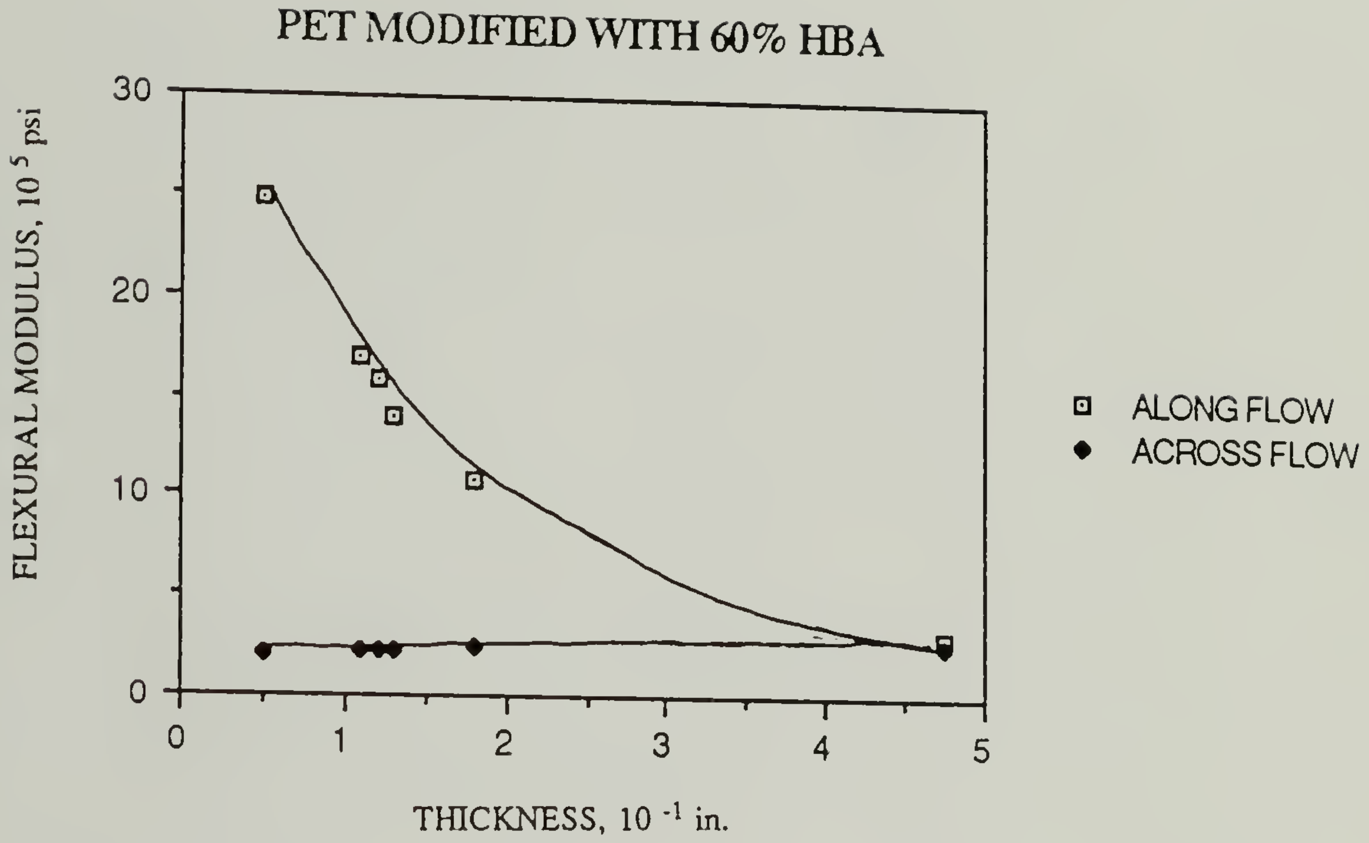


Figure 1.7 Properties of Eastman's X7G® liquid crystalline polyester (*Ref. 17*)

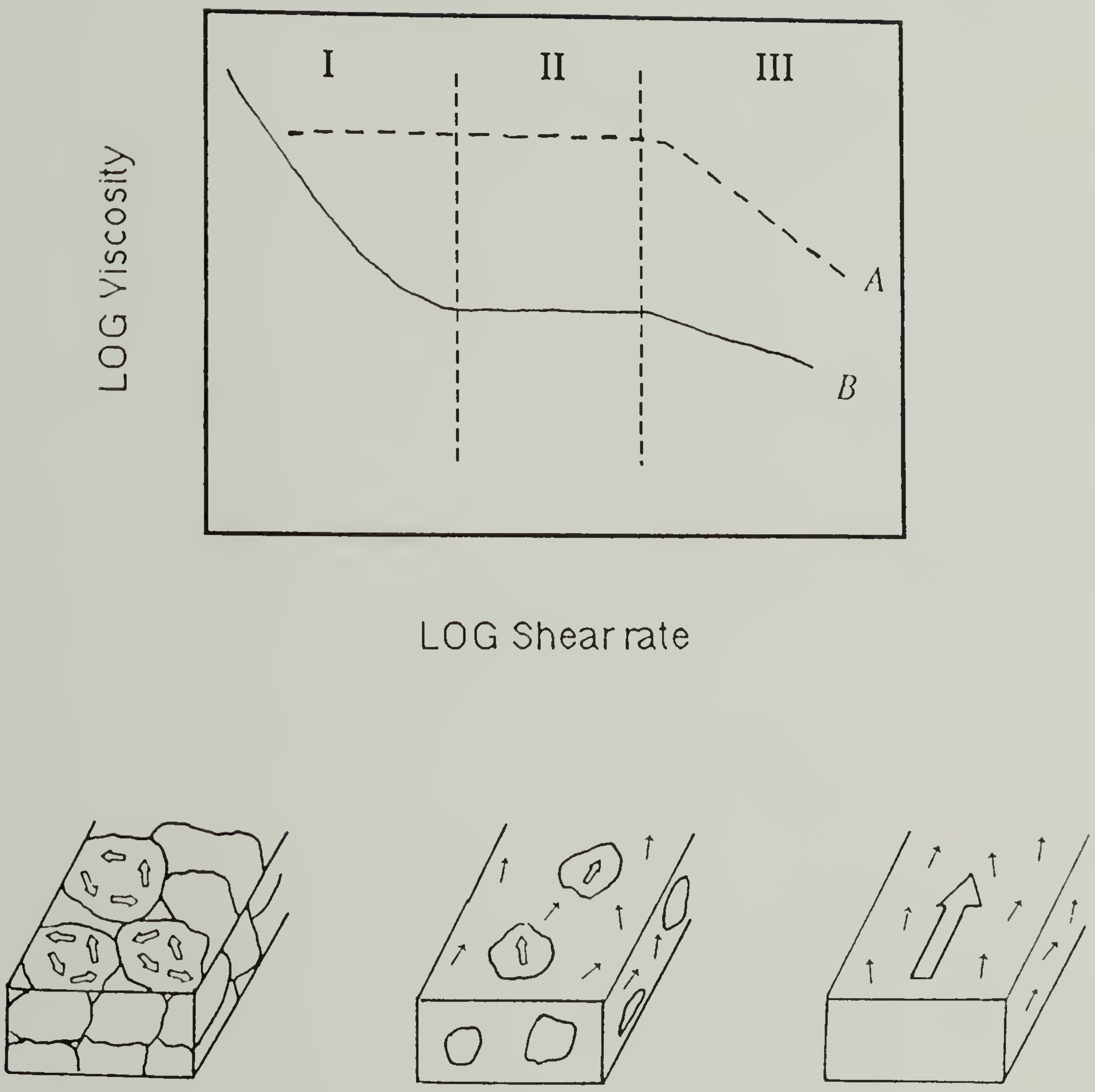


Figure 1.8 Asada's schematic for flow in a liquid crystalline polymeric system. *A*-conventional polymer, *B*-liquid crystalline polymer (*Ref. 93*)

the observation that at all shear rates, liquid crystalline polymers exhibit much lower viscosity melts than do conventional polymers. This lower viscosity is a result of more independent movement of one polymer chain relative to adjacent polymer molecules as compared to conventional non-liquid crystalline polymers. This lower viscosity also leads to the lower pressure needed for molding, which, coupled with a less compressible polymer, leads to zero or negative die swell (97).

The extensional orientation that develops during processing, and leads to exceptional properties in one direction, leads to anisotropy of other properties including thermal expansion, creep and abrasion resistance as well as all strength and modulus properties (98). For tensile properties perpendicular to the fiber direction, the stress is proportional to the cohesive energy density of the polymer (99). In composites using a liquid crystalline polymer as the reinforcing member, composite strength is limited by the compressive strength of the polymer (100).

The fiber geometry of lyotropics has been exploited in a number of applications where high strength and high modulus are needed. Kevlar® is annealed to remove defects and increase orientation, with the unannealed and annealed versions labeled Kevlar 29® and Kevlar 49®, respectively. As expected, the 29 has a lower modulus but higher elongation, and is used in high toughness applications such as body armor, protective helmets, ropes, cable coatings and tire cord (22, 101). The higher modulus Kevlar 49® is primarily used in composites for aerospace applications and sporting goods (22, 101).

As noted, the highest mechanical properties for thermotropics also come from fiber geometry, and here, the applications reflect the use of lyotropic polyamides. Although maximum mechanical properties are not obtained in other geometries (as seen in Figure 1.6), the properties remain better than for conventional thermoplastics, with values approximately the same as that of glass fiber reinforced polyester (21). Advantages result for molding, where the lower viscosity melt and very low die swell make possible the molding of more intricate parts (102).

For extensions of the one-dimensional properties of liquid crystalline polymers to more than one dimension, crosslinking (103), block copolymerization (104), biaxial orientation(105) and placing mesogens in both the side chain and the main chain of a polymer (47) have been researched. None of these methods has been realized to superior mechanical properties.

In summary the advantages and disadvantages of main chain liquid crystalline polymers are :

ADVANTAGES

- high strength and modulus
- low viscosity for processing
- low thermal expansion
- high toughness and abrasion resistance
- low creep

DISADVANTAGES

- anisotropy of all advantage properties
- difficulty of processing due to high melting points and limited solubility

A problem for all current commercial liquid crystalline polymers is processing. The lyotropic polyamides are processed from concentrated sulfuric acid. This is a corrosive solvent which requires extra safety considerations and special equipment for handling. Because of its high boiling point and interaction with the polymer it is difficult to remove from the coagulated polymer, produced by water precipitation of the wet spin. Thermotropic polyesters are not as difficult to process, but often the temperatures needed are higher than those normally encountered in thermoplastic injection molding, and special equipment is required. Lowering the melting temperature would assure no degradation and lead to faster mold turnover. In the case of both the lyotropic polyamides and the thermotropic polyesters, easier processing, without loss of mechanical properties, would be of utmost benefit.

Current research in main chain liquid crystalline polymers

As noted, commercial liquid crystalline polymers are relatively difficult to process because of high melting points for the thermotropics and the necessity of harsh solvents for the lyotropics. A great deal of research in the past two decades has been aimed at easing this processing. This staggering amount of research will be briefly summarized here and the interested reader is referred to several reviews (3, 21, 22, 26, 27, 38, 106-111). For lyotropics the research has centered on biological liquid crystalline systems and in the synthesis of very rigid, higher performance fibers, sacrificing, to an extent, ease of processing. In the thermotropics the concept of easing processing has dominated research and a wide variety of methods have been used to lower melting points. Thermotropics will be discussed first.

For a summary of the work on thermotropics, use is made of a classification schematic of Griffin and Cox, reproduced in Figure 1.9 (112). Here, the homopolymers are modified by frustrated chain packing or the incorporation of flexible spacers or nonlinear links. Frustrated chain packing is further divided into substitution of the mesogen and copolymerization of dissimilar mesogens. Although this schematic is an excellent one for many individual polymers, its use is limited for some research examples, in that two or more methods may be used to lower the melting point for a specific polymer.

The majority of work in thermotropic liquid crystalline polymers has been on polyesters with flexible spacers. An excellent review for these polymers was published in 1984 (106). That review included as spacers $-O-(CH_2-)_n-O$, $-OOC-(CH_2-)_n-COO-$, $-O-(CH_2CH_2-)_n-$ and siloxane. The number of phenylenes was two, three or four. Some examples of direct-linked *trans*-cyclohexane/phenylene mesogens were reported. Other reports include diphenylacetylene polyesters (113), polyethers (114-116), polyamides (117), polycarbonates (118) and polyurethanes (119). By using long siloxane spacers, liquid crystalline transitions as low as room temperature have been observed (120).

As previously mentioned, two methods may be used to lower the melting point, and the method of flexible spacers has been used in conjunction with substituted mesogens (19, 117, 121-123) and with nonlinear links (124). For nonlinear links and for nonsymmetrical mesogens, copolymers are of course formed. Less work has been done on lowering thermal transitions by frustrated chain packing (18, 21, 125-128) or by kinks alone (112, 124, 129-131). With these systems a much lower depression of melting point is seen, and hence, a thermotropic state is much more difficult to reach before the onset of degradation.

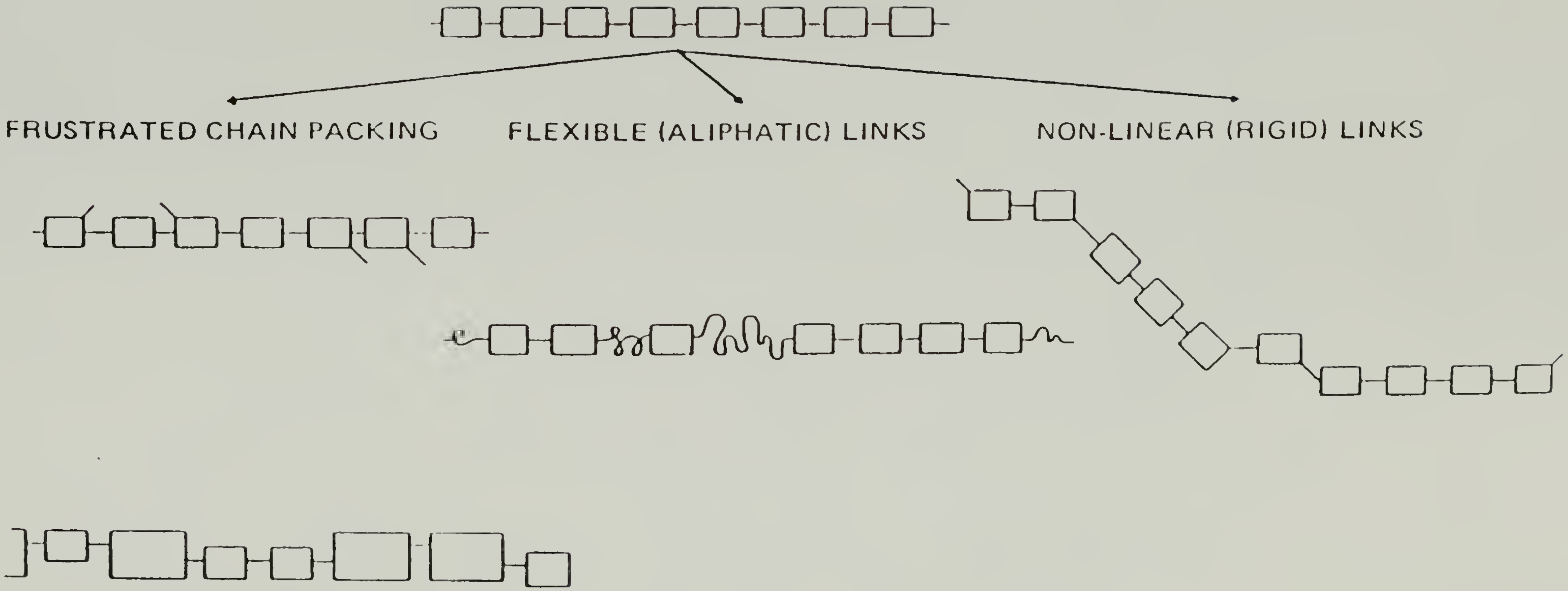
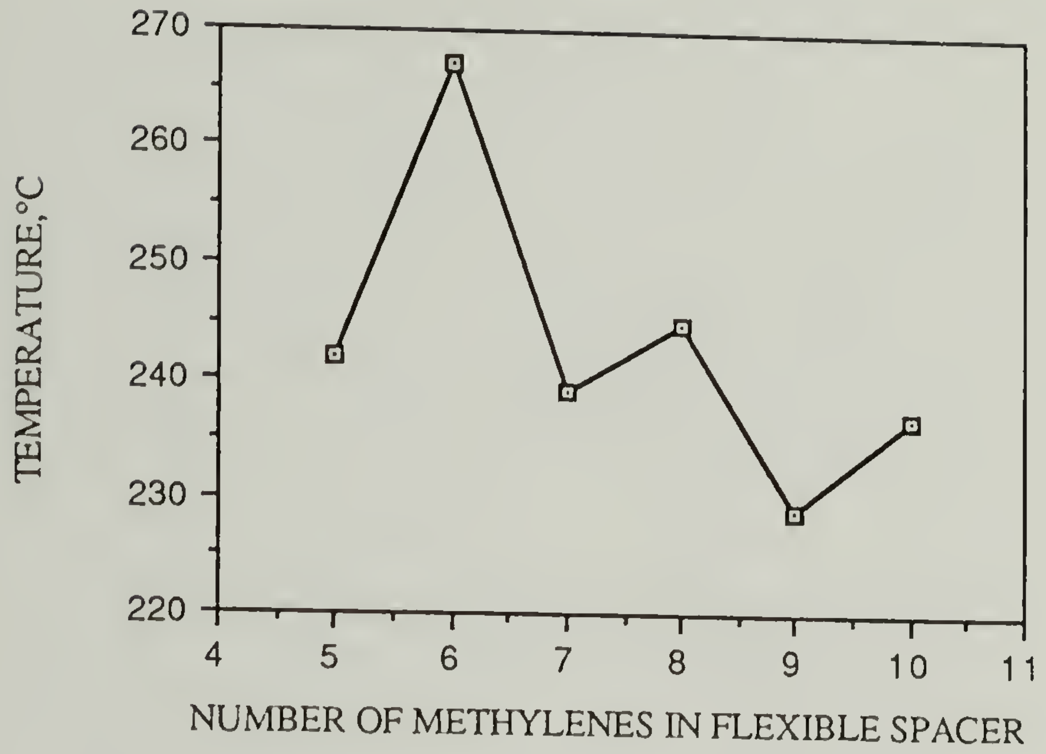


Figure 1.9 Methods for lowering the melting point of thermotropic liquid crystalline polymers (*Ref. 112*)

In the vast amount of work done on thermotropics, flexible spacer use has dominated the research as it is the easiest way of lowering melting points and insuring the preparation of a polymer with a liquid crystalline state. Melting point lowering is observed with increasing length and flexibility of the spacer and with decreasing length and rigidity of the mesogen. An odd/even effect is seen for flexible spacers, as illustrated in Figure 1.10, resulting from the decrease in linearity of adjacent mesogens with an odd number of links. Long spacers may enhance smectic formation. In short, the trends seen for flexible spacer main chain thermotropic liquid crystalline polymers mirror the trends seen in side chain liquid crystalline polymers (36-38). Frustrated chain packing, achieved either by substituting the mesogen or by copolymerization, lowers crystallinity and lowers the melting point. The more unsymmetrical the mesogen, the lower the melting point. Presumably, a lower melting point is also seen in more random polymers, but the decrease is probably small and an example of this behavior could not be found. Nonlinear links lower the melting point but, due to the rigidity, the effect is small as dictated by equation 1.3. At high nonlinear-link contents liquid crystallinity is lost.

From a mechanical viewpoint the favored methods of decreasing the melting point in thermotropic polymers are frustrated chain packing and the use of rigid, nonlinear links. This point is illustrated in the successful commercial thermotropic liquid crystalline polymers, Celanese's Vectra® (21) and Dart's Xydar® (24, 25). Nonlinear links may be as rigid chemically and hence stiff mechanically, but the loss of the liquid crystalline state precludes an easy method of obtaining alignment. Flexible spacers are detrimental to mechanical properties, although use of block



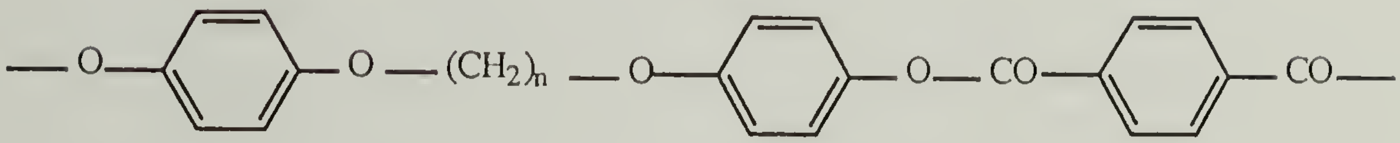


Figure 1.10 The effect on melting point for a main chain liquid crystalline polymer with a flexible spacer (*Ref. 121*)

copolymers with flexible spacers in liquid crystalline blends may be a favorable method of obtaining tie molecules to increase transverse strength.

As noted before, the majority of research with lyotropic polymers can be divided into work on naturally occurring biological polymers and on high performance, all-extended synthetic polymers. The distinction is also made between the two as true rigid rods and semiflexible liquid crystals, respectively (132). The first examples of polymeric liquid crystals were discovered in biological systems as described previously (9, 10). Other examples will not be described here, but include cellulose and derivatives (32-34, 133), deoxyribonucleic acid (134, 135), ribonucleic acid (136, 137) and polypeptides (138-140).

The initial report of lyotropic behavior in synthetic polyamides (12) started a fury of research activity in all aromatic polyamides. Much of this work, which included copolymers, polymers with substituted mesogens and polymers with nonlinear links, has been summarized by DuPont researchers (15, 141-143). Other examples of lyotropic polymers include polyisocyanates (144, 145), polyesters (146), *N*-substituted polyamides (147), polyazomethines (148), polyhydrazides (149) and several ladder (150) and semi-ladder type polymers (151) including bisoxazole (152), bisthiazole (153) and bisimidazole (154).

Although the amount of research in lyotropic polymers has been overshadowed in recent years by the amount of research on thermotropic systems, the lyotropic Kevlar® remains the standard for high mechanical performance by a polymeric fiber. However, in laboratories, even the high modulus of Kevlar® has been surpassed by some of the ladder type polymers (155, 156). That the experimental modulus is very close to the theoretical modulus (21) means that orientation is near perfect.

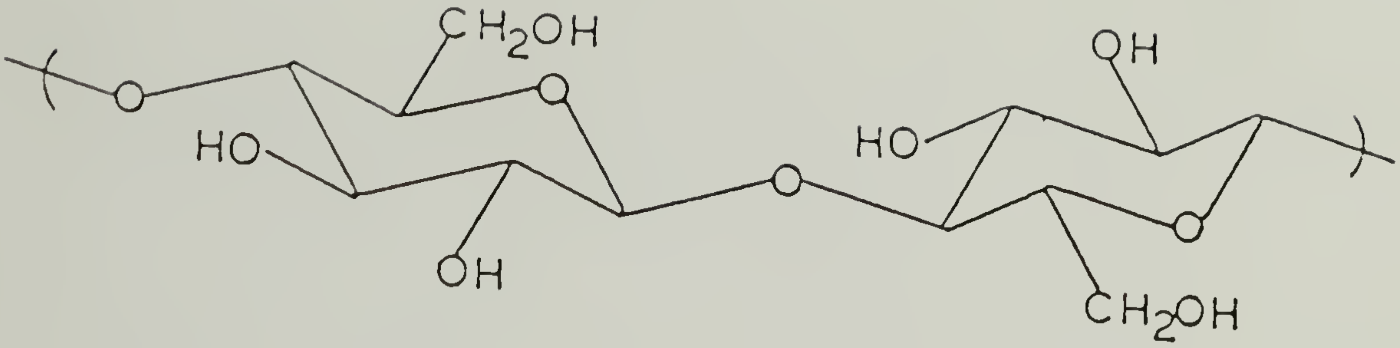
Rationale for research

The extended structure necessary for a polymer to exhibit liquid crystallinity leads to a ΔS of melting which is lower than for conventional polymers, and leads to the higher T_m. Research has been directed at lowering the melting transition by affecting both ΔH and ΔS according to equation 1.3. As discussed, the most common methods, with the main factor influenced in parentheses, are: incorporation of flexible spacers (ΔS), substitution on the mesogen (ΔH), incorporation of nonlinear, rigid units (ΔH) and frustration of chain packing with dissimilar, linear rigid units (ΔH). For the most part these methods, while easing processing, compromise mechanical properties. And the methods which minimize the compromise of mechanical properties, for example frustrated chain packing, also have the smallest melting point depression.

For liquid crystallinity the overriding necessity is rigidity and high axial ratio (54). Aromatic mesogens possess both these requirements. However, aromatic mesogens also have a relatively high intermolecular attraction (large ΔH) and no mechanism for becoming more flexible on melting (small ΔS). A great advantage would be a rigid, high-axial material with a low intermolecular attractive force and a degree of flexibility available on melting. Cyclohexane mesogens have these characteristics. Cyclohexane in a *trans*-1,4-linkage has a higher axial ratio than a *para*-linked benzene ring (157). Polarizability is decreased because there is no aromaticity, and this decrease leads to generally lower melting points and related properties such as lower viscosity, birefringence and dielectric anisotropy (158).

An example of a naturally occurring liquid crystal polymer is cellulose. Cellulose was reported as lyotropic as early as 1980 in *N*-methyl morpholine *N*-oxide (159) and has since been reported as lyotropic in other solvents (160). For cellulose the mesogen is not aromatic, but is a β-1,4-linked structure as seen in Figure 1.11. This mesogen differs from cyclohexane only in the ring oxygen. Decreasing hydrogen bonding by substituting the hydroxy groups results in polymers soluble in more common solvents, such as glacial acetic acid for ethyl cellulose (161), and ethanol and water for hydroxypropyl cellulose (162). Cellulose derivatives also form liquid crystalline melts (32-34).

The cyclohexane mesogen has been used in a variety of low molecular weight liquid crystals. The first report of a pure cyclohexane mesogen was for *trans*-4-substituted cyclohexane acids as in Figure 1.12 *A* with n values of 3-8 (163). The axial ratio necessary for thermotropic behavior was obtained by the known acid coupling mechanism due to hydrogen bonding. Since that time a number of other low molecular weight compounds using two or more cyclohexane linked in a *trans*-1,4-configuration have been reported as all-hydrocarbon (164), hydrocarbon with cyano end group (165) or ester-linked (166). Many more mixed cyclohexane/ aromatic liquid crystals have been reported (157, 158, 167) with two examples shown in Figure 1.12 *B* and *C*. In these cases the cyclohexane was also in a *trans*-1,4-configuration. Piperazine-containing aromatic liquid crystals have also been



- lyotropic in N-methyl morpholine N-oxide *Ref. 159*

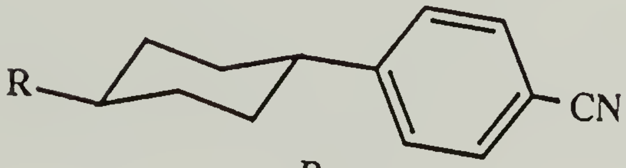
- EC is lyotropic in glacial acetic acid *Ref. 161*

- HPC is lyotropic in ethanol and water *Ref. 162*

Figure 1.11 The structure of cellulose

A

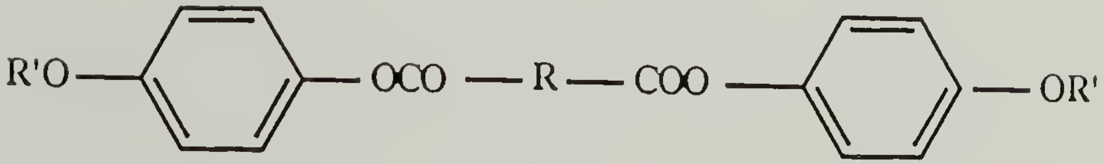
n=5 K 31 S 47 N 96 I *Ref. 163*



B

R= C_5H_{11} N 55 I

for Biphenyl N 35 I *Ref. 158*



C

R= CH K 142 N 245 I *Ref. 157*

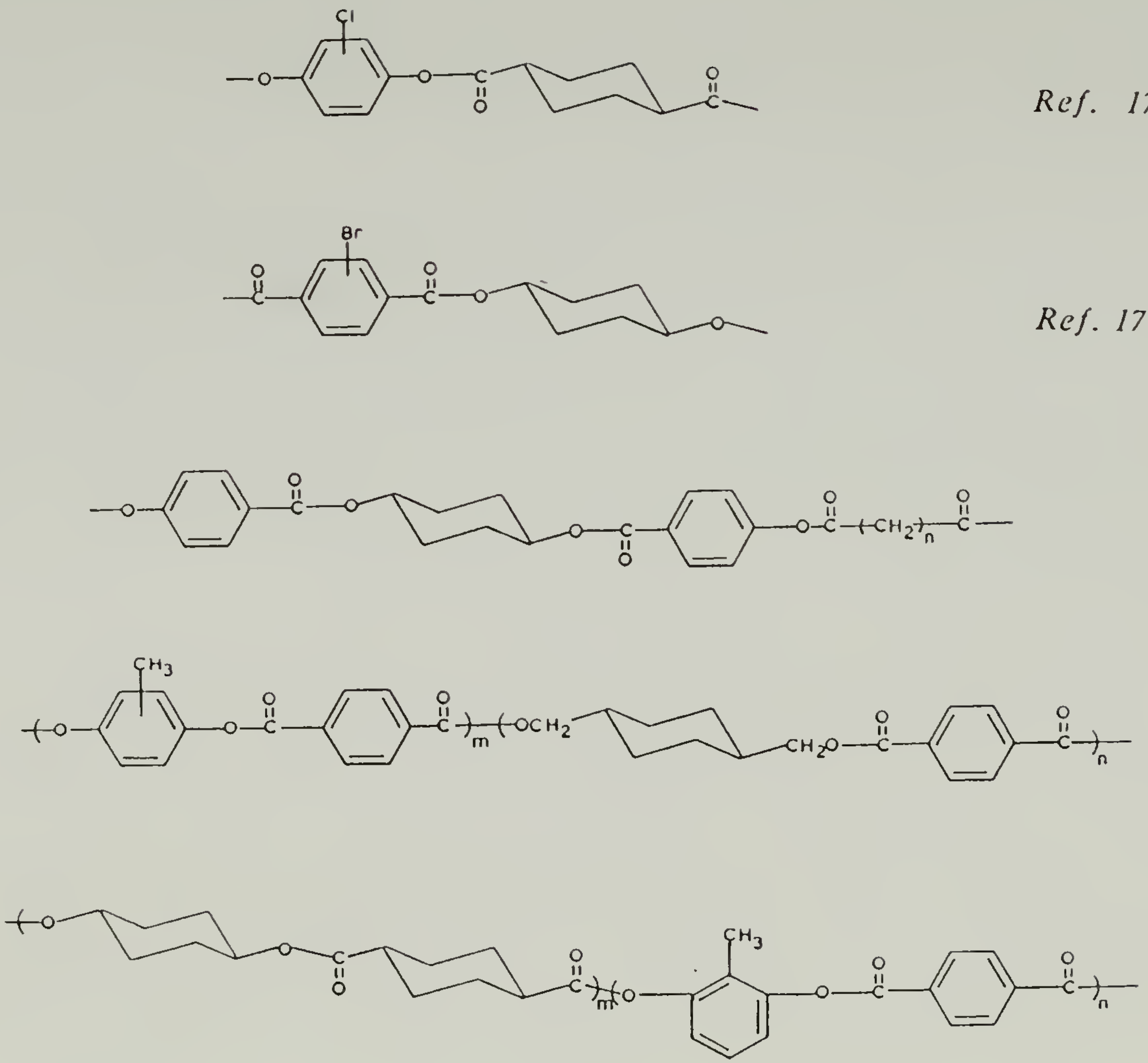
= AR K 209 N 285 I

Figure 1.12 Low molecular weight cyclohexane-based liquid crystals been reported linked either by an all-hydrocarbon group (168) or Schiff bases (169).

The fact that cyclohexane is a longer molecule than a phenyl ring can cause the lower melting members of these analogous series to exhibit the somewhat unexpected result that the cyclohexane compounds have the higher melting point (157, 158). An example of this behavior is seen in Figure 1.12 *B*. The longer axial ratio of the cyclohexane is observed to have an effect only at moderate temperatures (< 220 °C), above which the flexibility of the cyclohexane predominates and lower transition temperatures are seen, as shown in structure *C* of Figure 1.12 .

For polymers using cyclohexane as a mesogen, a number of mixed aromatic/cyclohexane polymers have been reported as liquid crystalline, as shown in Figure 1.13. For an all-cyclohexane polymer or for an all-non-aromatic liquid crystalline polymer there are two reports from esters in the literature as seen in Figure 1.14. For 1.14 *A* with a *cis/trans* ratio of 1:1 in the diol a 0.16 dL/g inherent viscosity polymer is reported to melt to a nematic at 295->300 °C by optical microscopy (171). For 1.14 *B* a transition to a nematic melt is reported at 288 °C by optical microscopy, but the author later cites 50% weight loss at 290 °C (174). Hence, the data in these two reports does not include a thermally stable, high molecular weight example of a liquid crystalline polymer.

For liquid crystalline polyamides, sulfuric acid solubility is the rule with some exceptions. For example, for the polymers seen in Figure 1.15 only the last example is soluble in a solvent other than sulfuric acid. These exceptions use high-boiling solvents such as *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidinone or hexamethylphosphoramide, usually with added lithium chloride (15, 175). For



Ref. 170

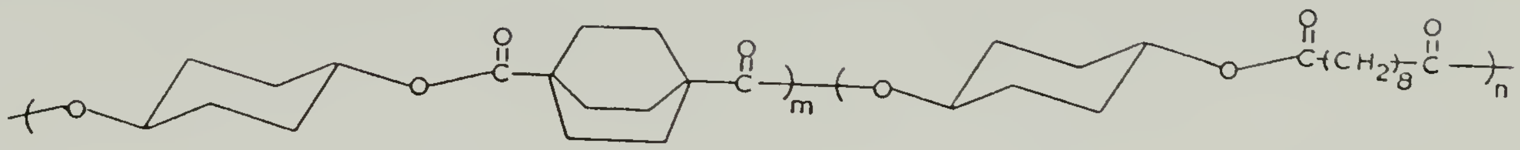
Ref. 171

Ref. 172

Ref. 173

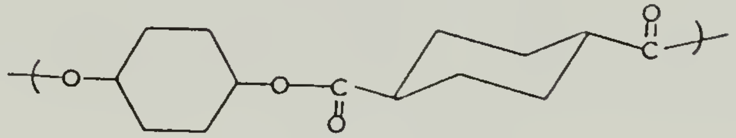
Ref. 146

Figure 1.13 Mixed aromatic/cyclohexane liquid crystalline polyesters



A

Ref. 174



B

Ref. 171

Figure 1.14 Non-aromatic liquid crystalline polyesters

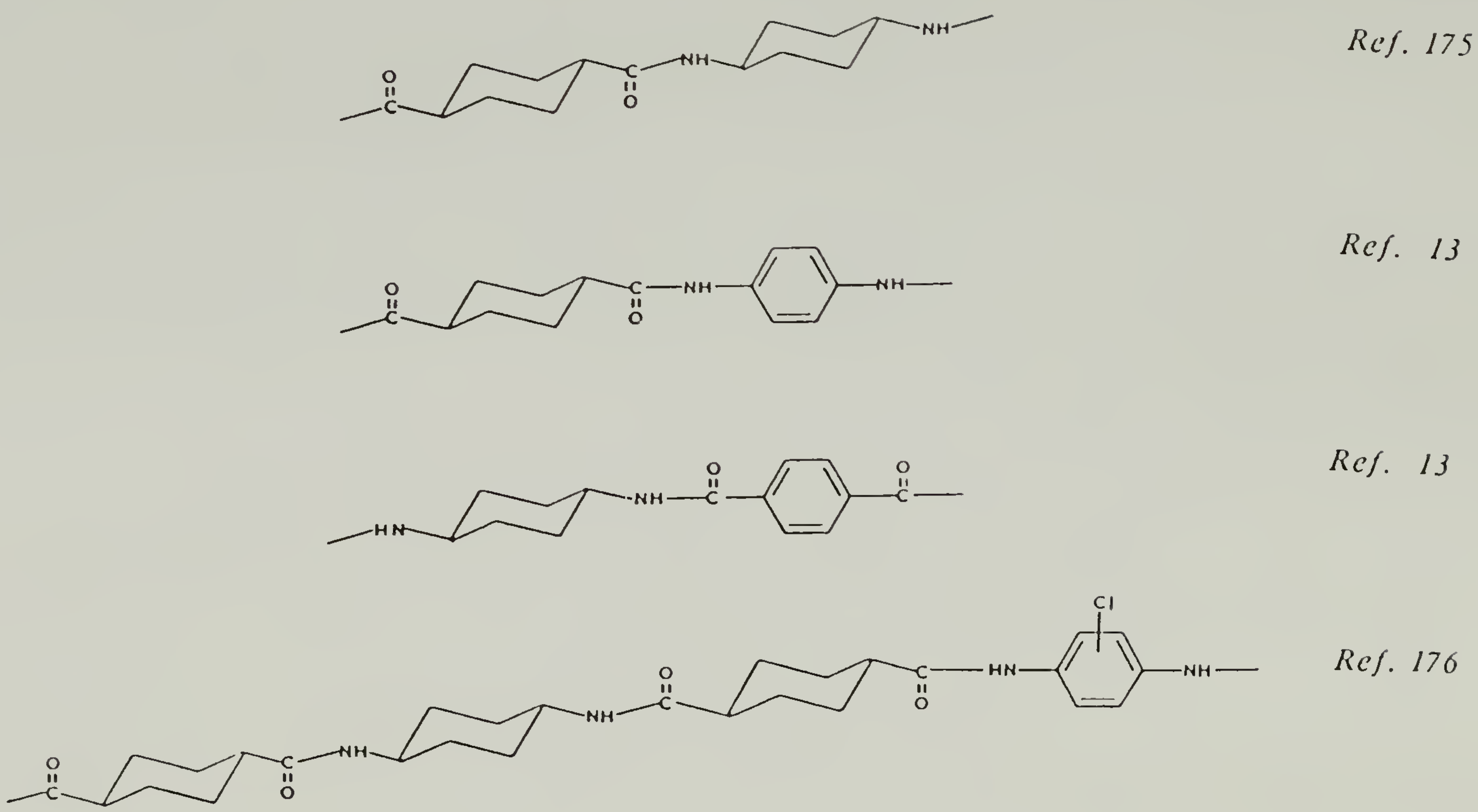


Figure 1.15 Mixed aromatic/cyclohexane-based liquid crystalline polyamides

non-liquid crystalline polyamides greater solubility is observed, and, particularly for polyamides made from a secondary diamine such as piperazine, solubility is observed in common solvents such as dichloromethane and methanol (177). Reports of thermotropic polyamides are limited to substituted mesogens with long flexible spacers (117).

In all scientific/technical endeavors there exists a compromise. In the area of liquid crystalline polymers the compromise is mechanical performance versus ease of processing. In addition, the existence of the liquid crystalline state is not *prima facie* proof for superior mechanical properties. From the vast array of liquid crystalline polymers that have been synthesized, it is evident in many, if not most, cases that the observation of a liquid crystalline state was the goal of the research. This pure goal has far-reaching applicability for an understanding of polymer liquid crystallinity. However, all liquid crystalline polymers are not mechanically equivalent, and these differences reflect the methods used to ease processing. The complexity of obtaining an easily processed polymer with minimal loss of mechanical properties has not been thoroughly researched. Ultimate mechanical performance exists, as Keller (88) has stated, with fully extended polymers, and methods that allow loss of this extreme, such as flexible spacers, compromise performance. (For example, compare the commercial development and use of Eastman's X7G® versus Dart's Xydar® polyesters.)

This research was initiated to synthesize high performance polymers. Liquid crystalline polymers are very high performance materials but, as described, the commercial liquid crystalline polymers are difficult to process. In low molecular weight liquid crystals, the use of cyclohexane mesogens, in contrast to aromatic mesogens, offers the advantage of a lower melting, less viscous liquid crystalline phase. The goal of this research was to exploit these characteristics in polymer analogs. By using cyclohexane mesogens, it was hoped that easily processed liquid crystalline polymers could be prepared with no sacrifice of mechanical properties. These polymers would be made without flexible spacers or substituted mesogens, but would have a low melting point based only on frustrated chain packing and the thermodynamic advantages of the cyclohexane mesogen.

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CHAPTER 2

MONOMER PREPARATION, PURIFICATION AND ANALYSIS

For cyclohexane compounds to exhibit mesogenic phases, linearity obtained by a *trans*-1,4-configuration is a necessity. The two methods of obtaining this configuration in polymers are stereochemical ring opening of bicyclo compounds and the polymerization of isomerically pure monomers. This section will address the preparation and ring opening polymerization reactions of bicyclo compounds, and the preparation, purification and analysis of isomerically pure cyclohexane monomers. Polymerization of cyclohexane monomers will be discussed in Chapters 3, 4 and 5.

Monomers for ring-opening polymerization

The [2.2.2] lactone and lactam can be prepared via the reaction schemes shown in Figure 2.1 (1, 2). The hydrogenations are performed on recrystallized

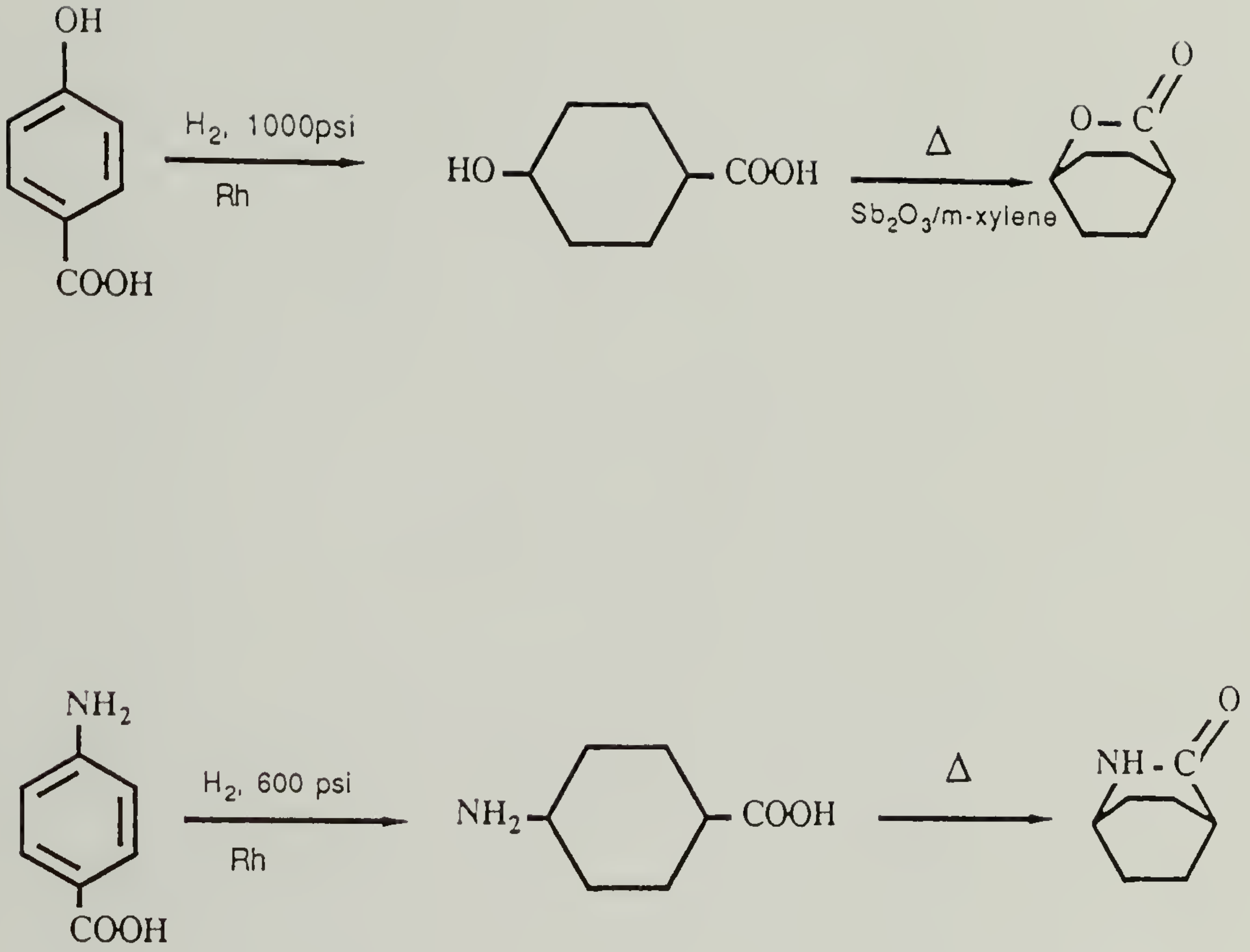

Figure 2.1 The synthesis of 2-oxabicyclo[2.2.2]octan-3-one and 2-azabicyclo[2.2.2]octan-3-one

materials, in a water solution, under approximately 1000 psi hydrogen pressure. The chemical composition and preparation of the catalyst may result in a change of *cis/trans* content in the resulting cyclohexane compound. In this reaction scheme, a high *cis* content was desired for the subsequent cyclization reaction. Active catalyst and high pressure were used to encourage the formation of this kinetic product. The conditions used resulted in *cis* contents of 92% for the hydroxy compound and 100% for the amino compound.

The cyclization of the amino compound was performed easily by reflux in diphenyl ether with subsequent water extraction of the cooled solution. The cyclization of the less basic hydroxy compound required more vigorous conditions. The literature method for cyclization of the lactone uses acetic anhydride reflux (1) to remove the reaction water. This method failed, as noted by other researchers (3, 4), giving only the acetate derivative, with a melting point of ~70 °C. Other conditions were tried by changing the catalyst and solvent, before a successful combination of antimony trioxide in *m*-xylene was discovered. Interestingly, another catalyst tested, zinc oxide, did not give the lactone, but isomerized the *cis/trans* mixture to 100% *trans* isomer, as shown by nuclear magnetic resonance (NMR) analysis and by melting point (146-148 °C). The relation of the melting points of the various derivatives and isomers is shown in Figure 2.2 (5).

An interesting result in the analysis of the lactone was the existence of two endothermic peaks as observed in differential scanning calorimetry (DSC) analysis as shown in Figure 2.3. This behavior was reported in an early paper and was attributed "...apparently to a change in crystal structure" (5). It is suspected that the lower transition is a transition into a plastic crystalline phase. The lactam does not display this behavior.

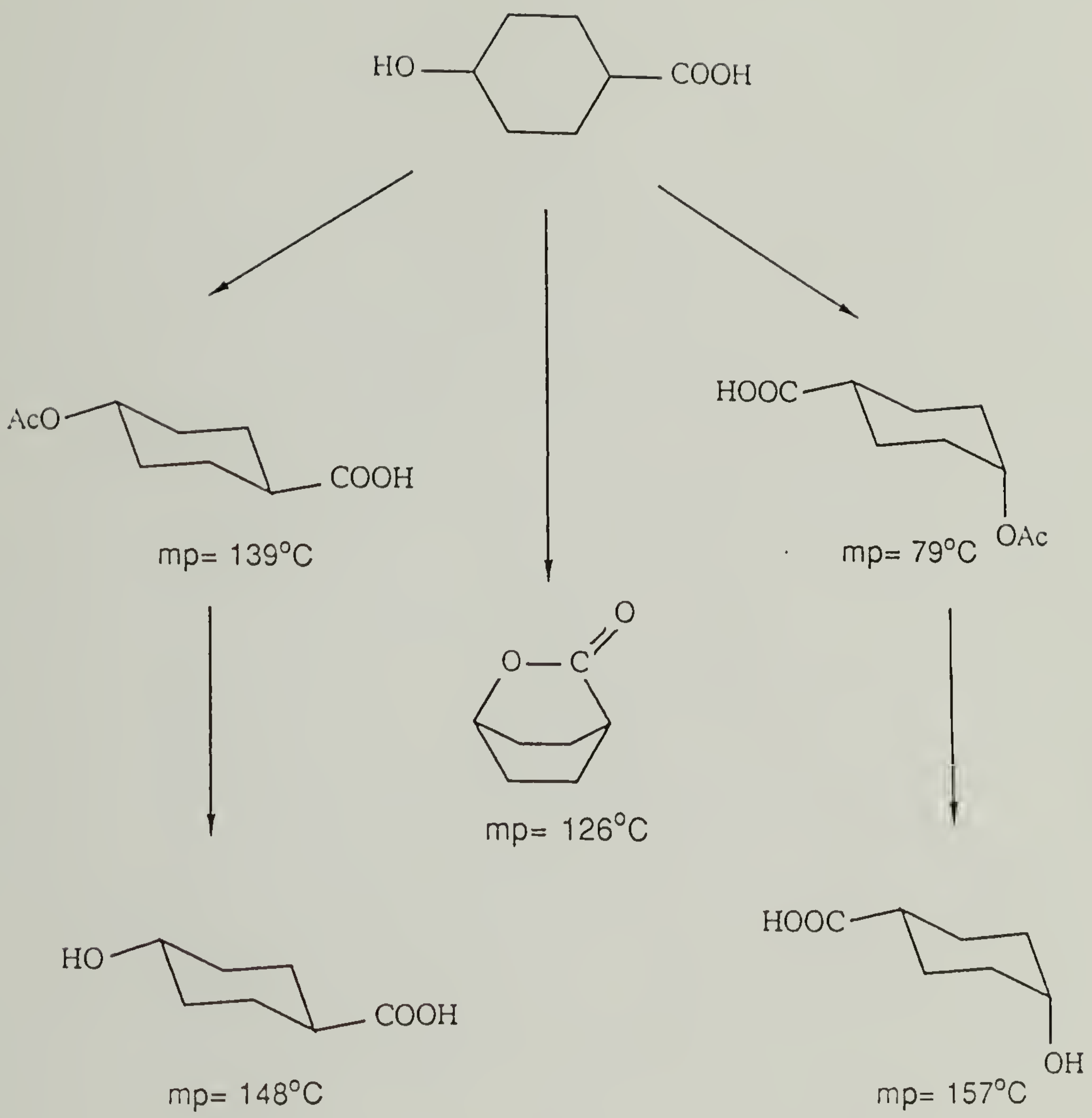

Figure 2.2 The melting point of 4-hydroxycyclohexanecarboxylic acid and derivatives (*Ref. 5*)

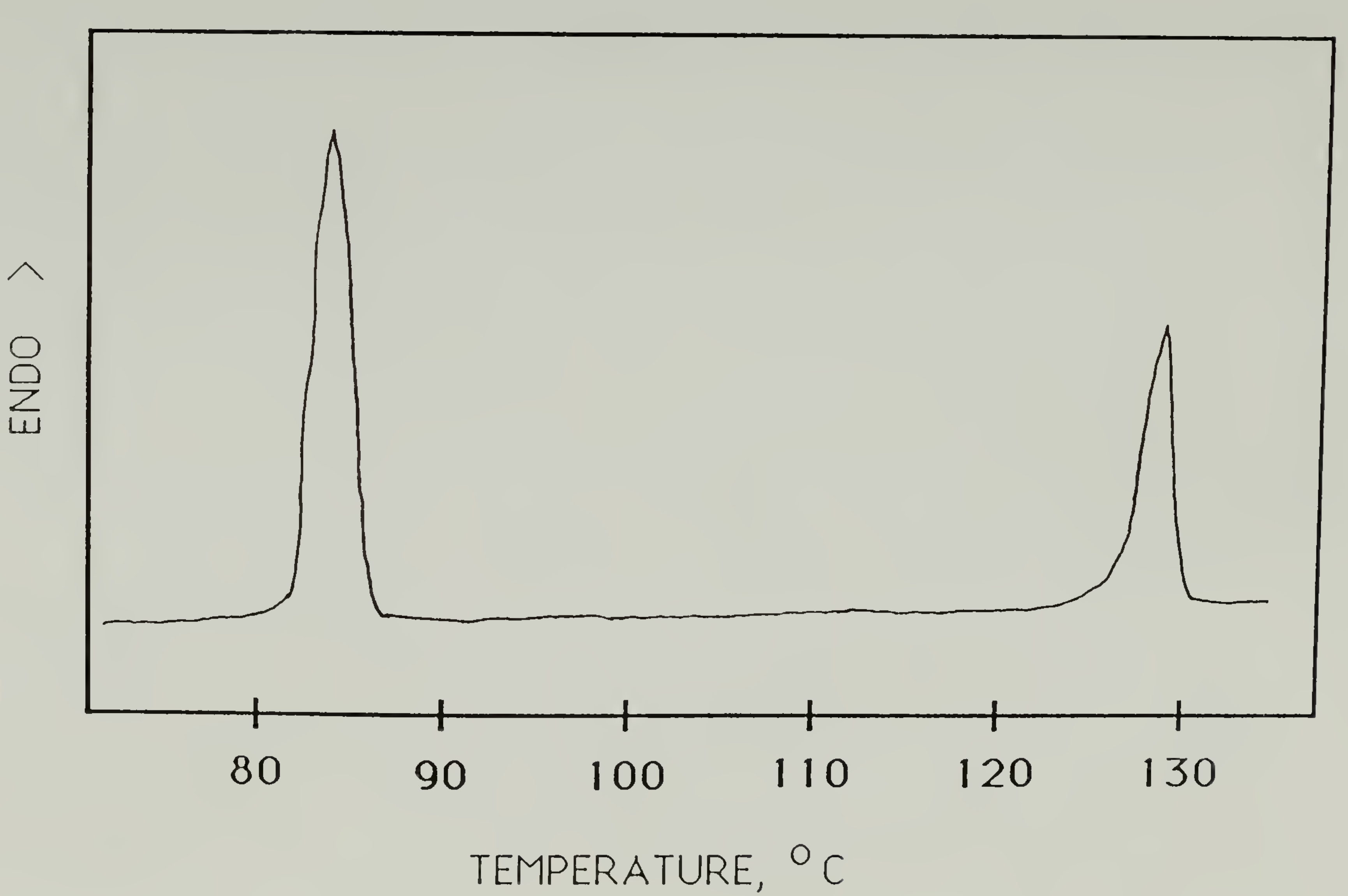

Figure 2.3 Differential scanning calorimetry curve of 2-oxa-bicyclo[2.2.2]octan-3-one

The two bicyclo monomers shown in Figure 2.1 are known, and the polymerization of them has been reported (6, 7). However, in these reports, strong base initiator was used, and a polymer high in *cis* content was formed (8). For liquid crystallinity, as desired in this research, weakly basic initiators are needed in order to encourage S_N2 attack at the bridgehead position leading to alkyl oxygen cleavage, rather than the acyl oxygen cleavage seen with the strong base initiation (9). This S_N2 initiation will lead to inversion of configuration with a resulting all-*trans* polymer. The initiators used for the lactone monomer were sodium acetate (with and without 15-crown-5), stannous octonoate and triethyl amine. Under a variety of conditions of temperature and solvents, none of these initiators produced polymer and, in all cases, monomer could be recovered from the polymerization attempt. Addition of a strong base initiator (*sec*-butyllithium) to a system which failed to polymerize with a weak base initiator, resulted in a polymer high in *cis* content.

It had been hoped that the bicyclo monomers would be polymerized by an S_N2 attack at the bridgehead, and that this propagation would lead to the all-*trans* structure. A number of substituted aromatics are available (10), and by incorporating the bicyclo compounds derived from these, it was hoped that copolymers could be made with accessible melting points. However, with the failed attempts to polymerize the simplest members of these classes, this approach of ring opening polymerizations was abandoned in favor of the method of condensation polymerization of isomerically pure monomers.

Monomers for condensation polymerization

Because liquid crystallinity with cyclohexane mesogens requires isolation of the linear isomer, the development of a method for the separation and analysis of these monomers is of utmost interest in this research. Although a number of cyclohexane monomers are available and specified as 100% *trans*-1,4, none are of the consistent high purity needed to prepare all-*trans* polymers. For example, for monomers purchased for this research, labeled as 100% *trans*, *cis* contents as high as 50% were found.

Cyclohexane diols for polyester synthesis

For polyester synthesis, the cyclohexane diols desired are shown in Figure 2.4. In all cases, the configurations shown in column II were the desired structures. Proton nuclear magnetic resonance (NMR) is a convenient method for determination of the stereochemistry. In the cases of all the monomers chosen, the amount of two isomers could be quantified by NMR. In the literature, various methods for isolation of cyclohexane isomers include recrystallization, column chromatography, solvent extraction, isomerization reactions and resin chromatography (11-13).

The 1,3-cyclohexanediol (1,3-CHD) was the most difficult monomer to separate into isomers, and the several methods attempted for purification provide an enlightening view of the general methods of isomer separation. Several

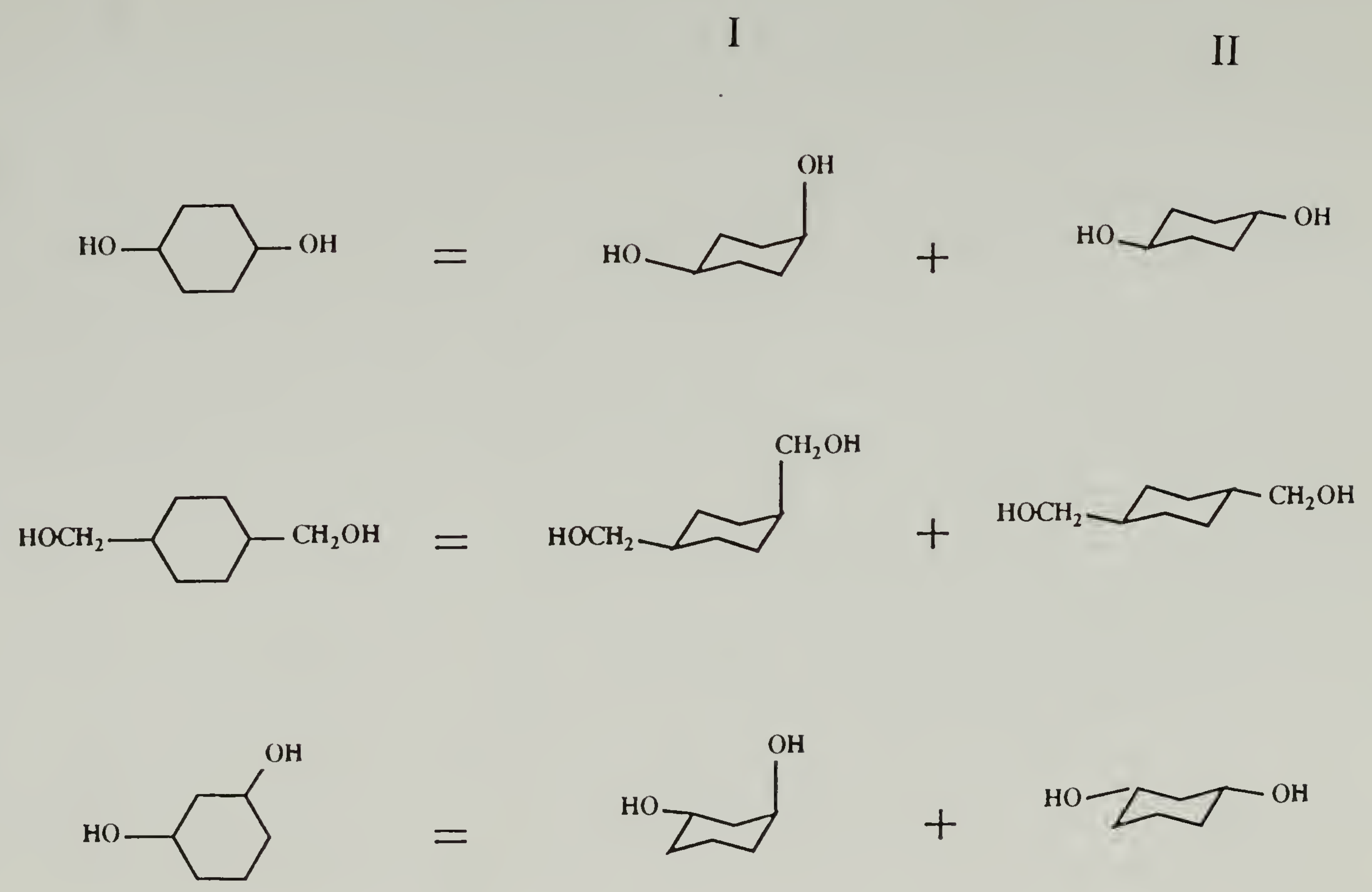

Figure 2.4 Isomeric structures of cyclohexane monomers

recrystallization solvents were tried, with cooling to room temperature or to -20 °C, with little increase in the desired isomer from the initial 50/50 isomer mixture. The diol was converted to the diacetate with acetic anhydride and this mixture separated by ether extraction. No significant difference in the two phases was seen, in contrast to that reported for the 1,4-cyclohexanediacetate or for the 1,4-cyclohexanedimethylene diacetate (13, 14). The 1,3-cyclohexanediol was prepared by the hydrogenation of resorcinol using either platinum or rhodium catalyst, in attempts to vary the isomer content of the resulting cyclohexanediol, but mixtures close to 50/50 were obtained. Separations by column chromatography with a variety of solvents gave only slight increases in *cis* content. Steam distillation gave no measurable separation. The known dehydration catalyst, Al_2O_3 (14), was used in an equilibrium isomerization reaction and a slight increase in *cis* content to approximately 65 percent was noted. A combination of the above methods, namely Al_2O_3 isomerization followed by several recrystallizations from ethyl acetate, gave the pure isomer. For the other diol monomers, the above methods were attempted and the most general (recrystallization) gave the highest purity isomer within the most reasonable time frame. The proper choice of solvent is of utmost importance. For the 1,4-cyclohexanediol (1,4-CHD), a 95/5 chloroform/ethanol mixture was used, and for the 1,4-cyclohexanedimethanol (CHDM), ethyl acetate was used; both purifications required at least five recrystallizations. Changing the solvent as the isomer content changed aided in achieving higher yields; for example, for 1,4-cyclohexanediol, ethyl acetate was a good recrystallization solvent once the *trans* isomer content reached approximately 75%. One caveat is that separations work poorly or not at all if the monomers or solvents are not anhydrous.

Nuclear magnetic resonance spectra of the three diol monomers are shown in Figure 2.5, before and after separation of the desired isomer. For the case of the 1,4-diols, the ring methylene hydrogens are observed as separate peaks in the *trans* configuration due to non-interconversion of axial and equatorial positions. One methylene peak is observed for the *cis* isomer due to interconversion of the two chair forms in the time scale of the NMR. The ring methine position shows one peak for the *cis* and one peak for the *trans*, with both peaks occurring in the isomer mixture. The methylene adjacent to the hydroxy in 1,4-cyclohexanedimethanol is seen as a doublet in the pure isomer and as two doublets in the isomer mixture. The NMR analysis of the 1,3-cyclohexanediol is more complex, with the loss of a plane of symmetry for this monomer as compared to the 1,4-isomers. But here, as with the 1,4-isomers, the methine region shows that only one isomer is present in the purified material. Detailed analysis of the methylene region allows unambiguous assignment of the *cis*-1,3-structure.

Cyclohexane diacids for polyester and polyamide synthesis

The *trans*-1,4-cyclohexanedicarboxylic acid chloride (CHDC) was prepared by conversion of the diacid to the diacid chloride, using thionyl chloride with added *N,N*-dimethylformamide. The *trans* form of the acid was isolated from the mixture, prior to preparation of the acid chloride, by recrystallization from water. The dimethyl ester was also used and conversion to the diacid was accomplished by reflux in water with H_2SO_4 catalyst. This reaction not only yielded the acid from the ester, but the resulting recrystallized product was pure *trans* isomer, with the

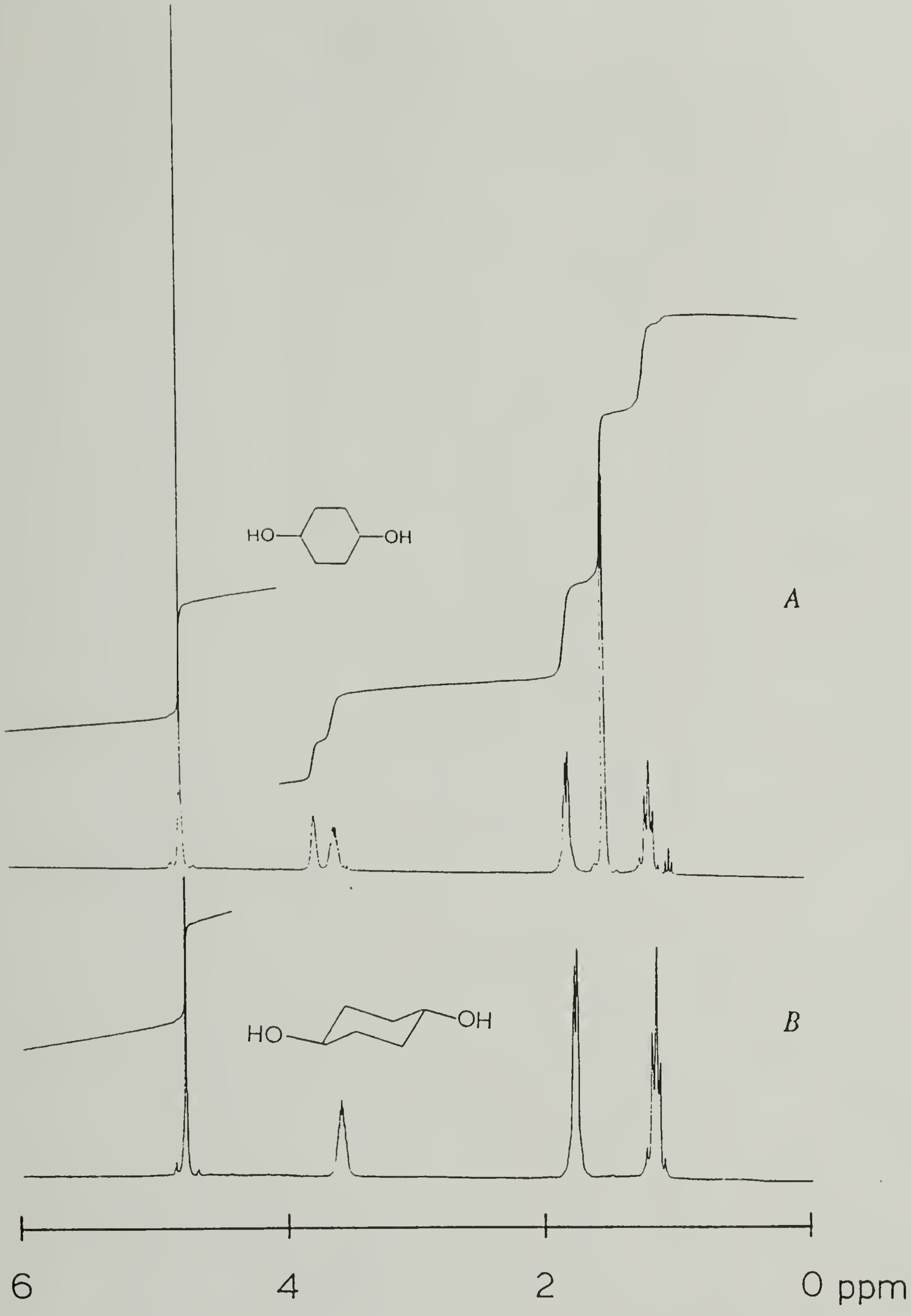

Figure 2.5 Nuclear magnetic resonance spectra of cyclohexane diols. *A*, *C* and *E* are isomer mixtures; *B*, *D* and *F* are the desired isomer (see Figure 2.4, Column II, and text)

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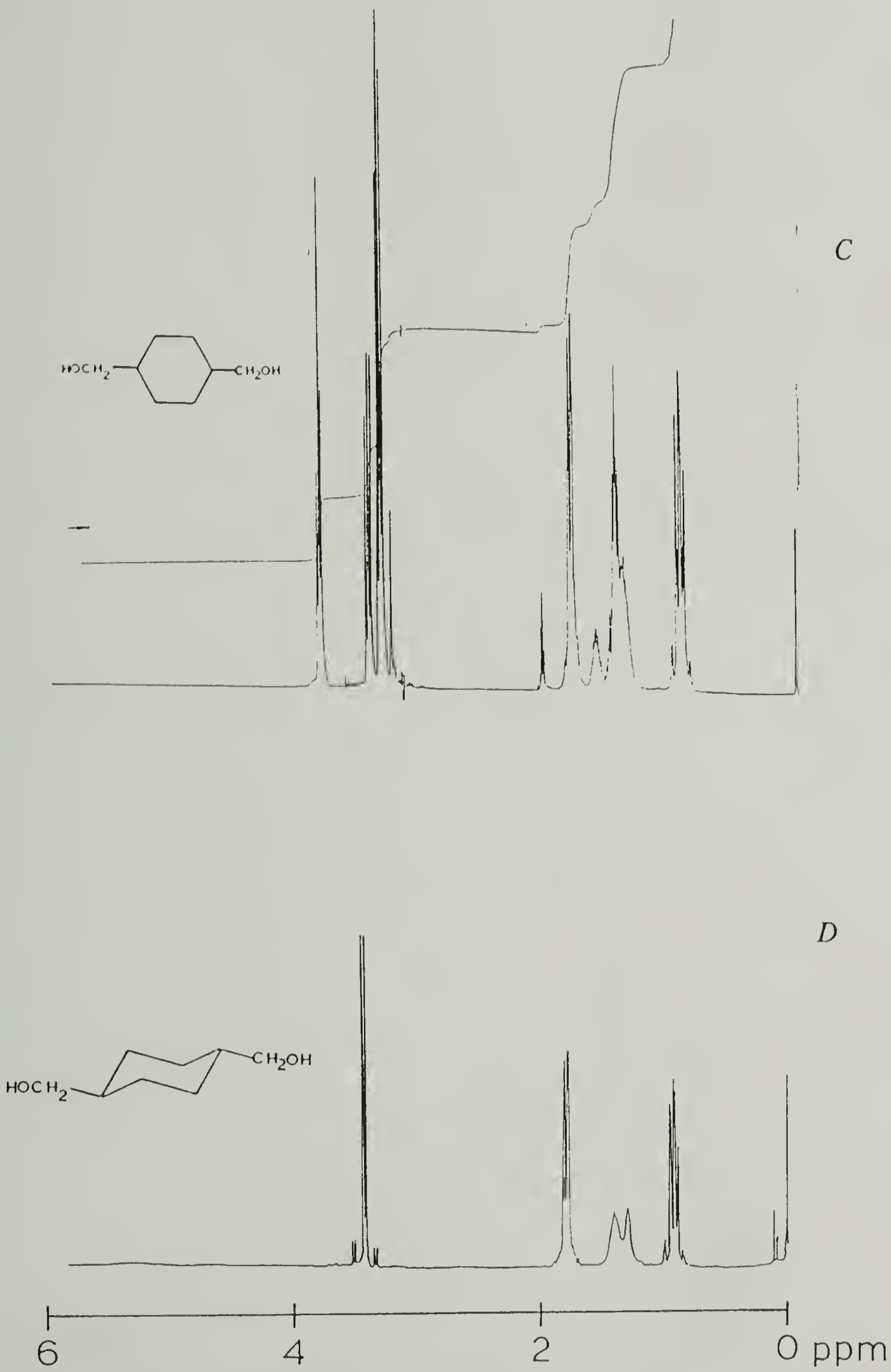

Figure 2.5 cont.

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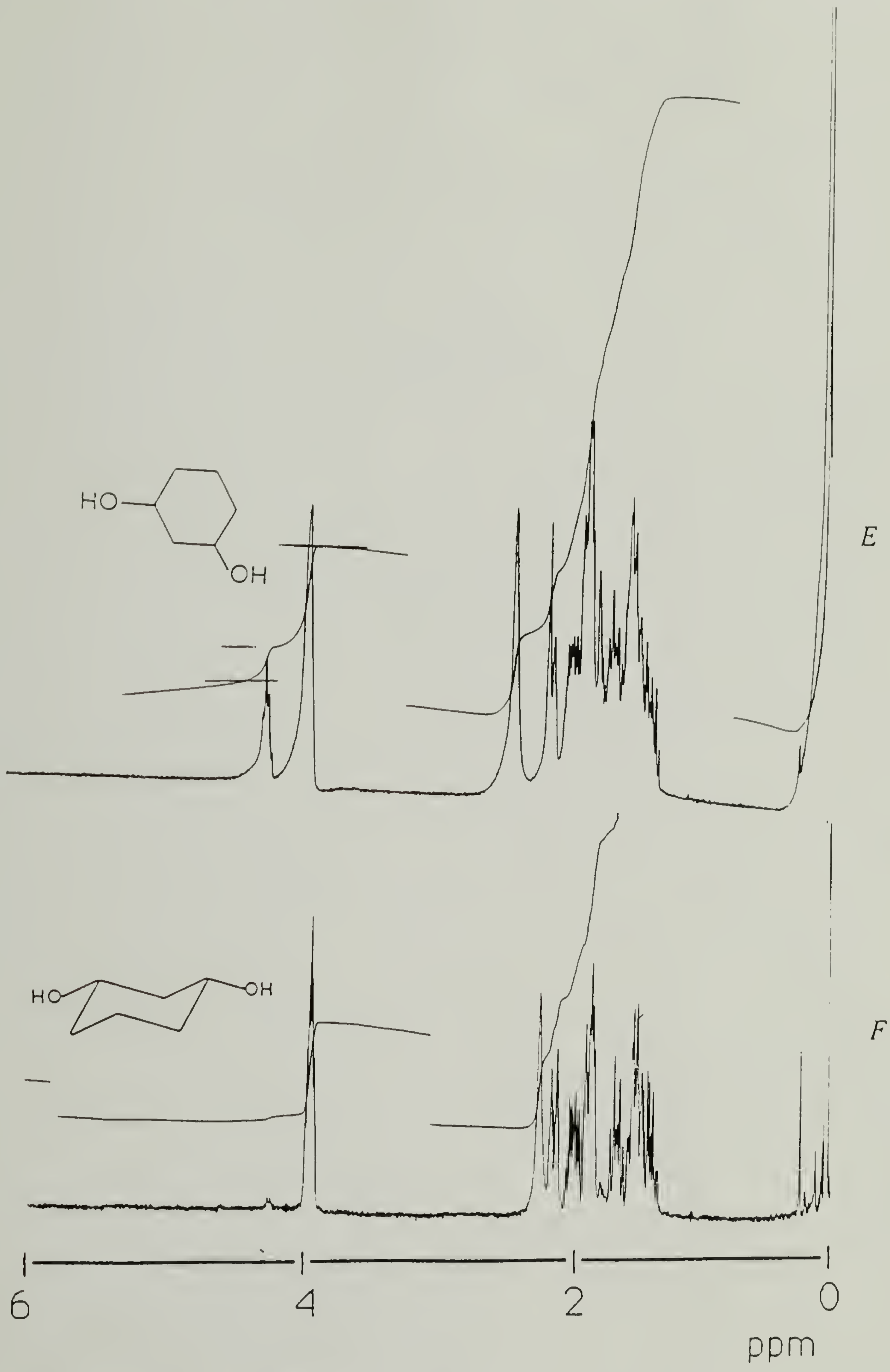

Figure 2.5 cont.

conversion being accomplished either by the recrystallization or the isomerization reaction (11). Conversion of the dimethyl ester to the diacid to the diacid chloride did not allow for reversion to the *cis* isomer, as evidenced by the NMR spectra shown in Figure 2.6. The analysis of the peaks is exactly analogous to that of the 1,4-cyclohexanediol above.

One other acid was prepared, the *trans*-1,4-cyclohexanediacetic acid (CHDAA), by the reaction scheme shown in Figure 2.7. This compound has apparently only been reported once before (15). In this case the synthesis was via the reaction of the ylide of diethyl(carboethoxy methyl)phosphonate with 1,4-cylohexanedione, followed by hydrogenation. In this research, the more direct scheme, shown in Figure 2.7, was used. This synthesis proceeds without reaction at the stereochemical center, such that the *trans*-1,4-cyclohexanedimethanol can only give the *trans* form of the diacid. Isomerically pure *trans*-1,4-cyclohexanedimethanol was converted to the dibromo (or diido) compound via the ditosyl derivative. The dihalo compound was converted to the diacid via either the cyanide reaction or the diGrignard reaction. Both methods gave the desired product, free of isomeric impurities; the diGrignard proceeded to higher yields. Initial attempts to prepare the dibromo compound from the dimethanol with aqueous hydrobromic acid gave the bromoalcohol as the predominant product, again in isomerically pure *trans* form.

The melting points of the above compounds, as measured in this investigation, agree well with literature melting points as seen in Table 2.1.

The purification of the other monomers used in this study is described in the experimental section at the end of this chapter.

Figure 2.6 Nuclear magnetic resonance spectra of *trans*-1,4-cyclohexanedicarboxylic acid and derivatives. *A* is the dimethyl ester, *B* is the diacid and *C* is the diacid chloride

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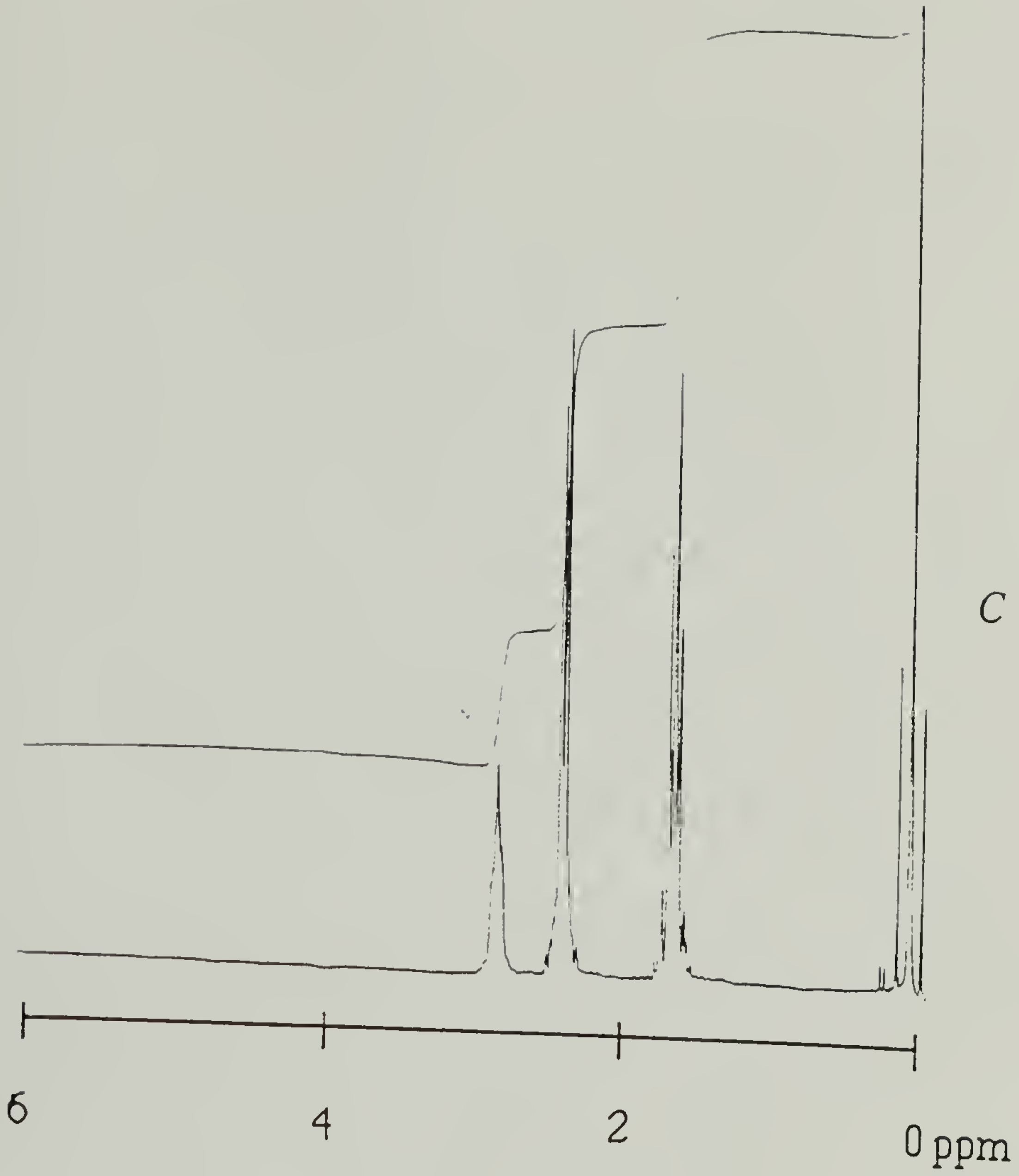


Figure 2.6 cont.

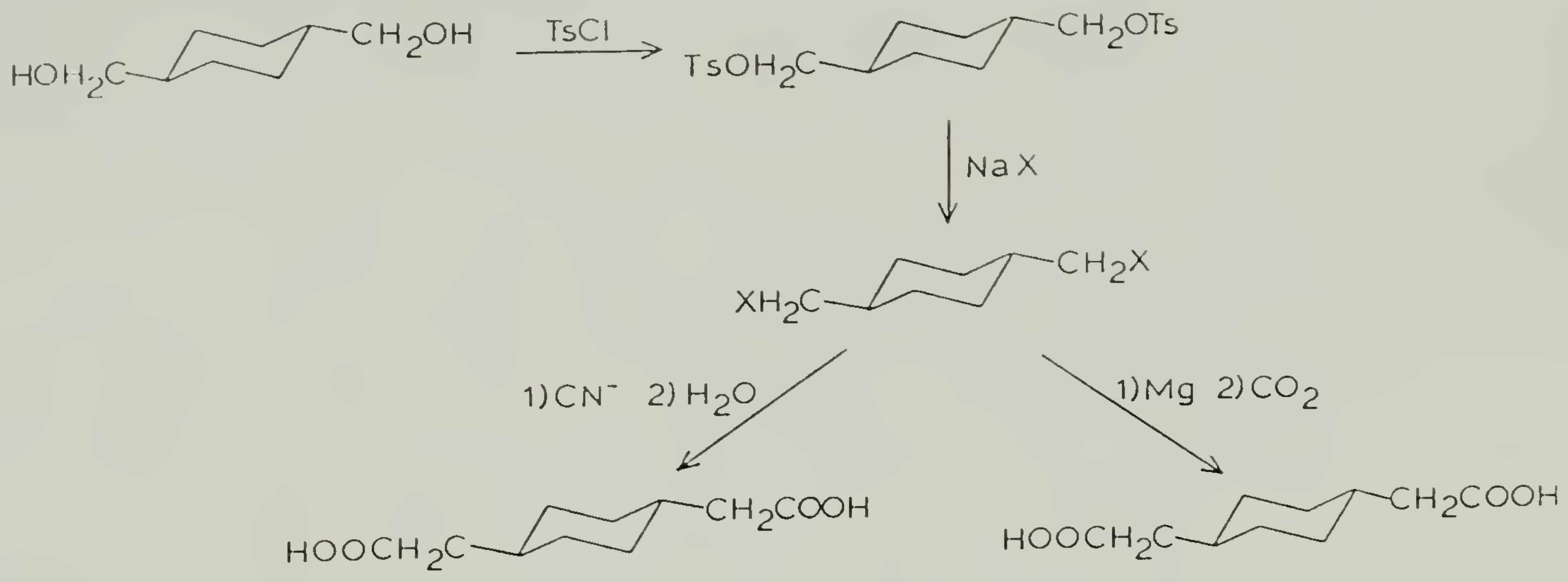


Figure 2.7 Synthesis of *trans*-1,4-cyclohexanediacetic acid

Table 2.1 The melting points of cyclohexane monomers used in this research

	Melting point of isomer mix	Melting point of Figure 2 isomer	Literature Value	Ref.
1,4-CHD	98-100	141-142	142	(14)
CHDM	wax	64.5-66	64	(13)
1,3-CHD	30	84.5 -86	84-85	(12)
CHDC	---	68-69	68-69	(16)

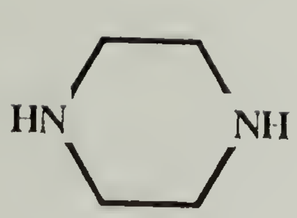
Secondary diamines for polyamide synthesis

The structures of three diamines of particular interest are shown in Figure 2.8. These three are among the most strongly basic of all diamines (17), and a CO_2 reaction has been reported for strongly basic diamines (18). For these monomers, CO_2 uptake could be seen by elemental analysis and NMR, and the evolution of the CO_2 could be seen on heating by DSC or thermogravimetric analysis (TGA).

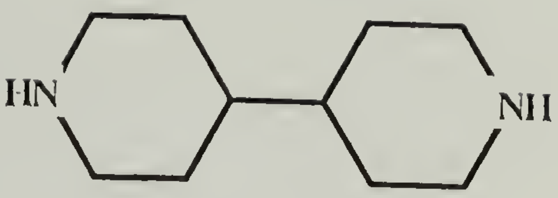
Carbon dioxide uptake occurred upon equilibration with ambient atmosphere. This uptake could be enhanced by dissolving the diamine in tetrahydrofuran and bubbling the CO_2 through the solution until precipitation of the carboxylated diamine occurred. By this method CO_2 extents of reaction of up to 70% (based on mole percent of the free diamine) could be obtained. Freshly sublimed diamine could be kept free of CO_2 only by handling the compound under an inert atmosphere. (As will be described in Chapter 4, the presence of carboxylated diamine does not preclude the preparation of polyamides by the reaction with diacid chlorides.) CO_2 contents could be determined by elemental analysis, but the analysis was complicated by nonequilibrium sample weight prior to analysis.

The release of CO_2 occurs on heating as seen in a TGA trace in Figure 2.9 for TMP-CO_2. This release can also be seen by DSC as a rather irregular endothermic process as shown in Figure 2.10. Subsequent DSC heating runs show melting with little or no subsequent endothermic peaks depending on how quickly the sample is cooled.

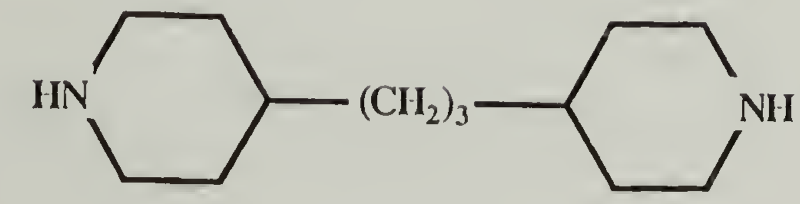
Examination of these materials by polarized optical microscopy (POM) showed nematic structures in a water solution of all three carboxylated diamines as



PIPERAZINE (PIP)



4,4'-BIPIPERIDINE (BP)



4,4'-TRIMETHYLENEDIPIPERIDINE (TMP)

Figure 2.8 The structure of some cyclic secondary diamines

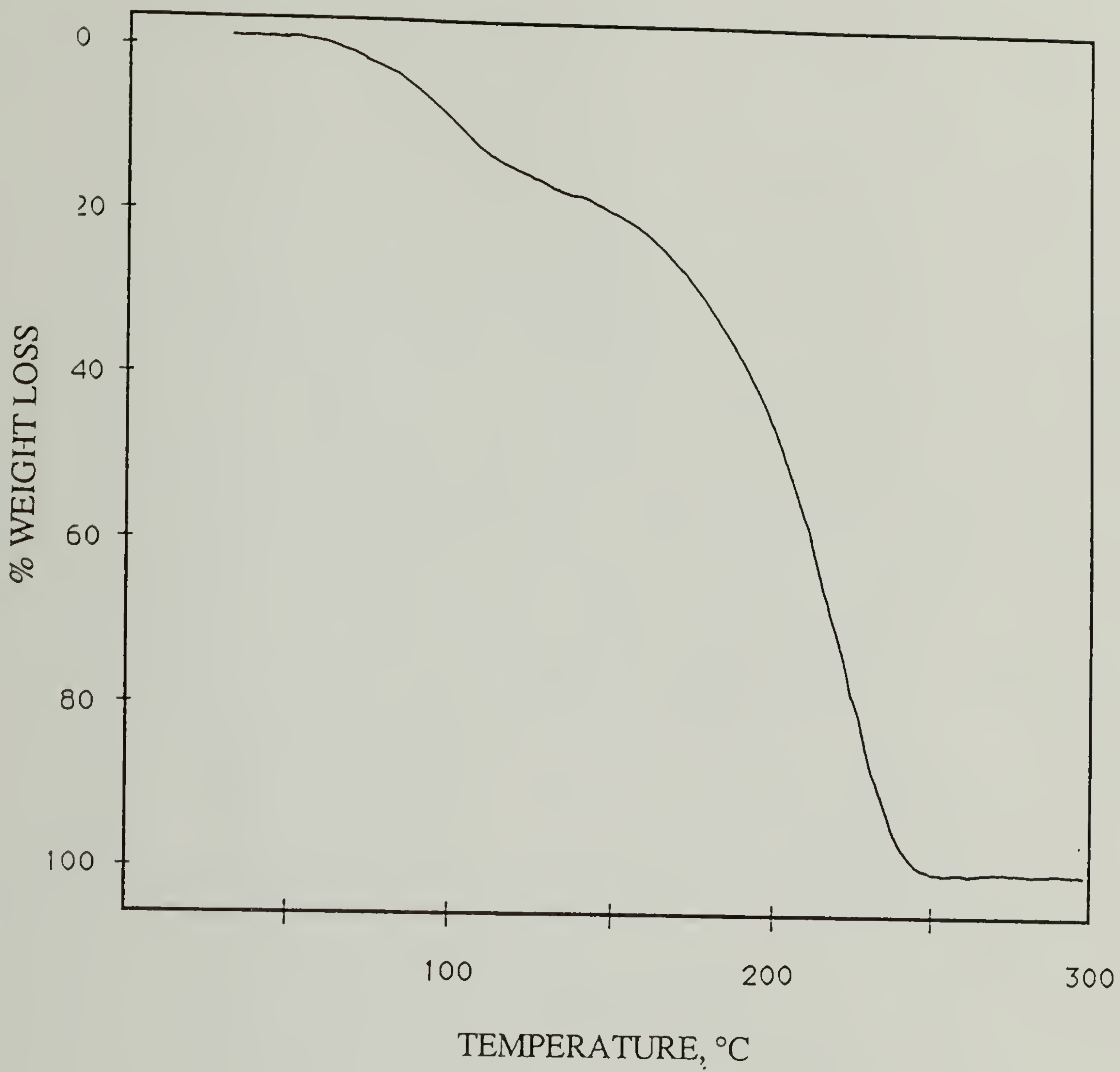


Figure 2.9 Thermogravimetric analysis of carboxylated 4,4'-trimethylenedipiperidine

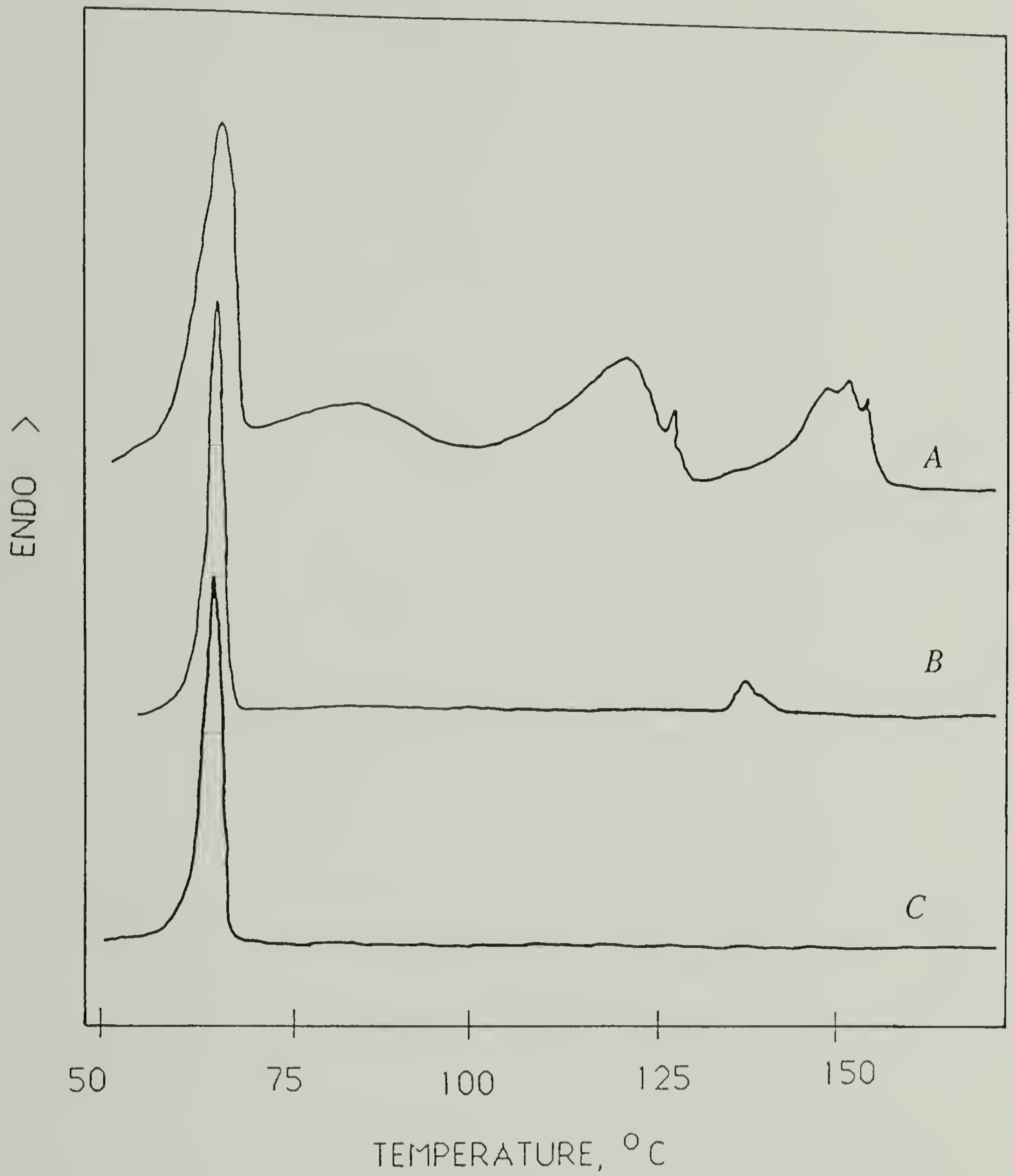


Figure 2.10 Differential scanning calorimetry of carboxylated 4,4'-trimethylenedipiperidine. *A* is first heating, *B* is second heating following quench cooling, *C* is second heating following slow cool

shown in Figure 2.11. The CO_2 contents of the examined diamines were 72%, 55% and 28% (based on mole percent of free diamine) for the piperazine, TMP and BP, respectively. On heating at a constant rate (10 °C/min) a nematic texture appeared above the diamine melting point, but this structure was not stable. This behavior can be seen more clearly at constant temperature, observing first the appearance, and afterward the disappearance, of a nematic texture, as seen in Figure 2.12 for TMP at 110 °C. This behavior is explained by the schematic of Figure 2.13 with an extended structure resulting from the ionic interaction of a diamine and a carboxylic acid. As the CO_2 evolves with heating, the ionic bonding decomposes, and evidence of an extended structure is not seen on subsequent heatings unless more CO_2 is absorbed.

Figure 2.14 summarizes the monomer structures used in this study, and will be referred to in future Chapters of this dissertation.

Monomer reactions and low molecular weight compounds

Several low molecular weight model compounds and intermediates were made in the course of this research and were routinely examined for liquid crystalline phases. Figure 2.15 lists several of these compounds. All of these derivatives melted to isotropic fluids.

The *trans*-1,4-cyclohexanediisocyanate (CHDI) is commercially available and is of high isomeric purity (19). This compound was used to prepare several

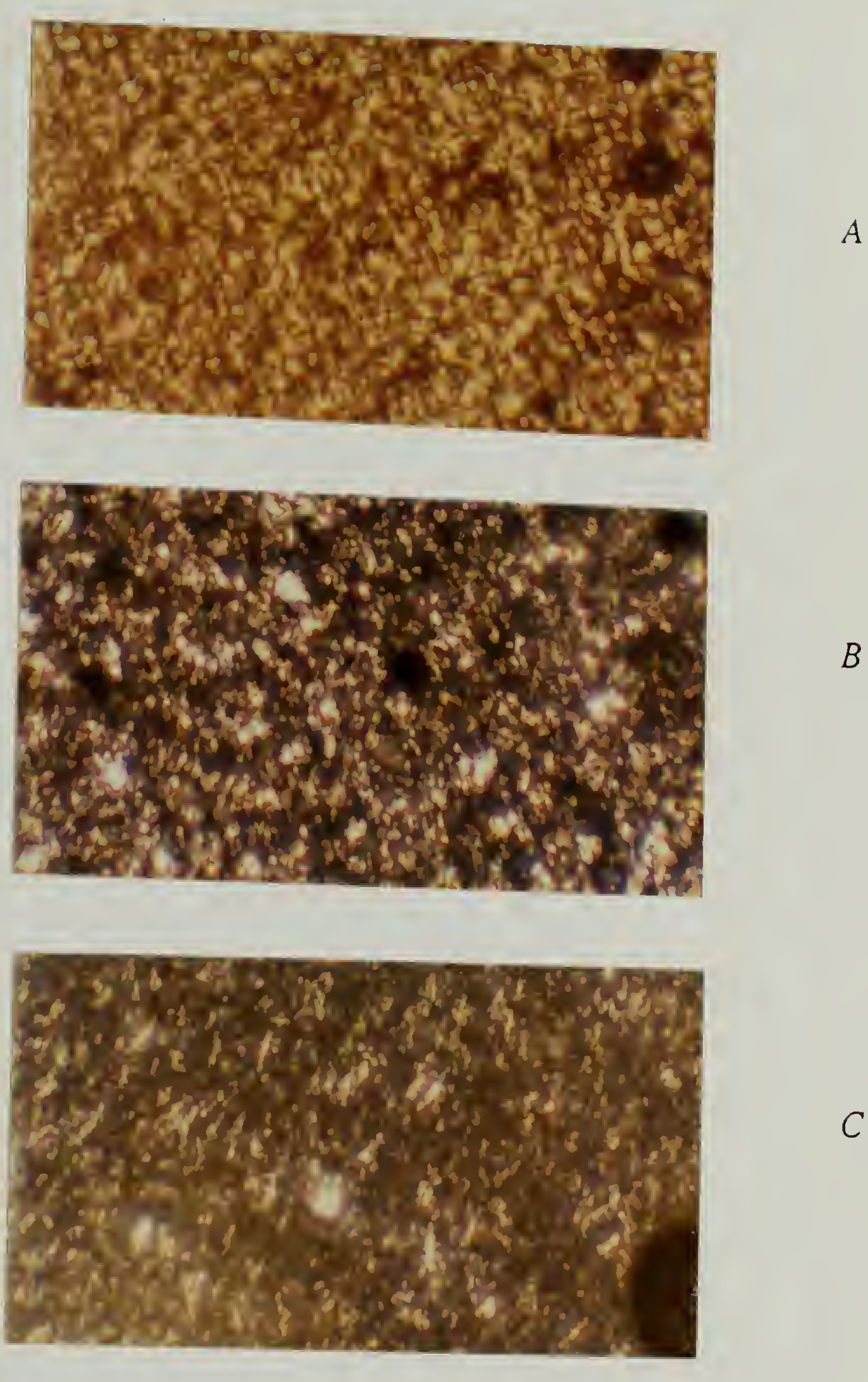


Figure 2.11 Polarized optical microscopy of carboxylated diamines in water solution. *A* is piperazine, *B* is 4,4' - bipiperidine, *C* is 4,4'-trimethylenedipiperidine

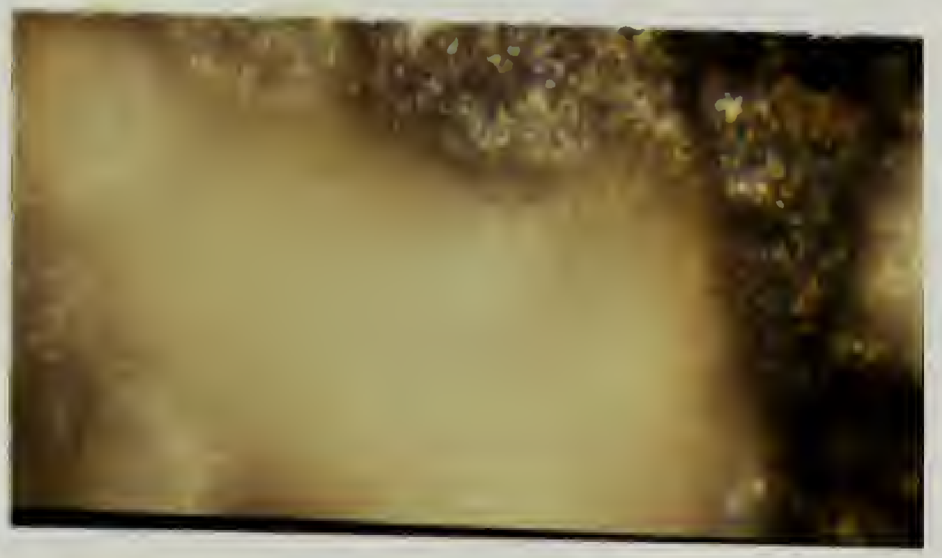


Figure 2.12 Polarized optical microscopy of carboxylated 4,4'-trimethylenedipiperidine held at 110 °C.
A-4.5 min; *B*-7 min; *C*-10.5 min; *D*-16 min, *E*-22 min

cont. next page

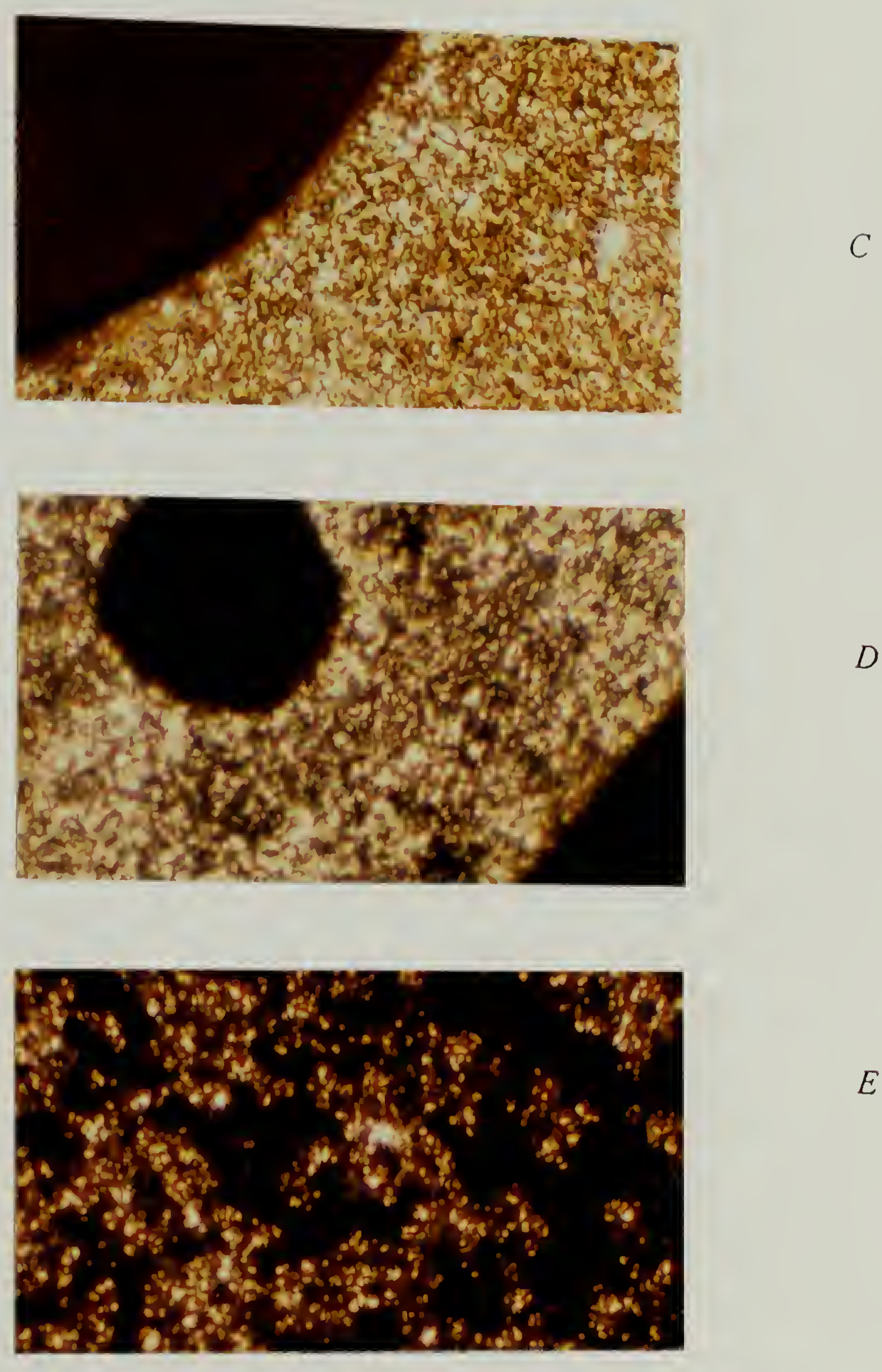


Figure 2.12 cont.

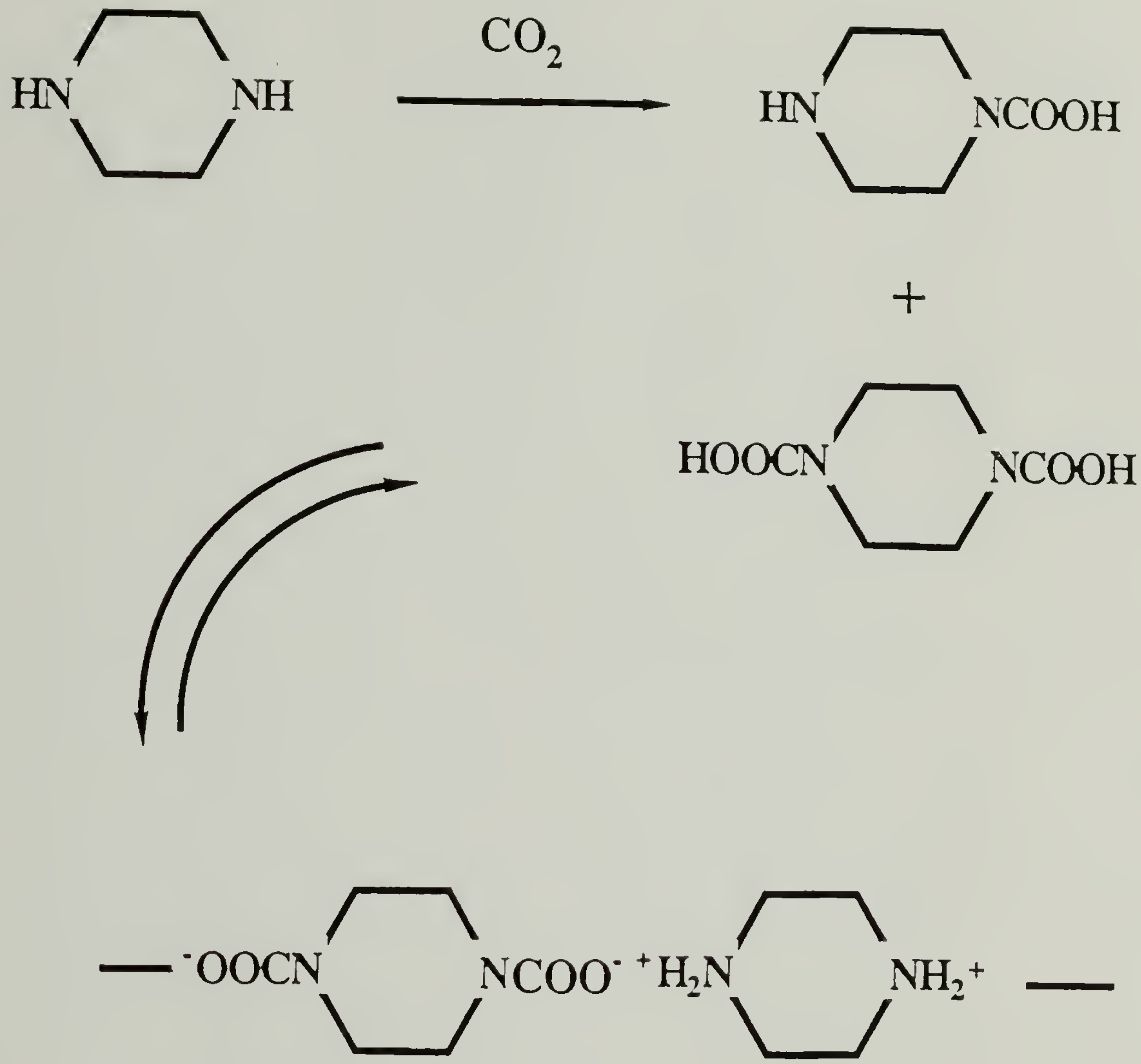
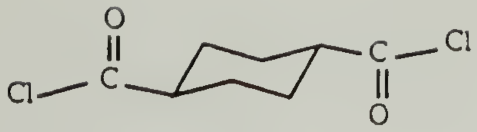
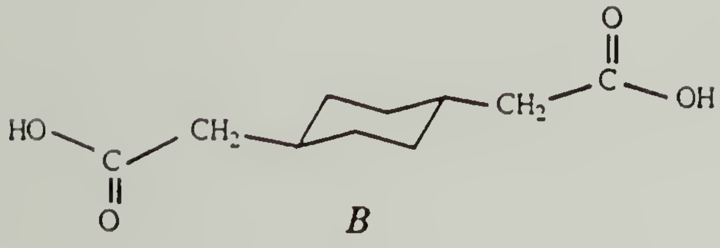


Figure 2.13 Extended structure of carboxylated diamines

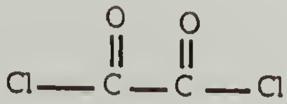
I



A

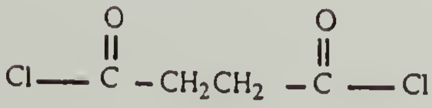


B



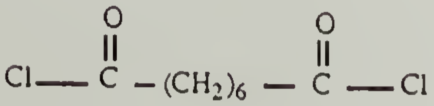
C

$\mathrm{Cl-\overset{\underset{\|}{O}}{C}-\overset{\underset{\|}{O}}{C}-Cl}$



D

$\mathrm{Cl-\overset{\underset{\|}{O}}{C}-CH_2CH_2-\overset{\underset{\|}{O}}{C}-Cl}$



E

$\mathrm{Cl-\overset{\underset{\|}{O}}{C}-(CH_2)_6-\overset{\underset{\|}{O}}{C}-Cl}$

II

F

G

H

$\mathrm{HO-(CH_2)_4-OH}$

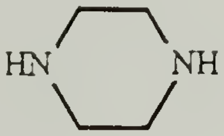
I

$\mathrm{HO-(CH_2)_6-OH}$

J

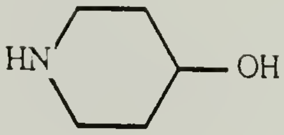
Figure 2.14 Structure of monomers used in this research
cont. next page

III IV V

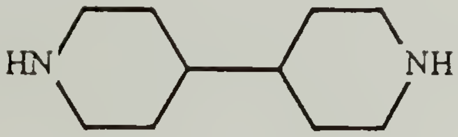


K

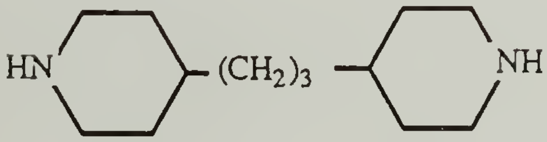
N



O



L



M

Figure 2.14 cont.

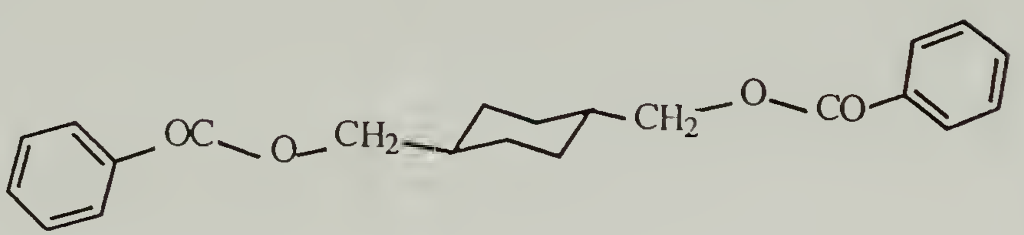
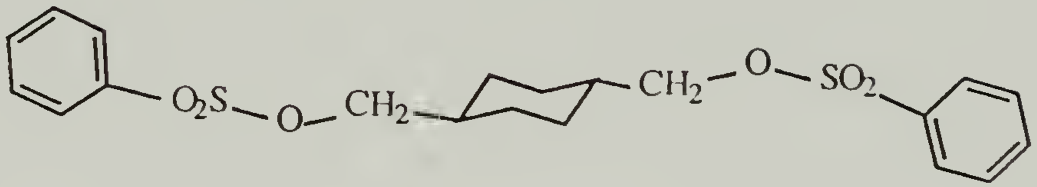
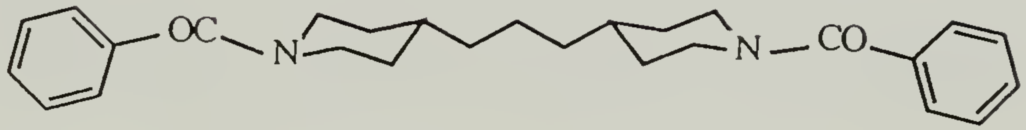
	MELTING POINT, °C
	121-122
	162-164
	112-115
	112-114

Figure 2.15 Melting points of some model compounds

foams by reacting it with ether diols of a molecular weight of 400 to 2000. These foams formed rapidly (in under 1 minute) and were tough materials. No liquid crystalline polymers were prepared from this monomer in light of the very high melting points observed for non-liquid crystalline polyurethanes. For example, the polymer prepared from CHDI and 1,6-hexanediol melted above 300 °C.

CHDI was used to prepare two diamine monomers. The *trans*-1,4-*N,N'*-dimethylcylohexane diamine was prepared via the lithium aluminum hydride reduction of CHDI. This compound had a melting point of 100-102 °C. The carboxylated version of this compound displayed liquid crystalline phases in water. The *trans*-1,4-cyclohexanediamine was isolated in the workup from the lithium aluminum hydride reaction, and could also be made by simple hydrolysis of CHDI.

Experimental

The following section gives experimental details for the purification of each of the monomers previously described, using specific examples where appropriate.

Equipment

Hydrogenations were performed in a glass-lined, Parr stainless steel reactor, model 4563. Melting points were determined on a Fisher-Johns melting point apparatus and/or a Perkin Elmer DSC 2. Nuclear magnetic resonance spectra were obtained on Varian XL 200 or 300 MHz instruments with an internal tetramethylsilane (TMS) reference. Polarized optical microscopy was performed with a Leitz-Wetzler microscope at a magnification of 320X. Thermogravimetric analysis was performed on a Perkin Elmer TGS-2 with a System 4 Microprocessor. Gas chromatography/mass spectrometry (GC/MS) was performed by Thomas Potter on a Hewlett Packard HP 5985B instrument with a fused silica capillary. Elemental analyses were determined by the Microanalytical Lab at the University of Massachusetts.

Materials

Catalyst preparation. 5% Rh on carbon was mixed with 0.4 M NaOH, heated to boiling, cooled and stirred overnight. The Rh/C was collected by filtration, washed with 0.5% acetic acid and dried at 65 °C under vacuum for 24 h.

2-Oxabicyclo[2.2.2]octan-3-one. *p*-Hydroxybenzoic acid was recrystallized from water. 45.0 g was mixed with 200 mL of water and 0.92 g Rh catalyst, and hydrogenated at 1000 psi. The catalyst was removed by filtering through Celite®, and the solution was concentrated until crystallization occurred. 29.8 g (64%) of the hydrogenated hydroxy acid was recovered, mp = 124-130 °C. Nuclear magnetic resonance analysis in D_2O showed singlets at 3.7, 3.4, 2.2 and 2.35, and a complex multiplet at 1.05-1.9. 7.02 g of this compound was mixed with 250 mL *m*-xylene and 0.8 g Sb_2O_3 and refluxed under a Barrett trap for 6 h. The *m*-xylene was removed by vacuum distillation and the resulting solid mixture was transferred to a sublimator. The sublimed material was recrystallized three times from sieve-dried cyclohexane. White, needle-like crystals were recovered with a melting point of 128-129 °C. Nuclear magnetic resonance analysis in $CDCl_3$ showed singlets at 4.7 and 2.6 and a multiplet at 1.65-2.1, in the ratio of 1:1:8. Microanalysis results: Theory: C = 66.65, H = 7.99; Found: C = 66.65, H =7 .98.

2-Azabicyclo[2.2.2]octan-3-one. *p*-Amino benzoic acid (11.0 g) was mixed with 200 mL water and 0.98 g Rh catalyst and hydrogenated at 600 psi. The catalyst was removed by filtering through Celite®, and the water solution was concentrated until crystallization was noted. The crystals were collected and washed with *N,N*-dimethylformamide (DMF) and methanol, yielding 3.8 g (34%), which decomposed without melting above 270 °C. Nuclear magnetic resonance analysis in D_2O showed singlets at 2.6 and 1.8 and a broad multiplet at 0.8-1.5. Microanalytical results: Theory: C = 58.7, H = 9.15, N = 9.78; Found: C = 58.52, H = 8.95, N = 9.76. 1.2 g of the hydrogenated amino acid was mixed with 30 mL of diphenyl ether, and refluxed for 15 minutes. The solution was cooled, diluted with 100 mL of heptane and extracted with water. The water extract was concentrated, and 0.2 g of a white crystalline solid was collected, with a melting point of 196-198 °C. NMR analysis in dimethyl-d_6 sulfoxide showed singlets at 3.2 and 2.2 and a multiplet from 1.5-1.8 in the ratio of 1:1:8.

trans-1,4-Cyclohexanediol (1,4-CHD) . 1,4-Cyclohexanediol was purchased from Aldrich as an isomer mixture. 28.5 g of this isomer mixture was recrystallized from 200 mL of a 95:5 $CHCl_3$/ethanol solution and hot filtered with activated carbon. The crystals were recrystallized twice more from the same solvent mixture, yielding 16.8 g of a white crystalline material. This material was recrystallized twice from ethyl acetate, yielding 10.4 g (36%) of 1,4-CHD with a melting point of 140.5-141.5 °C. NMR analysis in D_2O showed a singlet at 3.5, a doublet at 1.8 and a triplet at 1.2.

cis-1,3-Cyclohexanediol (1,3-CHD). Resorcinol (16.7 g) was purified by dissolving in 200 mL of water and filtering with activated carbon. To this clear solution was added 0.78 g of Rh catalyst. Hydrogenation was achieved at 1250 psi. The hydrogenation catalyst was removed by filtering through Celite and the water was removed by vacuum distillation. The resulting oily product was recrystallized three times from ethyl acetate, with cooling to -20 °C to induce crystallization. This white, amorphous material was dried by the addition and subsequent distillation of two 50 mL portions of *n*-butyl alcohol. 2.2 g of Al_2O_3 was activated by heating to 400 °C for 2 h. A mixture of diol and Al_2O_3 was loaded into a pressure tube and purged with Ar. After purging for 15 minutes, the tube was heated to 280 °C for 4 h with external agitation. The mixture was cooled, diluted with 100 mL of ethanol, and the Al_2O_3 was removed by filtration. The ethanol was removed by vacuum distillation. The resulting crystals were purified by four recrystallizations from ethyl acetate. After drying, 5.6 g (32%) of 1,3-CHD was collected with a melting point of 83-84 °C. Nuclear magnetic resonance analysis in

$CDCl_3$ showed singlets at 3.9 and 2.2, a doublet at 2.1 and a complex multiplet at 1.3-2.0.

trans-1,4-Cyclohexanedimethanol (CHDM). CHDM was purchased from Aldrich as an isomer mixture. 88.9 g was recrystallized five times from ethyl acetate, yielding 8.40 g (27% based on *trans* content) , with a melting point of 64.5-66 °C. NMR analysis in $CDCl_3$ showed doublets at 3.4 and 1.8, a singlet at 1.25 and 1.4 and a triplet at 0.9.

trans-1,4-Cyclohexanedicarboxylic acid chloride (CHDC). A sample of dimethyl-1,4-cyclohexane dicarboxylate was received from Eastman (lot X 10508-128-2). 81.24 g of this diester was mixed with 1200 mL of water and 2 mL of concentrated H_2SO_4 and refluxed for 30 h. After refluxing, the volume was reduced to 800 mL and the sample allowed to crystallize overnight. 54.2 g of the diacid sample was collected (78%). NMR analysis in D_2O/acetone-d_6 showed a singlet at 2.35, a doublet at 2.05 and a triplet at 1.45 in a ratio of 1:2:2. The diacid was loaded into a 500-mL 2-neck round-bottom flask equipped with a reflux condenser and an Ar purge inlet tube. 100 mL of thionyl chloride (1.2 molar excess) was added slowly by cannula to the stirred sample. After the thionyl chloride addition was complete, 1 mL of DMF was added by cannula. The sample was refluxed for 6 h with a continual Ar purge. Initial HCl evolution was rapid, but slowed after the first hour and could not be detected after 4.5 h. The residual thionyl chloride was removed by vacuum distillation. The slightly yellow product was recrystallized three times from sieve-dried cyclohexane. The resulting needle-like crystals were dried under vacuum yielding 44.7 g (67%) of CHDC with a melting point of 67-68.5 °C. NMR analysis showed a singlet at 2.8, a doublet at 2.35 and a triplet at 1.65.

Other monomers. 1,6-Hexanediol, 1,4-butanediol, oxalyl chloride, succinyl chloride, adipoyl chloride and 4-hydroxypiperidine were purified by vacuum distillation. Piperazine (PIP) was purified by sublimation, recovering a product with a melting point of 110.5-112 °C. 4,4'-trimethylenedipiperidine (TMP) was recrystallized from cyclohexane and sublimed immediately prior to use in polymerizations (melting point = 65-66.5 °C). 4,4'-Bipiperidine (BP) was purchased as the dihydrochloride and was sublimed after neutralization (melting point = 162-164 °C). 1,4-Bis-(2-hydroxyethyl) piperazine (BHEP) was recrystallized from toluene, giving a product with a melting point of 134.5-136 °C.

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CHAPTER 3
POLYESTER SYNTHESIS AND CHARACTERIZATION

Introduction

Polyesters are the most commercially successful condensation polymers, with poly(ethylene terephthalate) (PET) accounting for a majority of sales (1). The reason for this success is not difficult to understand, as PET can be processed into fibers or films with outstanding strength and modulus, high impact strength, high tear strength and good thermal and solvent resistance (2). Processing is easy because PET can be melt processed at temperatures under 300 °C.

It is no coincidence that one of the earliest reports of a thermotropic liquid crystalline polymer was modified PET. PET already has a relatively high linear aromatic content, and when the linear aromatic content is increased, liquid crystalline phases are observed. Jackson and co-workers (3) post-polymerized PET with 4-hydroxybenzoic acid (HBA) in a transesterification reaction, and observed liquid crystallinity at HBA contents above 35 mole percent. Some of the properties of these polymers were discussed in Chapter 1 (see Figure 1.7). Since this early report of a thermotropic liquid crystalline polymer, polyesters have remained the most researched polymeric systems for thermotropic liquid crystallinity. A vast number of polyester systems have been researched using various diols and diacids. Most of these have been all-aromatic systems.

As described in Chapter 1, some mixed aromatic/cyclohexane liquid crystalline polyesters have been synthesized (4, 5-9). No all-cyclohexane based liquid crystalline polyester has been well documented. This chapter will describe several examples of this behavior.

The preparation and purification of monomers was described in Chapter 2. The relevant monomers for the polyesters described in this chapter are shown in Figure 2.14, columns I and II. The method for polyester preparation was the reaction of diols and diacid chlorides, chosen because the reaction proceeds at rapid rates at relatively low temperatures. Low temperatures are necessary to avoid isomerization as will be described in this chapter. For all the polyesters described in this chapter, unless otherwise stated, the diacid component used in the synthesis was *trans*-1,4-cyclohexanedicarboxylic acid chloride.

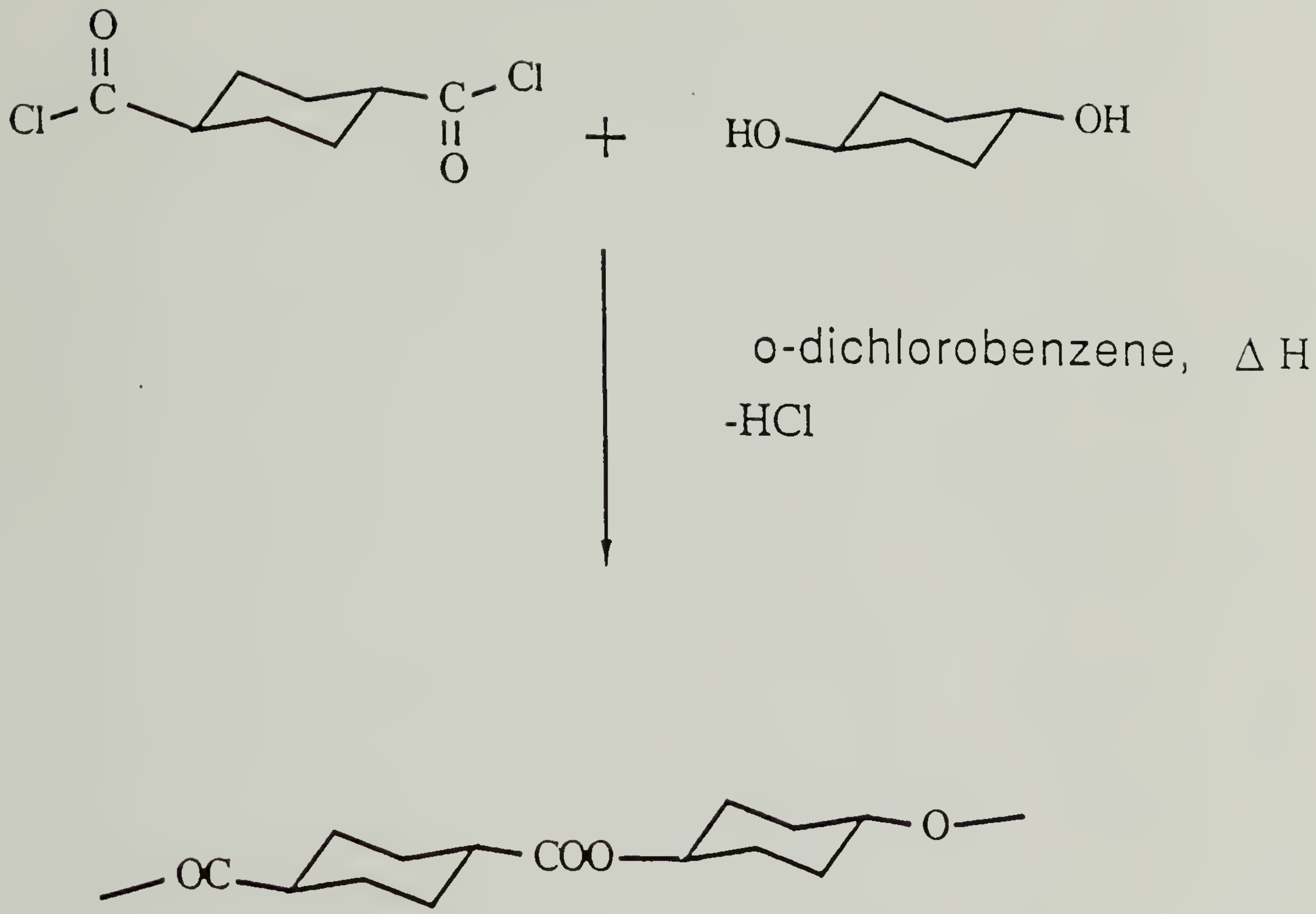
Copolymers of *trans*-1,4-cyclohexanedicarboxylic acid, *trans*-1,4- cyclohexanediol and *cis*-1,3-cyclohexanediol

Much of the older literature that describes preparation of cyclohexane polymers does not describe the nuclear magnetic resonance (NMR) spectra of the monomers, or of the polymers, as a check for isomer purity. From the experience of this research, monomers must be scrupulously purified to be free of residual isomer, and the monomers must be polymerized in solution to avoid isomerization of the acid component.

The most rigid, linear homopolyester from the Figure 2.14 monomers, that is, the *AF* polymer, was synthesized via the schematic of Figure 3.1. As expected, this homopolymer did not melt without considerable degradation. Because of its high melting point (390 °C by differential scanning calorimetry) routine analysis of this polyester by X-ray diffraction and polarized optical microscopy (POM) could not be performed. Films of this polymer cast from hexafluoroisopropanol (HFIP) solution display a liquid crystalline texture by POM at room temperature, in that no spherulites are present and disclination lines are evident. No lyotropic phases were evident in the HFIP solution.

From the POM observation of this polymer it was evident that the linearity necessary for liquid crystallinity was present, although the high melting point of the polymer precluded direct observation of a liquid crystalline phase. The melting point must be lowered by at least 100 °C to observe true liquid crystalline phases. The polymer is relatively stable thermally as noted by thermogravimetric analysis (TGA) of the above polymer which showed 1.0% weight loss at 190 °C and 7.0% weight loss at 400 °C. Interestingly, a polymer with the same structure, but with 20% of the CHDC in the *cis* form, showed greater weight loss at intermediate temperatures, but approximately the same weight loss at high temperatures. For this polymer 1.0% weight loss was observed at 105 °C, and 6.5% at 400 °C. The difference is apparently due to different amounts of crystallinity.

Given the high melting point of this homopolymer, and using the rationale of melting point lowering as described in the Figure 1.9 schematic, it was decided



Polymer precipitated into methanol

Redissolved in trifluoroacetic acid/ dichloromethane

Reprecipitated into methanol

Figure 3.1 The synthesis of polyesters

to investigate the effects of lowering the melting point by several methods, as illustrated by the polymer structures shown in Figure 3.2, *A-D*. The first method that will be described will be a copolymer system which incorporates a rigid cyclohexane comonomer, *cis*-1,3-cyclohexanediol (1,3-CHD) shown in Figure 2.14 *H*.

It was not expected that the *cis*-1,3-cyclohexanediol would display liquid crystallinity because it is not a completely linear monomer. This assumption was correct, and the homopolymer melted to an isotropic fluid at 145 °C.

Three copolymers were made in order to observe the thermal behavior in the region of copolymer ratio between the two homopolymers. The three ratios chosen were in the high *trans*-1,4-cyclohexanediol (1,4-CHD) content to insure a linear structure. The melting behavior of this series of copolymers is seen in Figure 3.3. An approximate linear drop of melting point is observed with an increase in molar content of the 1,3-monomer. The decrease is explained by the nonlinearity of the 1,3-monomer, and the linearity of the decrease, by isomorphic behavior.

Detailed thermal examination of all polymers with greater than 50% of the 1,4-cyclohexanediol was impossible, because melting was accompanied by severe degradation. The 50/50 copolymer was examined by POM and was observed to form a nematic melt at 220 °C as noted in this laboratory and in the laboratories of Idemitsu Petrochemical. The POM photograph of this polymer is shown in Figure 3.4. No clearing is seen to temperatures as high as 300 °C, but severe degradation is noted at temperatures above 250 °C, or at the melting point after 10 minutes. For the other copolymers in the series, films cast from HFIP solution display nematic textures at room temperature, as do those from the 1,4-cyclohexanediol

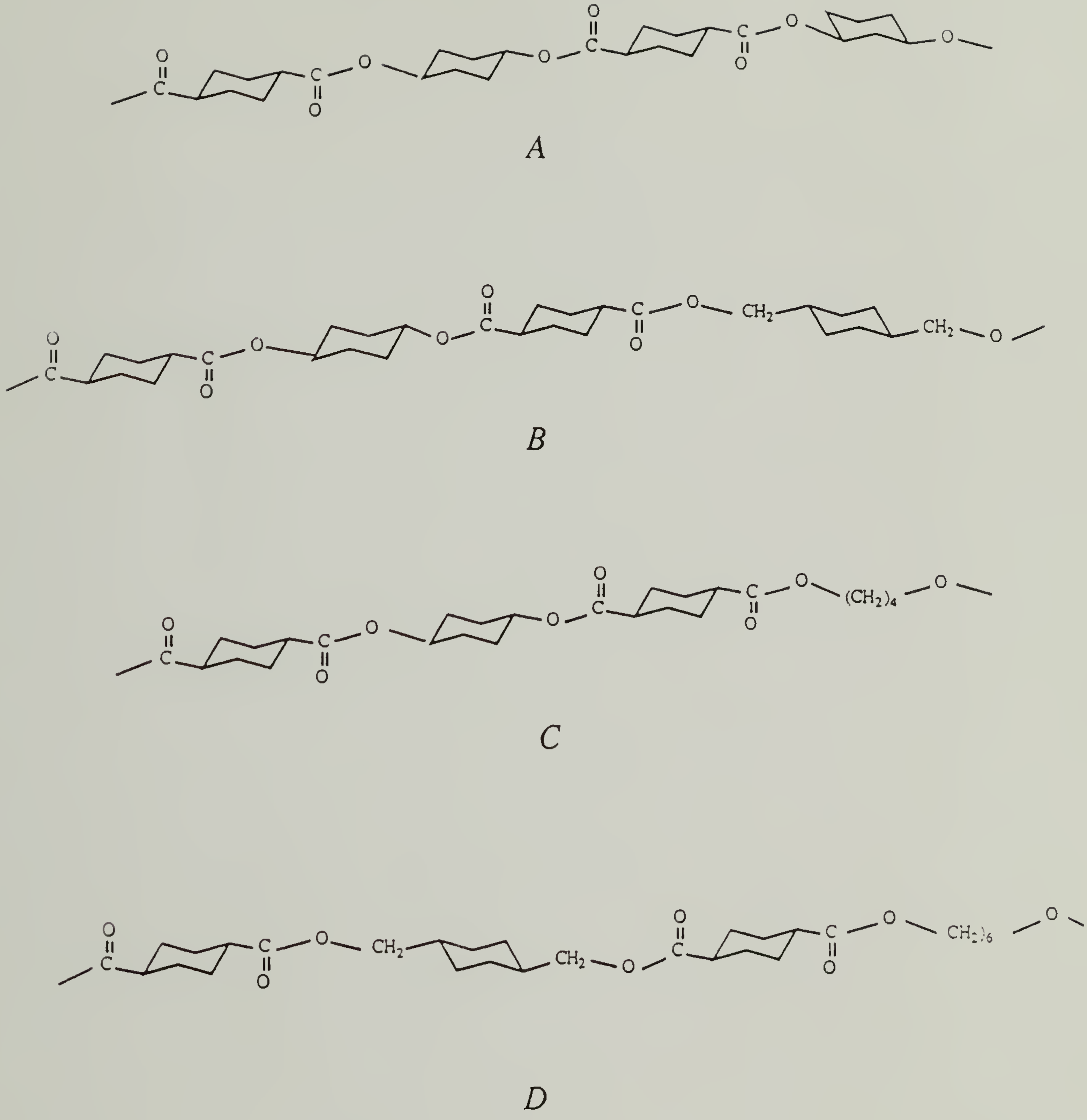


Figure 3.2 Polyesters synthesized in this research

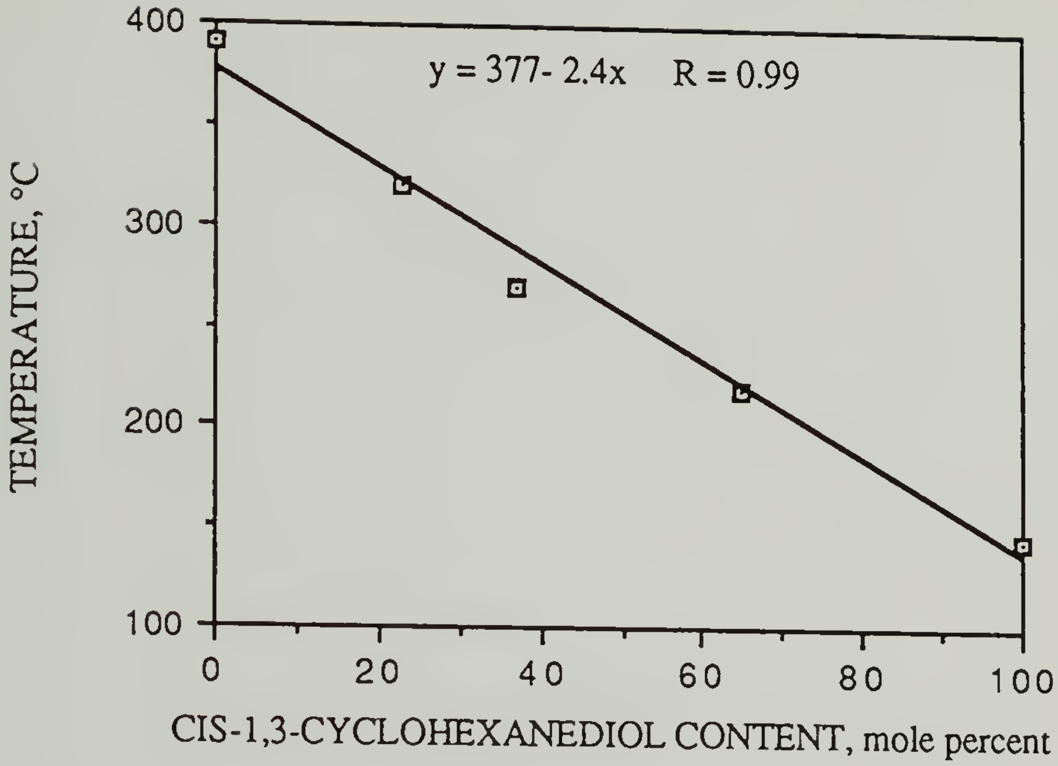


Figure 3.3 Melting point versus composition for Series 3.2 *A* polyesters

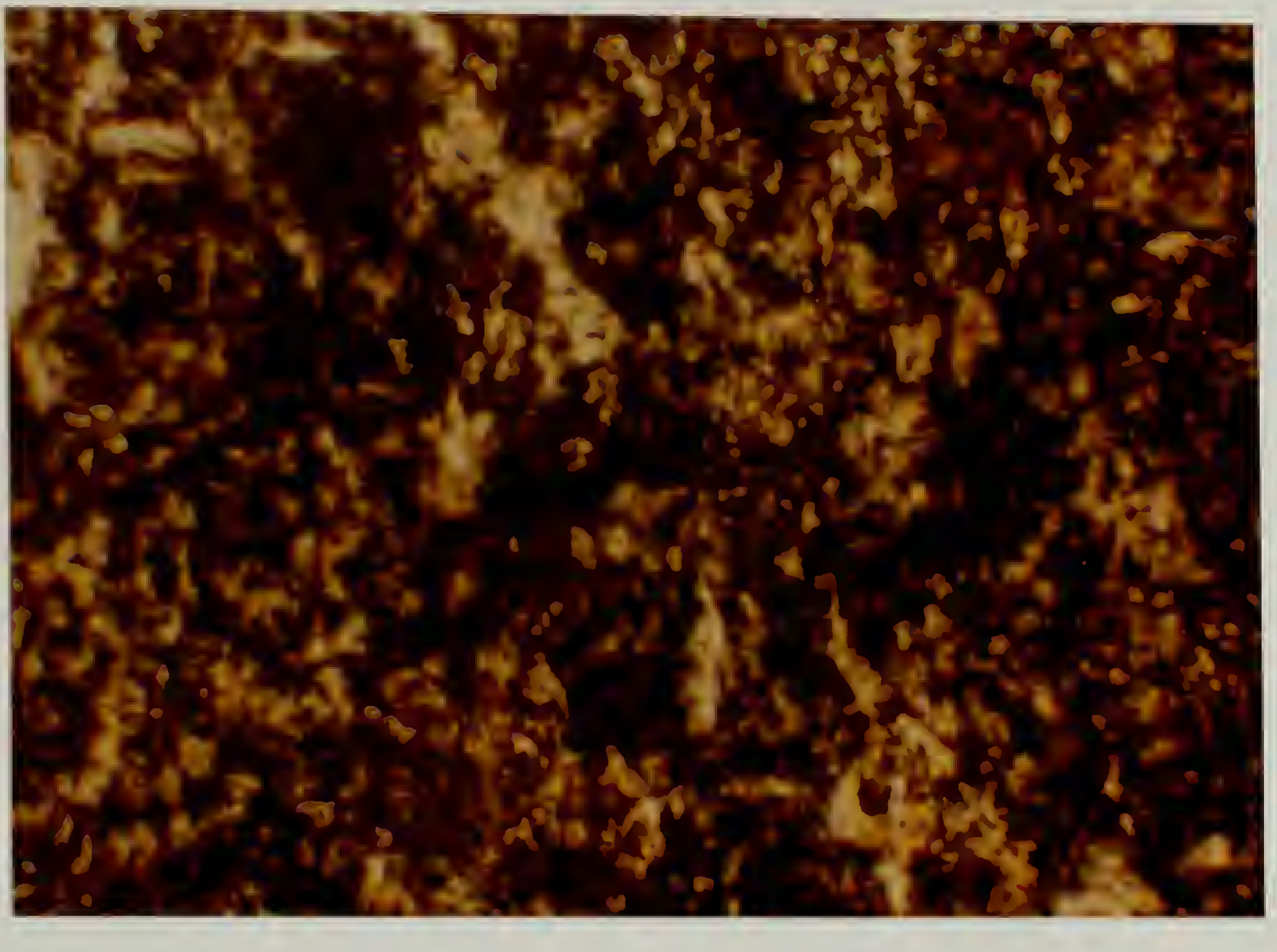


Figure 3.4 Polarized optical microscopy of a Series 3.2 *A* polyester. 50% 1,3-CHD sample at 240 °C

homopolymer, described above. Like the homopolymer, these copolymers show no evidence of lyotropic behavior.

The thermal behavior of this series of copolymers is summarized in Table 3.1. An interesting trend is seen with a drop in molecular weight, noted by a drop in inherent viscosity, with an increase in molar content of the 1,3- cyclohexanediol monomer. Exhaustive purification of monomers prior to polymerization did not yield an increase in the molecular weight of the resulting polymer; in all cases a polymer with an inherent viscosity of less than 0.50 dL/g was obtained. A side reaction for the 1,3-cyclohexanediol would explain this phenomenon. A possible such reaction mechanism is seen in Figure 3.5.

For this series, only the 50/50 copolymer can unequivocally be said to be nematic. The evidence for this claim is the POM schlieren textures observed and the low viscosity melt observed on a melt point apparatus. It is expected that incorporation of the more linear 1,4-cyclohexanediol also leads to nematic polymers, but the nematic state cannot be examined as such, because of the rapid degradation of these polymers at high temperature. Films of these polymers with greater than 50% 1,4-cyclohexanediol content cast from HFIP solution display a nematic structure when examined at room temperature.

Table 3.1 Properties of Series 3.2 *A* polyesters

% 1,3-CHD feed	% 1,3-CHD actual *	IV **, dL/g	Mp, °C, comments
0	-	1.51	390 by DSC, nematic film at RT
20	23	0.86	320 by DSC, nematic film at RT
30	37	0.73	270 by DSC, nematic film at RT
50	65	0.31	220 to nematic, no clearing
100	-	0.22	145 to isotropic melt

* actual molar contents were determined by NMR in $CDCl_3$/ CF_3COOD

** IV's were measured in 3:1 CF_3COOH/CH_2Cl_2 at 30 °C at a concentration of 0.5 dL/g.

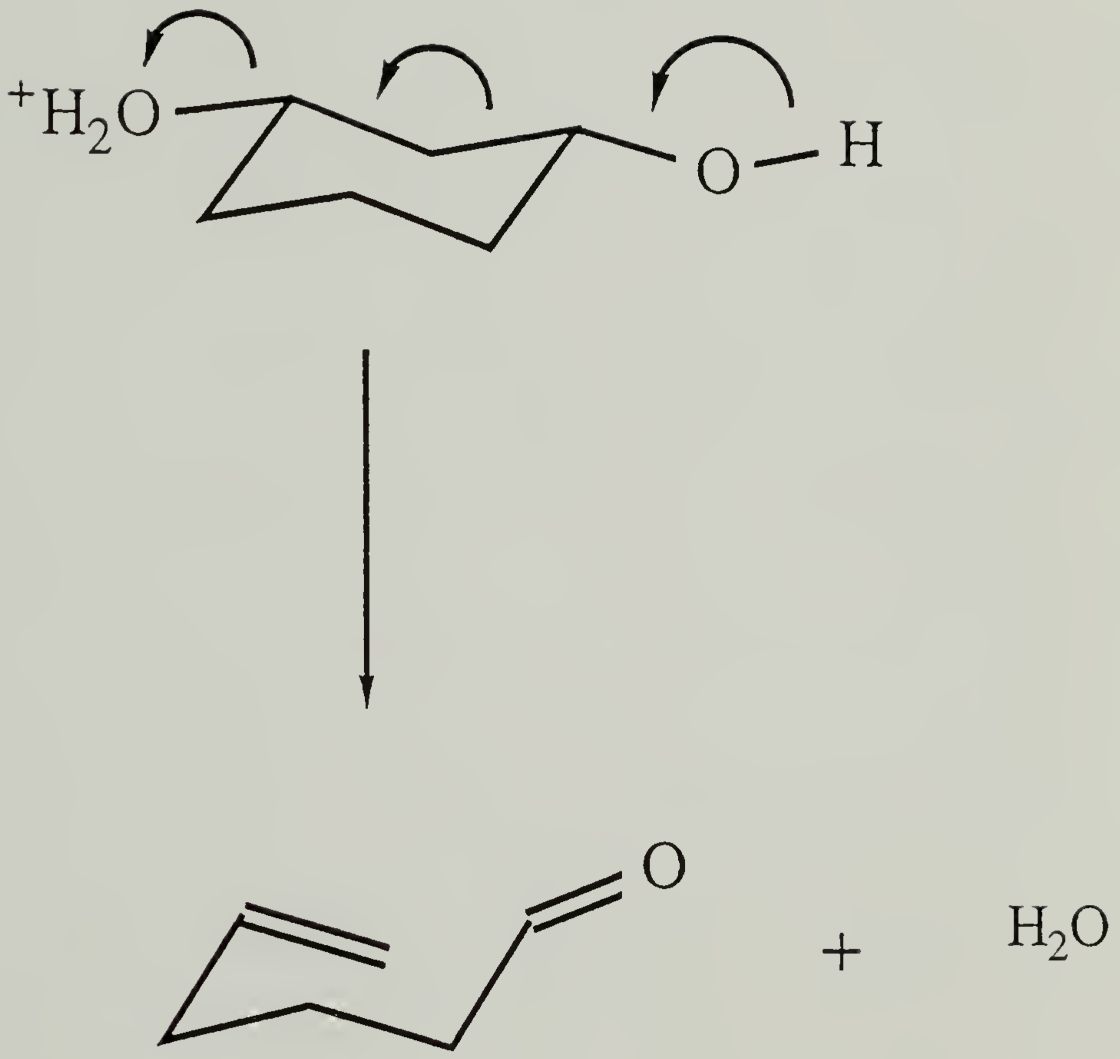


Figure 3.5 A degradation mechanism for 1,3-cyclohexanediol

Copolymers of *trans*-1,4-cyclohexanedicarboxylic acid, *trans*- 1,4-cyclohexanediol and *trans*-1,4-cyclohexanedimethanol

Properties of copolymers

A linear monomer can be used to frustrate chain packing in copolymers, and one such monomer used in this research is the *trans*-1,4-cyclohexanedimethanol (CHDM) (Figure 2.14 *G*). As with the above series, the CHDM homopolymer was not expected to be liquid crystalline, because it had been synthesized before with no description of anomalies in melting point (9). This assumption was not completely justified as will be described below. In this series, as with the 1,3-cyclohexanediol series, a linear drop in melting point was observed. The more linear CHDM gave a smaller slope for the melting point drop curves than for the preceding series, as seen in Figure 3.6. Once again the linear decrease indicates isomorphic behavior.

As with the preceding series, the higher melting copolymers of the series---in this case, the copolymers with above 25% 1,4-cyclohexanediol---melted too high to observe a nematic melt. The 25% 1,4-cyclohexanediol copolymer melted to a nematic at 270 °C, but this melt was accompanied by rapid degradation, and X-ray analysis was impossible. POM was performed on rapidly heated samples, with texture evident in the birefringent fluid up to 300 °C, as shown in Figure 3.7. Both differential scanning calorimetry (DSC) and POM showed no evidence of an isotropization temperature.

The CHDM/CHDC homopolymer proved to be a very complex system with changing behavior dependent on molecular weight and thermal history. The properties of this polymer will be discussed in the next section.

Table 3.2 summarizes the properties of these polymers.

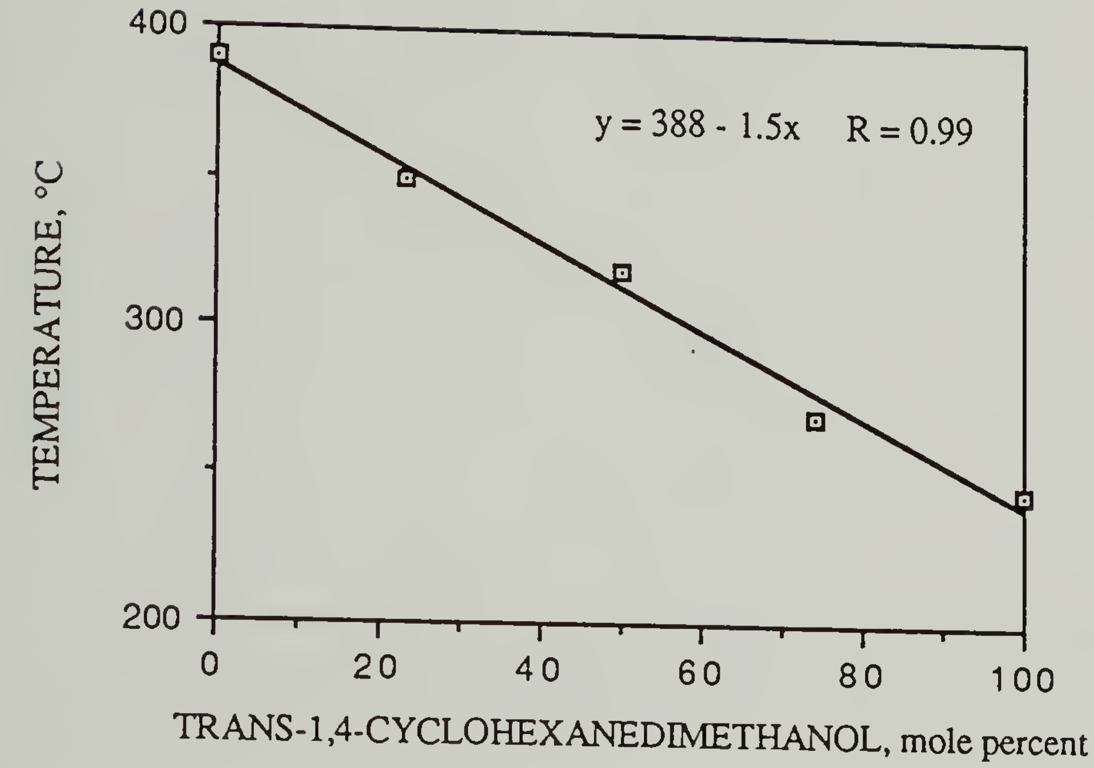


Figure 3.6 Melting point versus composition for Series 3.2 *B* polyesters

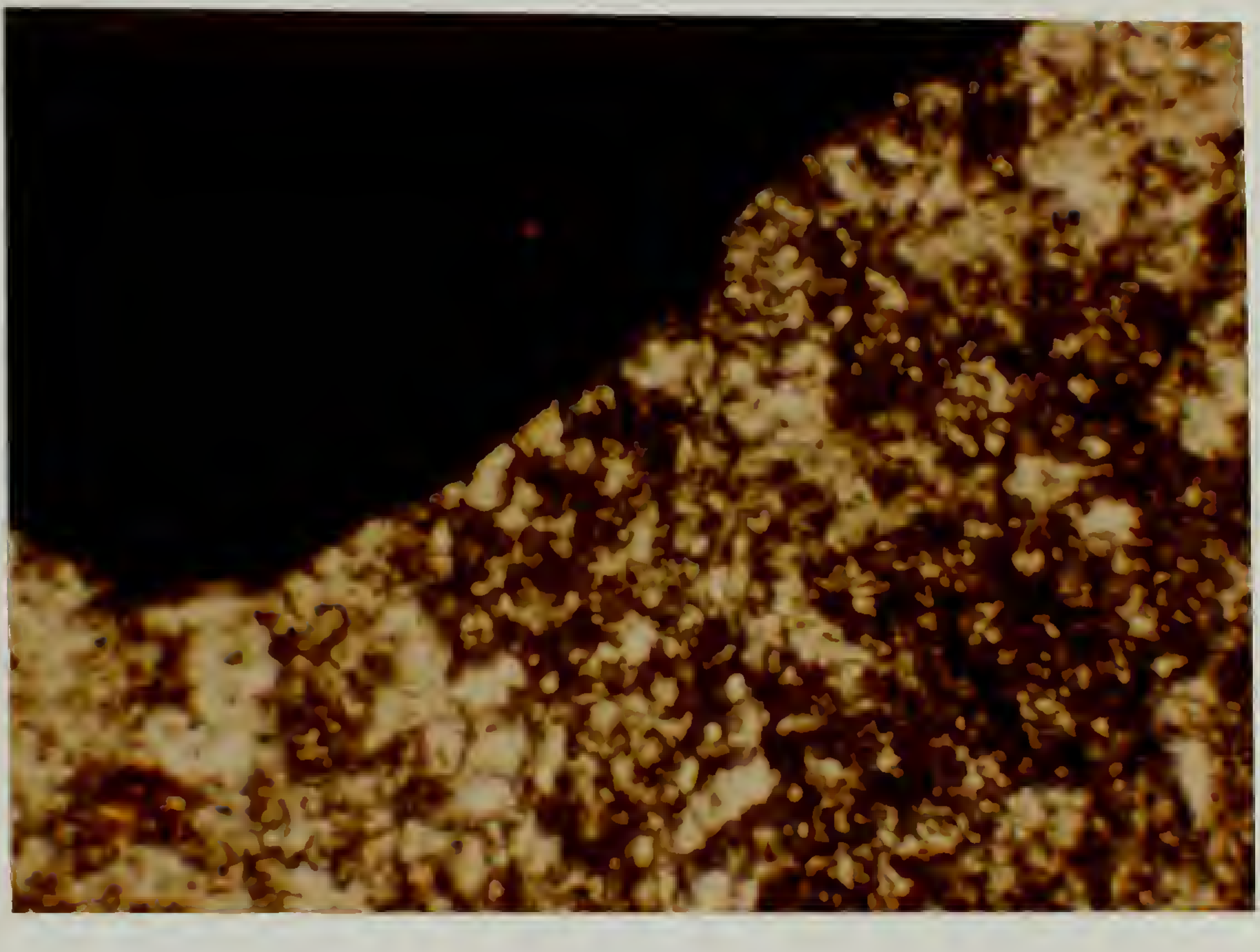


Figure 3.7 Polarized optical microscopy of a Series 3.2 *B* polyester. 75% CHDM sample at 300 °C

Table 3.2 Properties of Series 3.2 *B* polyesters

% CHDM feed	% CHDM actual*	IV**, dL/g	Mp, °C, comments
0	-	1.51	390 by DSC,nematic film at RT
25	23	1.02	350 by DSC, nematic film at RT
50	50	0.71	320 by DSC, nematic film at RT
75	74	1.13	270 to nematic, no clearing
100	-	0.81	K 230 N 245 I (see text)

* actual monomer contents were determined by NMR in $CDCl_3/CF_3COOD$

** IV's were measured in 3:1 CF_3COOH/CH_2Cl_2 at 30 °C at a concentration of 0.5 dL/g.

Properties of trans-*1,4-cyclohexanedimethanol polymers*

Preliminary evaluation of the CHDM homopolymer indicated a nematic melt. The result was surprising in light of Eastman workers reporting no anomalous behavior in melts of this polymer (9). In this research, DSC and POM results were seen to vary with sample thermal history and with isomer content. These two effects are related because the isomer content can change with thermal history, due to the isomerization reaction at elevated temperatures. This isomerization has been noted by other researchers (5, 10). The two effects will be discussed separately where possible.

The 100% *trans*-1,4-cyclohexanedicarboxylic acid monomer used to make polymer in this research can isomerize under reaction conditions and yield a polymer with a *trans* isomer content of less than 100 percent. In this research, no evidence of isomerization was noted in a large range of polymer syntheses in either $CHCl_3$ or *o*-dichlorobenzene solution. At temperatures above 220 °C, isomerization was noted, proceeding via the enolate, as shown in Figure 3.8. The extent of this isomerization can be quantified by proton NMR. For CHDC/CHDM polymers made in the melt, *cis* isomer was formed in increasing amounts with increasing temperature, as would be expected from entropic considerations. Isomerization equilibrium will be discussed in more detail later in this chapter. The isomer content could also be varied by preparing a polymer in solution from a *cis/trans* mixture of the monomeric diacid. From this data, a melting point versus isomer content can be plotted as seen in Figure 3.9. A linear decrease is seen, once again indicating isomorphic behavior.

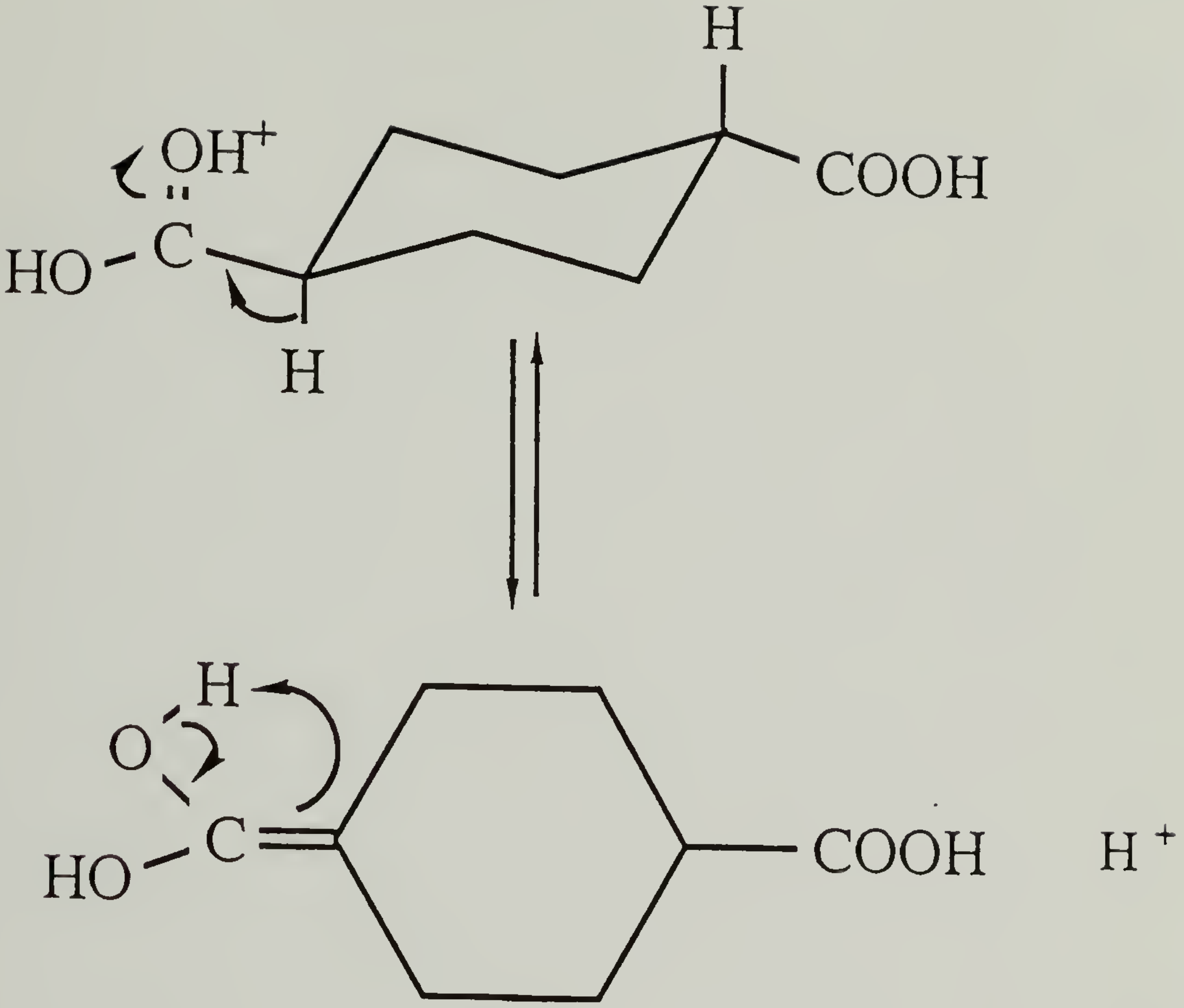


Figure 3.8 Isomerization mechanism for *trans*-1,4-cyclohexanedicarboxylic acid via the enolate

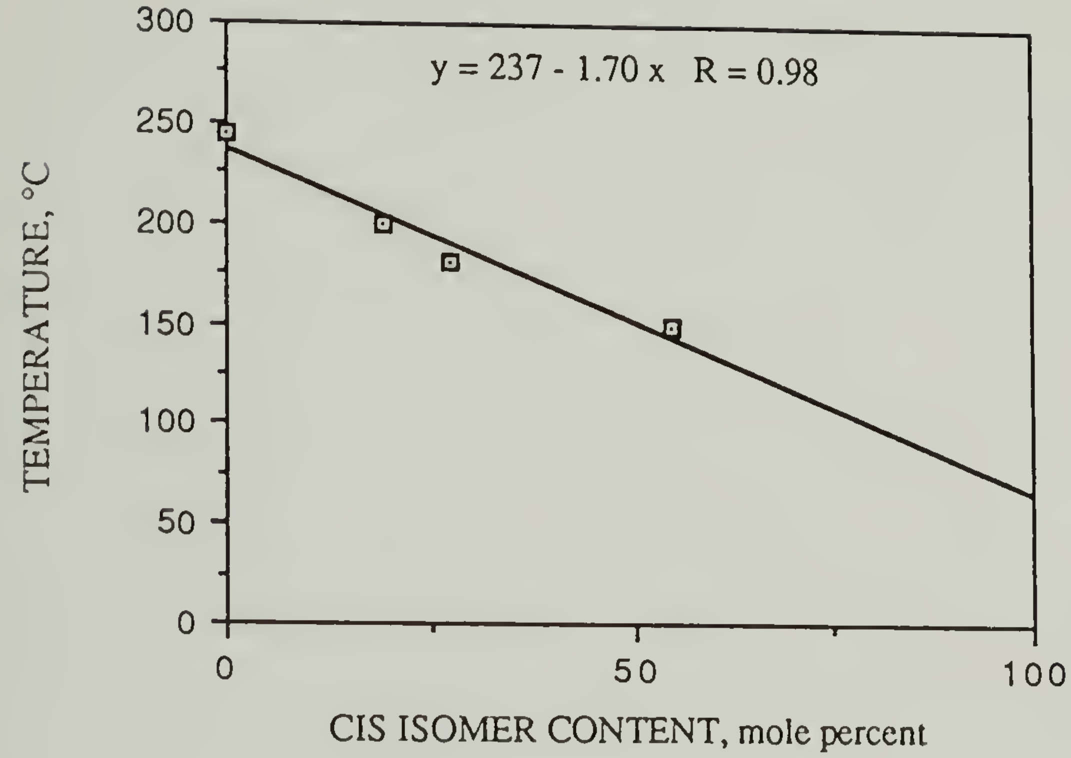


Figure 3.9 Melting point drop with increasing amount of *cis* isomer for the *trans*-1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexanedimethanol polyester

On first DSC heating, the low molecular weight versions of these polymers displayed two peaks (examples of DSC traces are seen in Figure 3.10), which merged to a large broad peak on subsequent heatings. Observations made by POM of the polymer in the thermal region between the two peaks showed a nematic schlieren texture as seen in Figure 3.11. A nematic phase was not substantiated, however, by the disappearance of the lower temperature peaks on subsequent heatings or by the high viscosity of the sample in the thermal region between the two DSC peaks. The viscosity decreased markedly after the second endothermic peak. DSC cooling curves for these polymers showed only one exotherm, again indicating that a nematic structure was not present, as two transitions would be expected.

Molecular weight effects were important as seen for two polymers with 80% *trans* isomer shown in Figure 3.12. Here, a lower molecular weight sample was seen to have two transitions on first heating, in contrast to the higher molecular weight samples which showed only one peak on the first heating.

To separate isomer effects from molecular weight effects, three samples of the all-*trans* homopolymer were made, with various molecular weights, adjusted by adding a stoichiometric excess of the diacid component. These three polymers were analyzed by NMR, and found to be isomerically pure, as seen in Figure 3.13 (compare Figures 2.5 and 2.6). The molecular weights were measured by size exclusion chromatography (SEC) in chloroform and were compared to polystyrene standards, with the data shown in Table 3.3. POM of these samples showed no evidence of a nematic melt, although all three samples displayed a nematic texture in solid films as seen in Figure 3.14. These films were made by

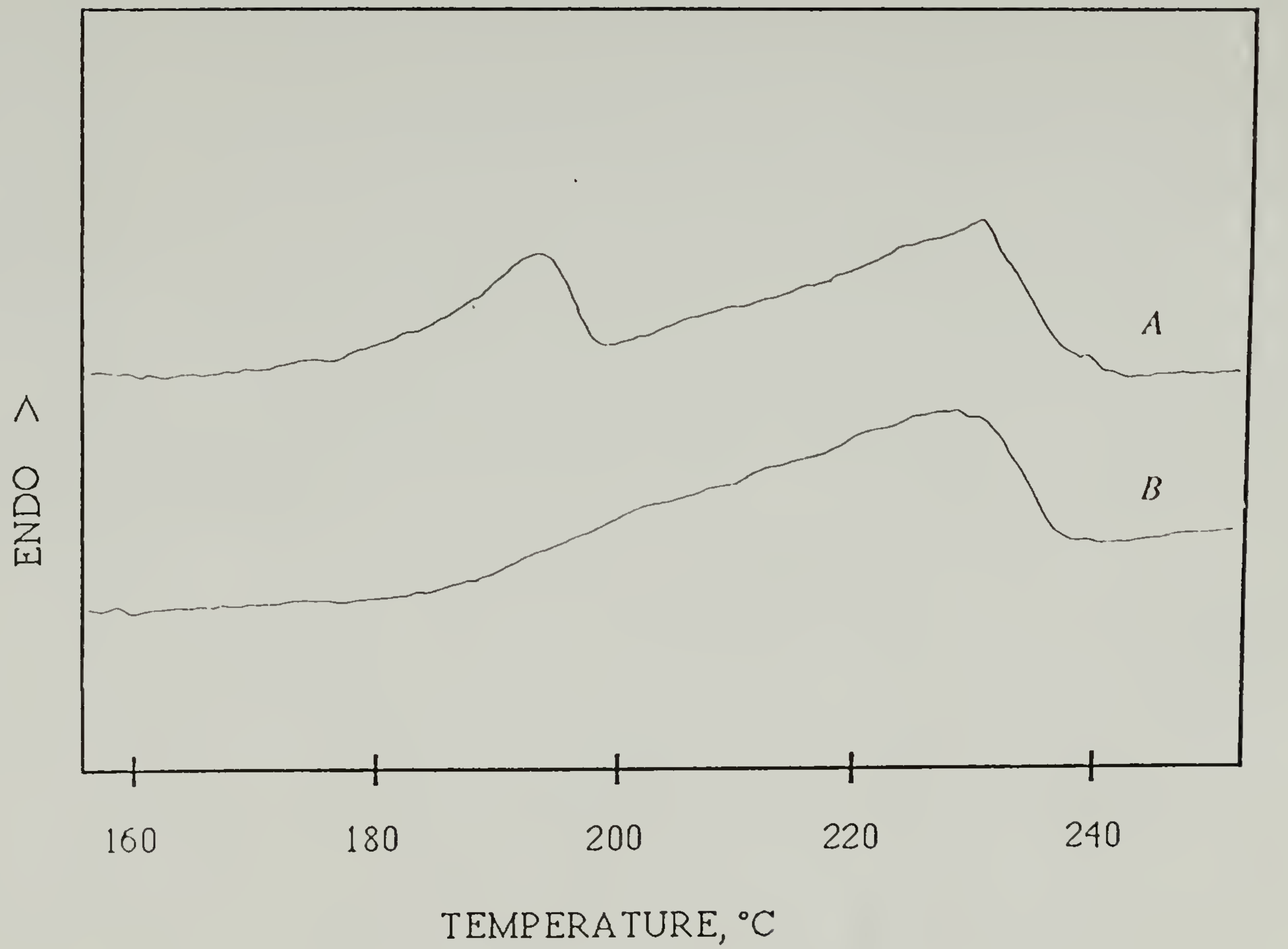


Figure 3.10 Differential scanning calorimetry curve for a low molecular weight *trans*-1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexanedimethanol polyester.
A-first heating
B-second heating

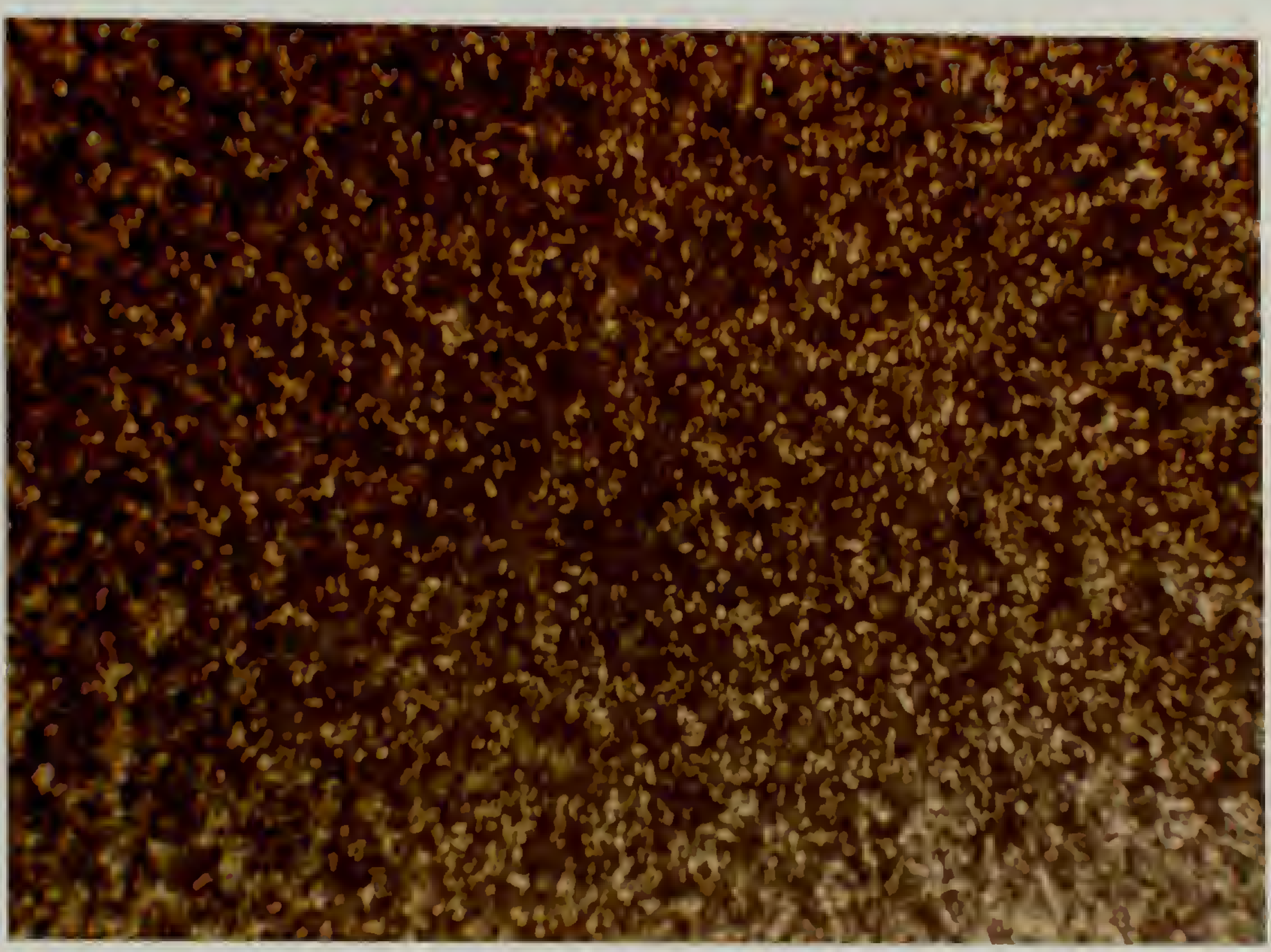


Figure 3.11 Polarized optical microscopy of a low molecular weight *trans*-1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexanedimethanol polyester

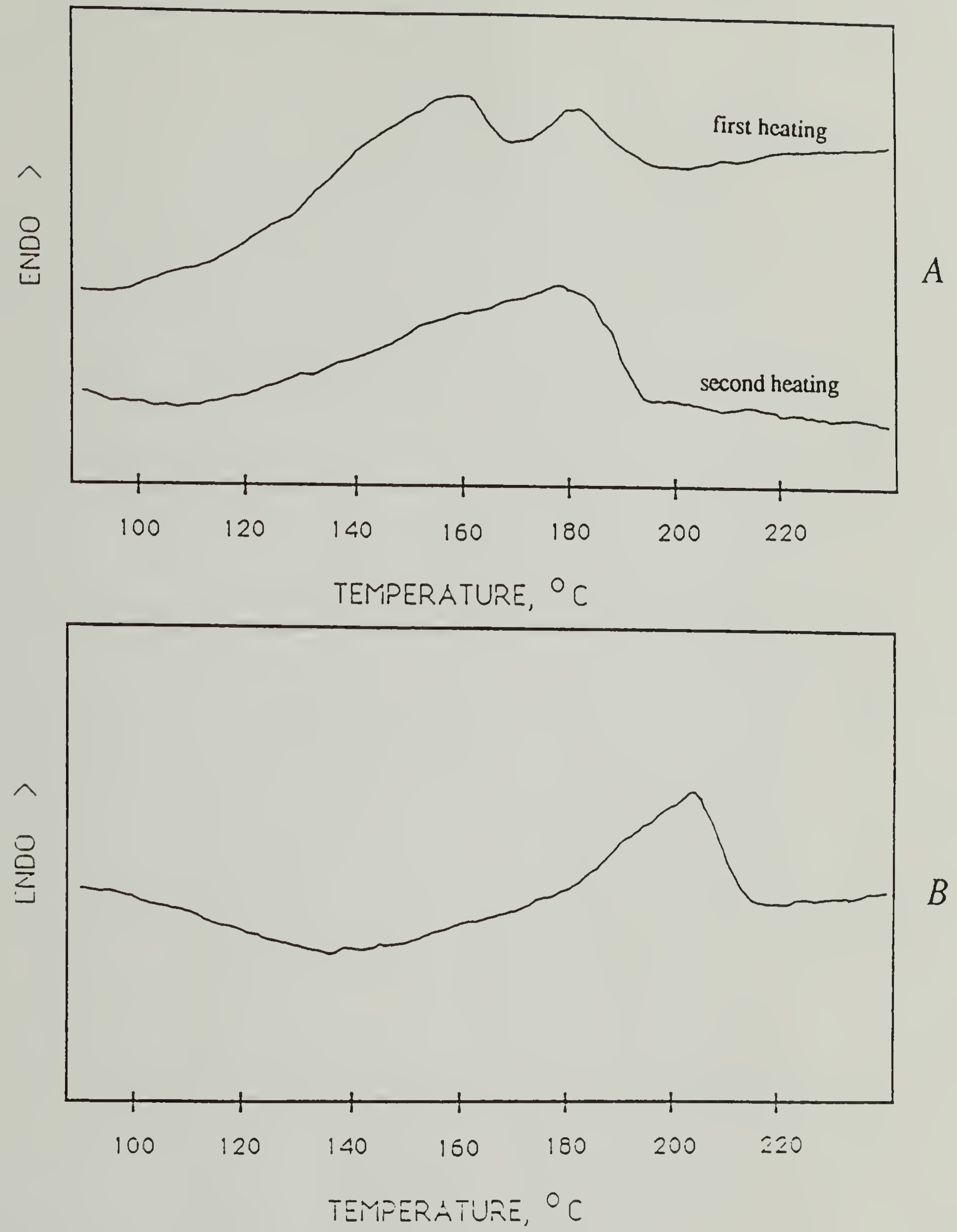


Figure 3.12 Differential scanning calorimetry results for low (*A*) and high (*B*) molecular weight samples of 1,4-cyclohexanedicarboxylic acid/ *trans*-1,4-cyclohexanedimethanol polyester with 80% of the CHDC in the *trans* form

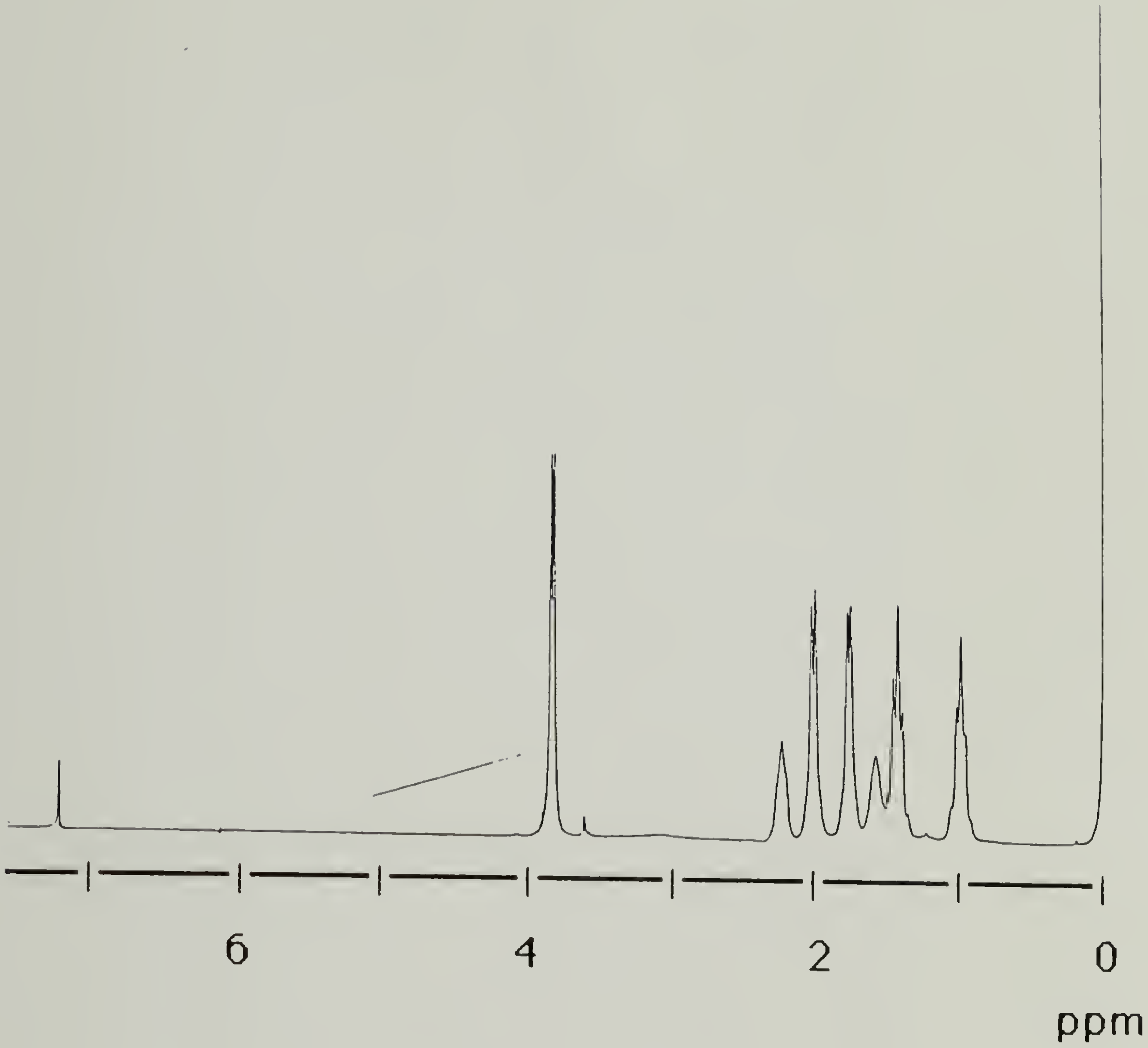


Figure 3.13 Nuclear magnetic resonance of *trans*-1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexanedimethanol polyester

Table 3.3 Size exclusion chromatography data for *trans*-1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexandimethanol polymers

Sample Number	M_n	M_w	M_w/M_n
3.3-1	33,800	55,700	1.65
3.3-2	138,000	275,000	1.99
3.3-3	216,000	335,000	1.55

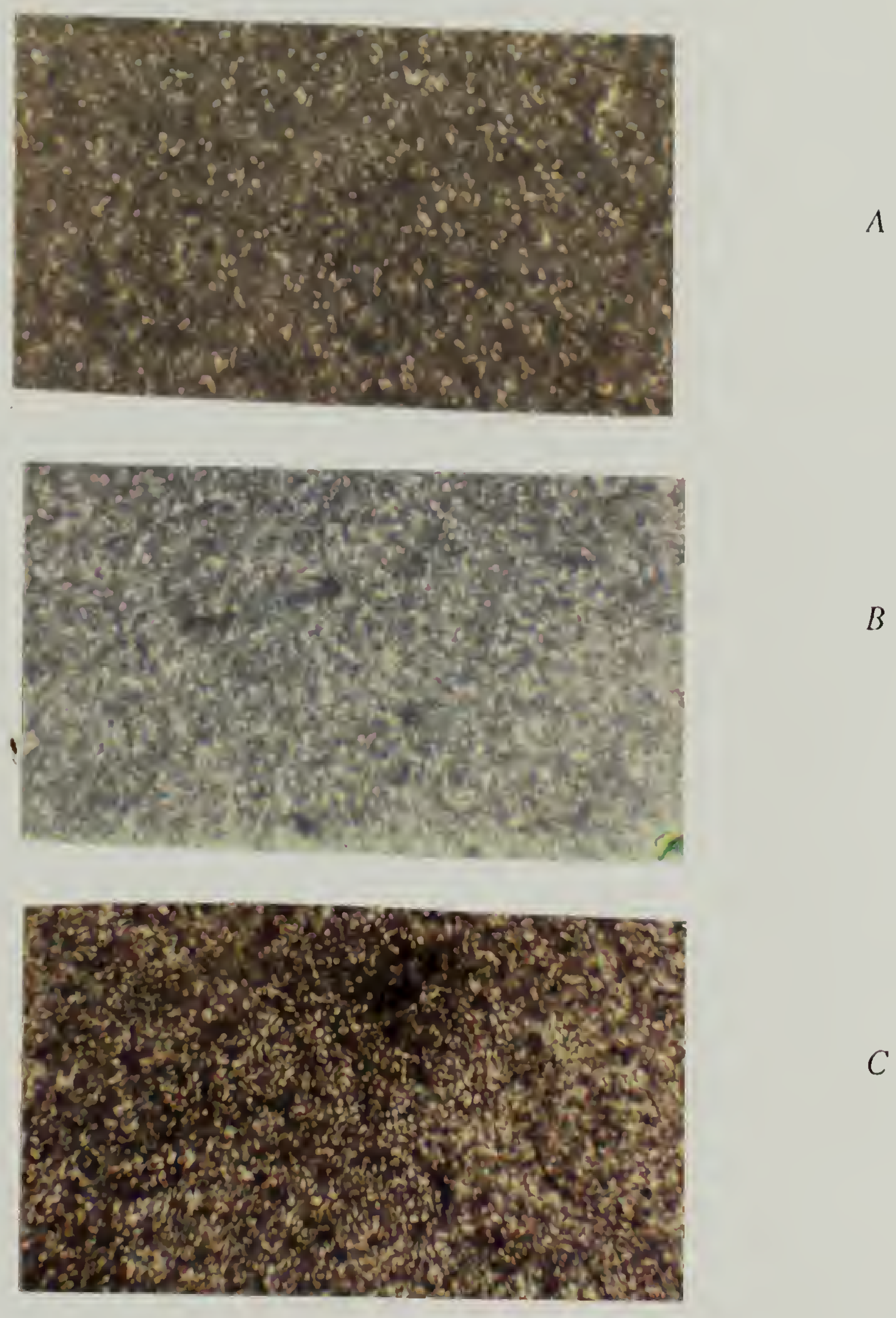


Figure 3.14 Polarized optical microscopy of three different molecular weight samples of *trans*-1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexanedimethanol polyester.
A-high molecular weight
B-medium molecular weight
C-low molecular weight

cooling the melt at 2 °C per minute, and POM examination showed disclination size in inverse proportion to molecular weight, as would be expected.

DSC examination of these polymers showed a very interesting result, with the data shown in Figure 3.15. The first heating scans for all molecular weight samples show single peaks for all samples. Single peaks were also seen in cooling curves for all samples, with the higher molecular weight samples showing more undercooling (45 and 49 °C) than the low molecular weight sample (34 °C), at a cooling rate of 10 °C/min. On second heating each of the two higher molecular weight samples again showed only one peak. In contrast, the low molecular weight sample showed two peaks on second heating. The behavior of all three polymers on third heating was consistent with that observed in second heating, in that the higher molecular weight samples again showed one peak and the lower molecular weight sample showed two peaks. Only one peak is observed for all samples on all cooling scans.

NMR was performed on all three samples after DSC. The two higher molecular weight samples---the ones that displayed only one peak in DSC traces---showed no isomerization. The lower molecular weight sample did show isomerization of 6%. This result was interesting because it indicated that a small amount of isomer was present in the two-peak DSC sample, but presumably not enough to be a *direct* cause of the observed thermal behavior. (The enthalpies of the two transitions were approximately equal. More description of the thermal history effects of similar polymers will be discussed in the next section.)

Although POM of these three samples did not show evidence of a nematic phase, examination of the post-DSC low molecular weight sample showed a nematic texture in the temperature range between the two peaks. This fluid was very

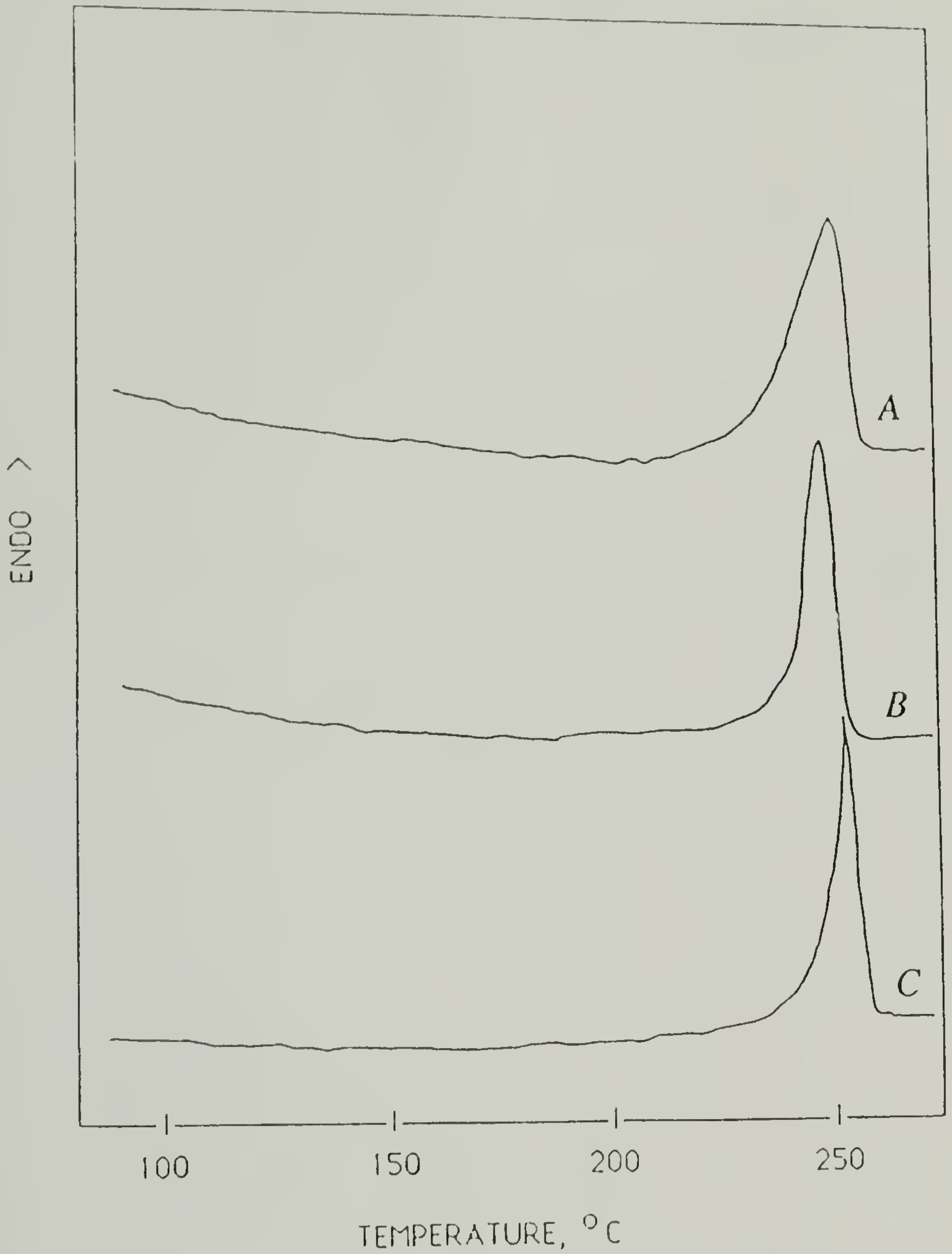


Figure 3.15 Differential scanning calorimetry scans for *trans*-1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexanedimethanol polyesters.
A-high molecular weight, first heating
B-medium molecular weight, first heating
C-low molecular weight, first heating
D-high molecular weight, second heating
E-medium molecular weight, second heating
F-low molecular weight, second heating

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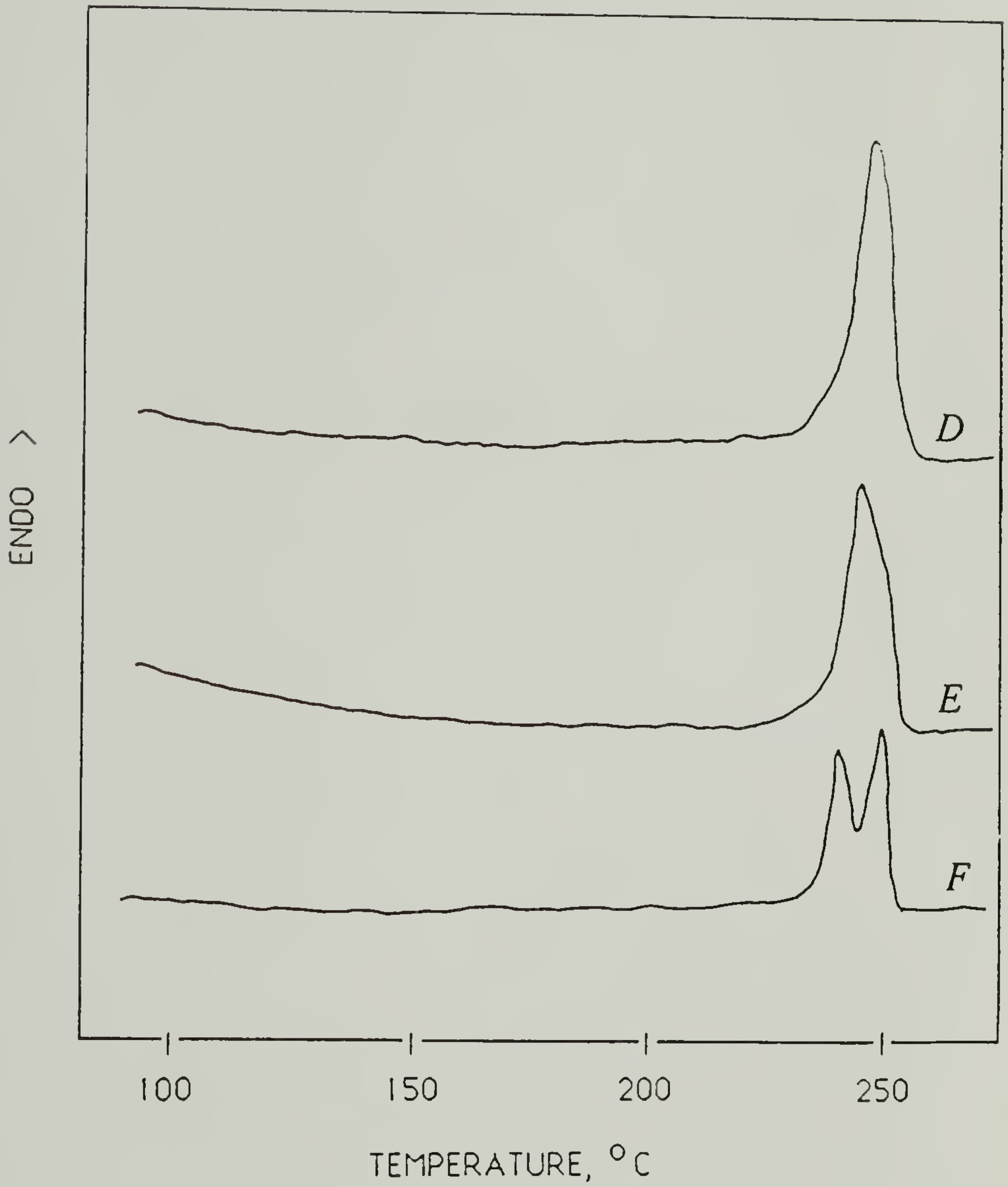

Figure 3.15 cont.

viscous, an observation that agreed with all other observations of melts of this polymer that displayed texture.

Wide angle X-ray scattering (WAXS) was performed on these samples to determine whether liquid crystallinity was present at temperatures higher than the lower DSC endotherm. Samples as first prepared showed identical patterns independent of molecular weight. After heat cycling in DSC, the higher molecular weight samples that showed only one peak on subsequent heatings were unchanged. However, as shown in Figure 3.16, the low molecular weight sample that displayed two endothermic peaks on second heating showed a more complex crystal structure. The additional diffraction bands that were observed are equivalent to diffraction bands in a high *cis* (22%) sample. At a temperature above the first DSC endotherm, sharp bands remained, indicating crystallinity rather than liquid crystallinity.

It is unlikely that 6% isomerization of a polymer sample to a different configuration could account for the resolution of an endothermic peak into two peaks of approximately equal enthalpy. Exhaustive X-ray analysis on several methylene cyclohexane polymers (11, 12) indicates that two crystal forms are possible, with the different forms shown in Figure 3.17 *A* and *B*. The methylene hydrogens experience less steric crowding in conformation *B*, explaining why this form can coexist with the generally lower energy all-linear, planar-zigzag form of conformation *A*. The two isomeric forms of the CHDC are shown in Figure 3.17 *C* and *D*. For an *A*-*D* repeat unit the length measured on space-filling models is 183 millimeters, while for *C*-*B* the length is 182 millimeters. X-ray evidence indicates that a small amount of *A*-*D* form encourages *B*-*C* formation. These two forms

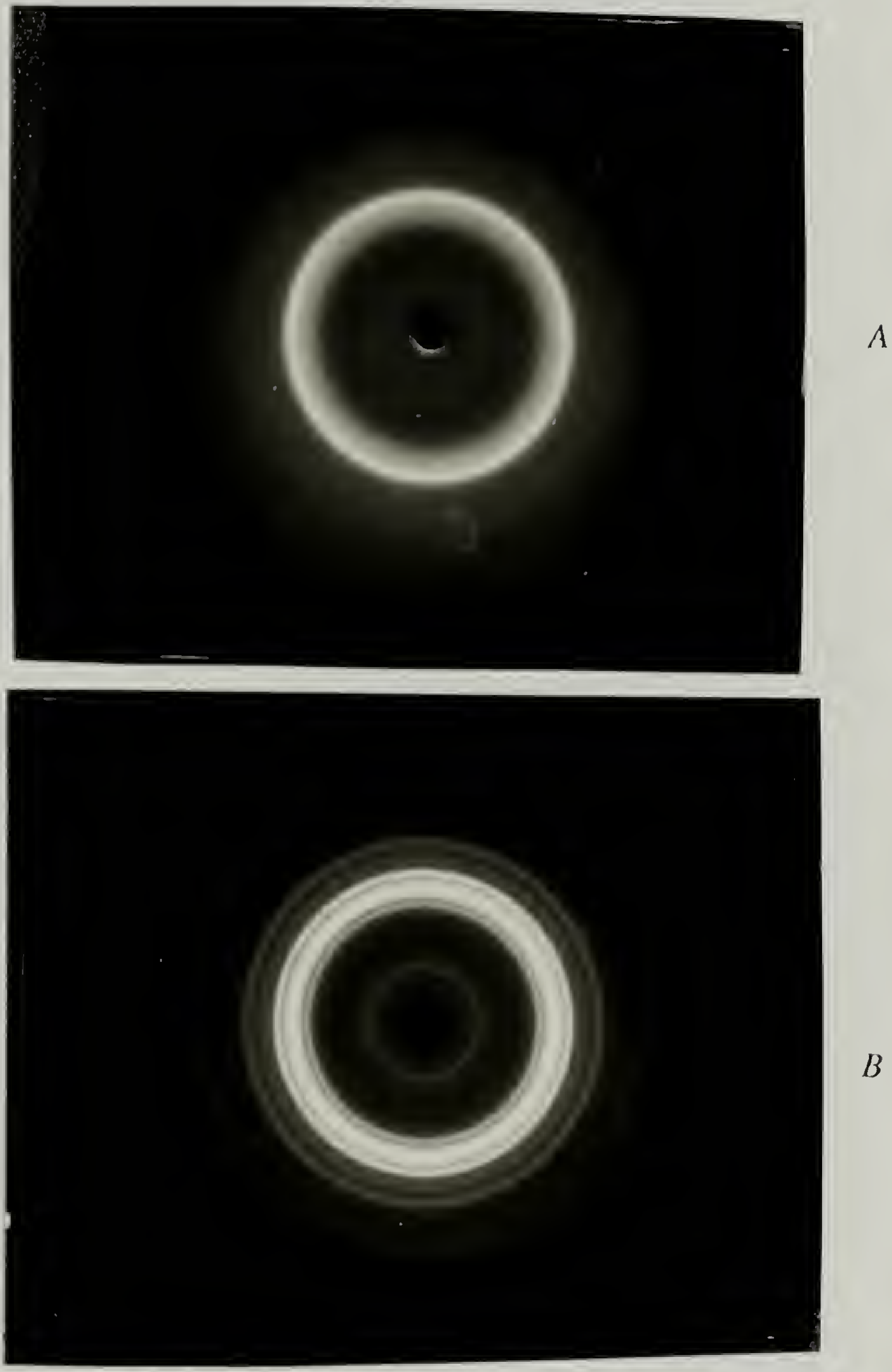

Figure 3.16 X-ray analysis of 1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexanedimethanol polyester.
A-100% CHDC in *trans* form
B-post-DSC sample, 94% CHDC in *trans* form
C-sample with 78% of CHDC in *trans* form
D-sample B at 242 °C

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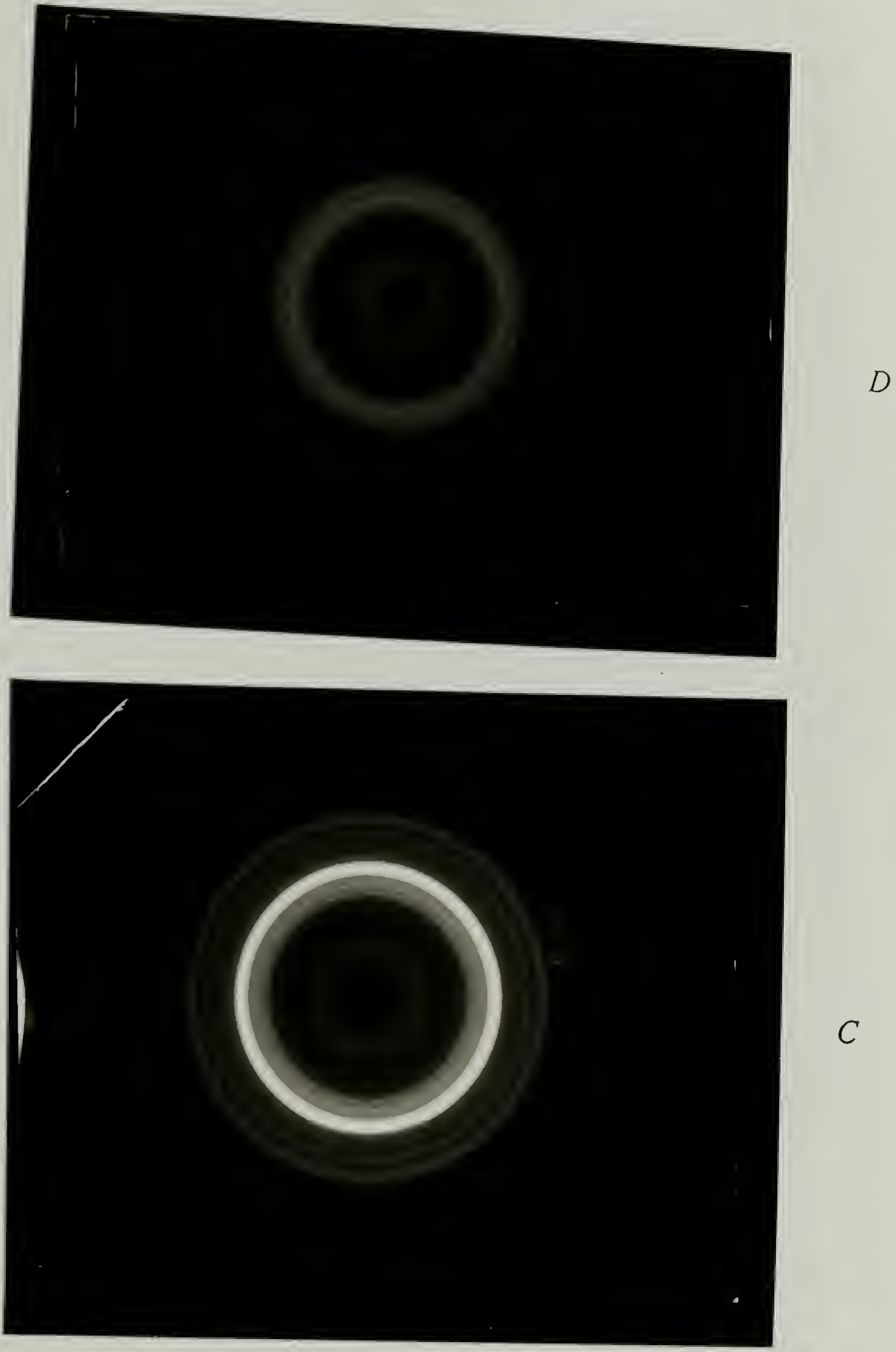

Figure 3.16 cont.

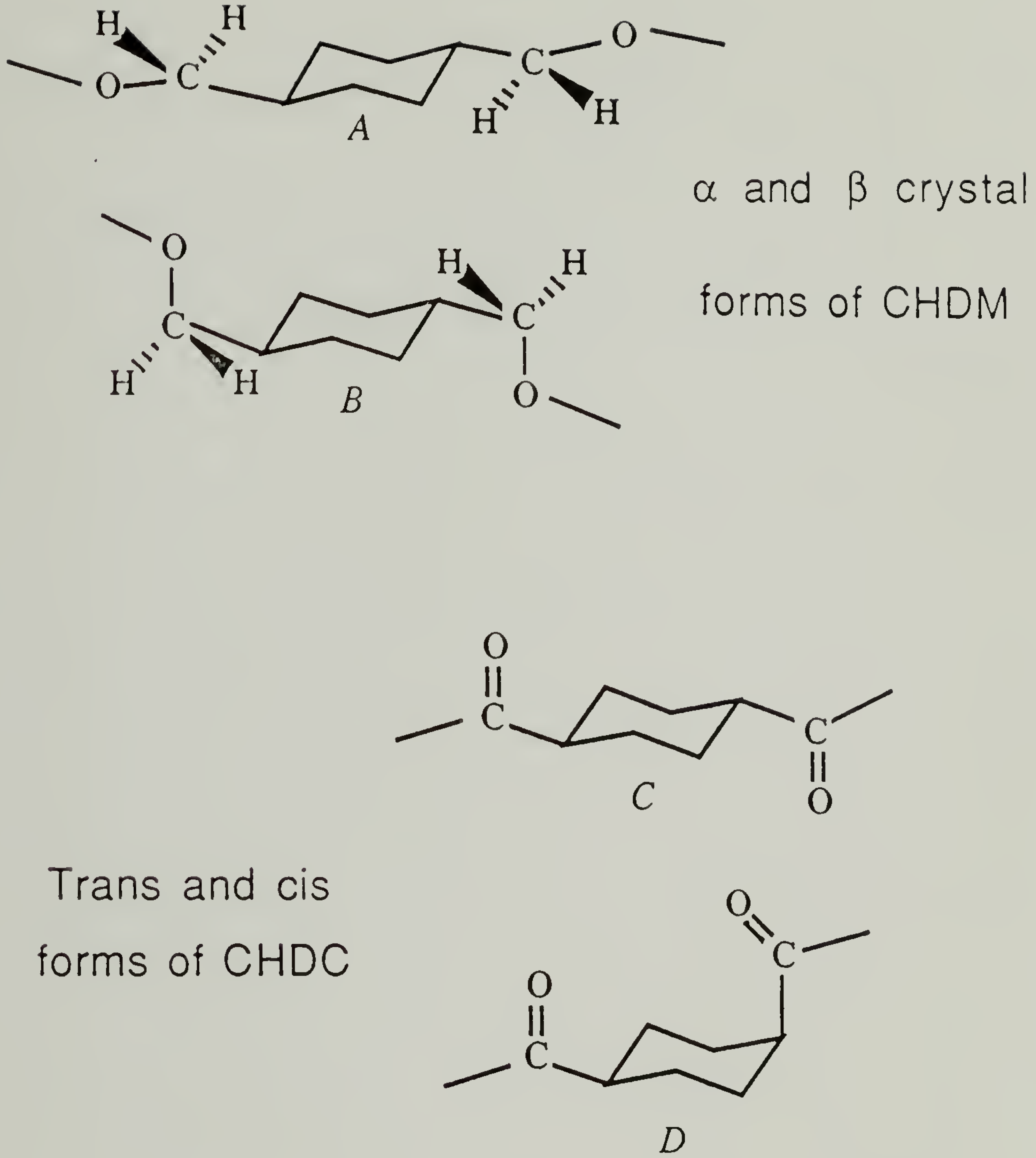

Figure 3.17 Possible crystal modifications for the 1,4-cyclohexanedicarboxylic acid/*trans*-1,4-cyclohexanedimethanol polyester

would be isomorphic. The remaining material would be the all-linear *A-C* repeat unit polymer. (The *B-D* repeat unit is sterically forbidden.)

The isomerization of the acid in the polyester occurs only at a temperature greater than 220 °C. The free diacid is a known catalyst for the methyl ester (13). The acid-terminated samples that are of the lower molecular weight will display the most isomerization, as a result of a higher concentration of end groups. On a practical level, it is difficult to prepare small samples of high molecular weight polymer with known termination by nonstoichiometry of monomer feeds. In this system, the addition of diol upon completion of the polymerization reaction is not feasible due to side reactions of the acid chloride such as hydrolysis and transesterification. In fact, it is likely that all high molecular weight samples have acid functionality end groups.

To summarize the behavior of this polymer, isomerically pure samples displayed single melting points, with slightly higher melting for the lowest molecular weight sample. If small amounts of *cis* isomer are present, two DSC peaks are observed on the second and subsequent heatings. The appearance of the additional peak can be attributed to three phenomena: the transition into a liquid crystalline phase, a crystal/crystal transition or the presence of two crystal forms. True liquid crystallinity is not likely, as noted by crystalline reflections seen by X-ray analysis, at a temperature above the lower peak. The existence of two possible crystal forms is shown in Figure 3.17. This hypothesis provides a reasonable explanation for the observed behavior. Large amounts of *cis* component decreased the melting point in a linear fashion, with two peaks seen in some samples. This behavior was particularly evident in low molecular weight samples where lower viscosity would allow separation of a crystalline phase from a molten phase (previously of a different crystalline form). For these samples a nematic-like texture is seen that can be explained by a dispersed crystalline form. The combined area of the two peaks was approximately equal to the area of the initial melting peak. Acid functionality, present as end groups, would be an effective catalyst for isomerization (10). All samples at room temperature in film form displayed a nematic texture.

An attempt was made to prepare a low molecular weight sample of this polymer with alcohol end groups by using a stoichiometric excess of the diol component. Analysis of such a polymer would test the hypothesis that the isomerization was catalyzed by acid end groups. A relatively low molecular weight polymer was formed (both M_n and M_w were within 10% of the low molecular weight, acid-terminated sample), but this polymer behaved as did the low molecular weight, acid-terminated sample. DSC analysis showed one melting peak on first heating, but subsequent heatings showed two peaks. NMR analysis of a sample treated exactly as the above sample showed 5% isomerization to the *cis* form of the diacid. A sample annealed for one hour at 242 °C showed isomerization to the *cis* form of 19%. (This amount is equivalent to the equilibrium content, as described later in this chapter.) This sample showed two peaks, as did the sample that had a lower *cis* content.

This experiment to separate polymer properties due to molecular weight from those due to *cis* isomer content failed insofar as all low molecular weight polymers isomerized during analysis by DSC. It is not known if this isomerization occurs only with an appreciable concentration of acid functionality. This possibility could be tested by end group analysis of all low molecular weight polymers. In this research, *no* samples showed multiple peaks by DSC analysis that did not also have a detectable *cis* isomer content. The two crystal forms, present even in aromatic/CHDM polymers (14), occur in the polymers of this research only in conjunction with the *cis* isomer of CHDC, although no causality has been established.

Polyesters with isomorphic flexible spacers

This research was undertaken with the desire to synthesize liquid crystalline polymers that maintain an all-rigid backbone. As stated in Chapter 1, liquid crystalline polymers are not used as liquid crystalline materials, per se. The advantage of a liquid crystalline state for a polymer is that it offers a method for obtaining the parallel linearity needed for advantageous processing and excellent mechanical properties. Rigidity for a bulk sample originates in molecules having no weak links for rotational disorder. Any completely-oriented, 100%-crystalline polymer will have exceptional properties in one dimension, independent of the chemical nature of the polymer, as evidenced by oriented polyethylene (15-17). With these thoughts in mind, two flexible spacers were copolymerized with the cyclohexane monomers. It was hoped that these flexible monomers would adopt the conformations seen in Figure 3.18, and that this arrangement would lead to isomorphism and cocrystallinity in the sample. The flexible spacer would have a larger ΔS on melting, and hence, lower the melting point.

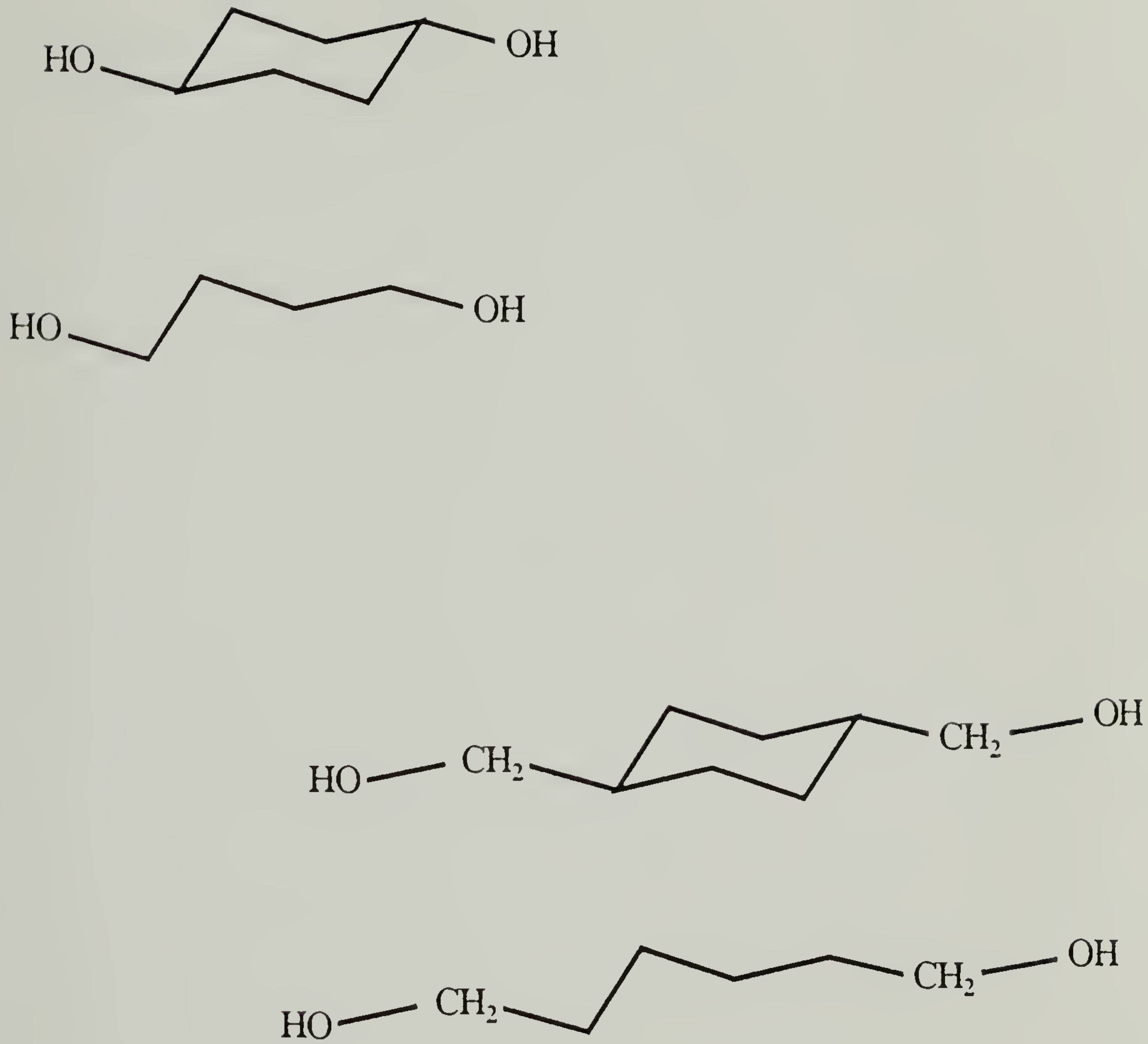

Figure 3.18 Isomorphic structures of butanediol with *trans*-1,4-cyclohexanediol and of hexanediol with *trans*-1,4-cyclohexanedimethanol

For CHDC/1,4-CHD polymers, relatively large amounts of flexible spacers were incorporated to lower the melting point. The polymer with 25% 1,4-butanediol (BD) degraded before it melted, and an investigation for liquid crystallinity in the melt was impossible. The polymer with 50% BD melted at 280-285 °C, again with degradation, but this melt was birefringent, and remained so until the sample completely degraded at temperatures as high as 300 °C (Figure 3.19). A graph of the melting point versus composition shows a fairly linear graph. It is interesting to note that the sample with 50% BD gives approximately the same melting point as a polymer with 50% of the cyclohexanediol in the *cis* form, as noted by Osman (6), but without the kinks of approximately 90° which would lead to a loss of strength in the bulk polymer.

For the *trans*-1,4-cyclohexanedimethanol polymers, less lowering of melting point is needed. When the work in this dissertation with the flexible spacers, 1,4-butanediol and 1,6-hexanediol (HD), was begun, initial investigations indicated that the CHDC/CHDM homopolymer had both a liquid crystalline transition and a transition to an isotropic fluid. Because these transitions were below 250 °C, only small amounts of flexible spacer were incorporated in attempts to lower the melting point to ~ 200 °C.

The first attempt to make these polymers in 10 and 20% HD contents was done in the melt. It was hoped that the lower melting point of these polymers would allow melt polymerization temperatures low enough that isomerization did not occur. However, a temperature of 245 °C was necessary during polymerization for complete melting and the resulting polymer showed isomerization in the acid position, in amounts of 25 and 23% for the 10 and 20% (HD) polymers, respectively.

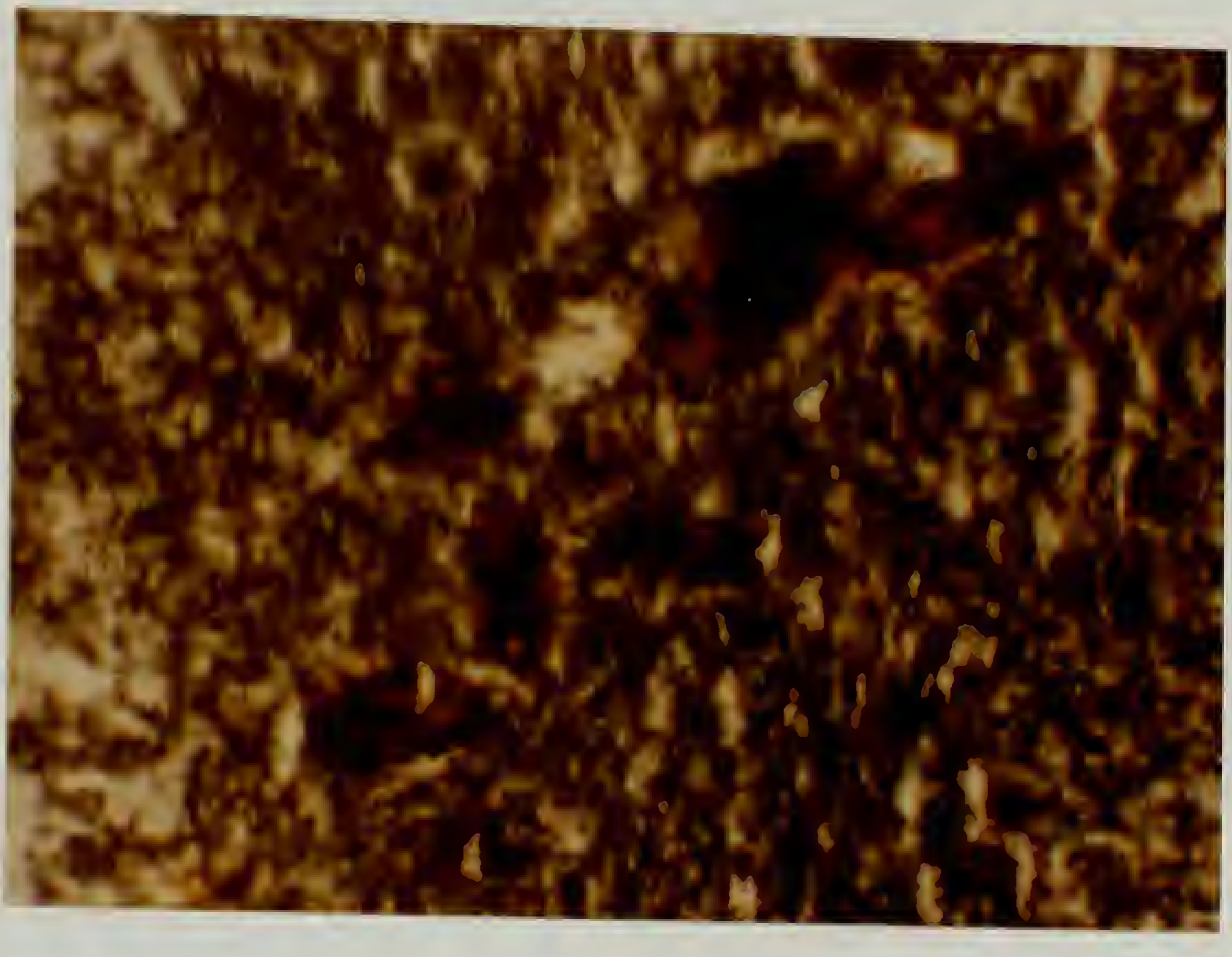

Figure 3.19 Polarized optical microscopy of a butanediol/*trans*-1,4-cyclohexanediol/*trans*-1,4-cyclohexanedicarboxylic acid polyester. 50% BD polymer at 290 °C

A DSC trace of one of these polymers is shown in Figure 3.20. The thermal behavior of these copolymers is similar to the behavior of a *trans*-1,4-cyclohexanedimethanol homopolymer with an equivalent amount of isomerization, in that two DSC peaks are observed. Polarized optical microscopic examination of these polymers in the region between these two peaks showed a nematic-like texture but, as with the *trans*-1,4-cyclohexanedimethanol homopolymers, this phase was a viscous liquid which showed a drop in viscosity at temperatures above the second thermal transition.

Reasoning by analogy to the *trans*-1,4-cyclohexanedimethanol polymers, it was thought that the greater range would be noted in low-molecular weight, high *trans* content polymers, so these polymers were resynthesized, this time in chloroform solution, with a slight stoichiometric excess of the diacid component. These polymers behaved as did the low molecular weight *trans*-1,4-cyclohexanedimethanol homopolymers, in that the analysis showed one peak on first heating which separated into two peaks on subsequent heatings, as shown in DSC traces in Figure 3.21. This low molecular weight polymer was annealed at different temperatures with the resulting DSC traces seen in Figure 3.22. Annealing at a point below both peaks sharpened and increased ΔH for both peaks, indicating an increase in crystallinity. Annealing at a point between the two peaks enhanced the higher peak only. This result indicated that more ordering of a liquid crystalline phase was not taking place, as would be expected if a smectic phase were present. X-ray analysis of this polymer gave results exactly analogous to those for the *trans*-1,4-cyclohexanedimethanol homopolymer, in that crystallinity was present after the first DSC endotherm.

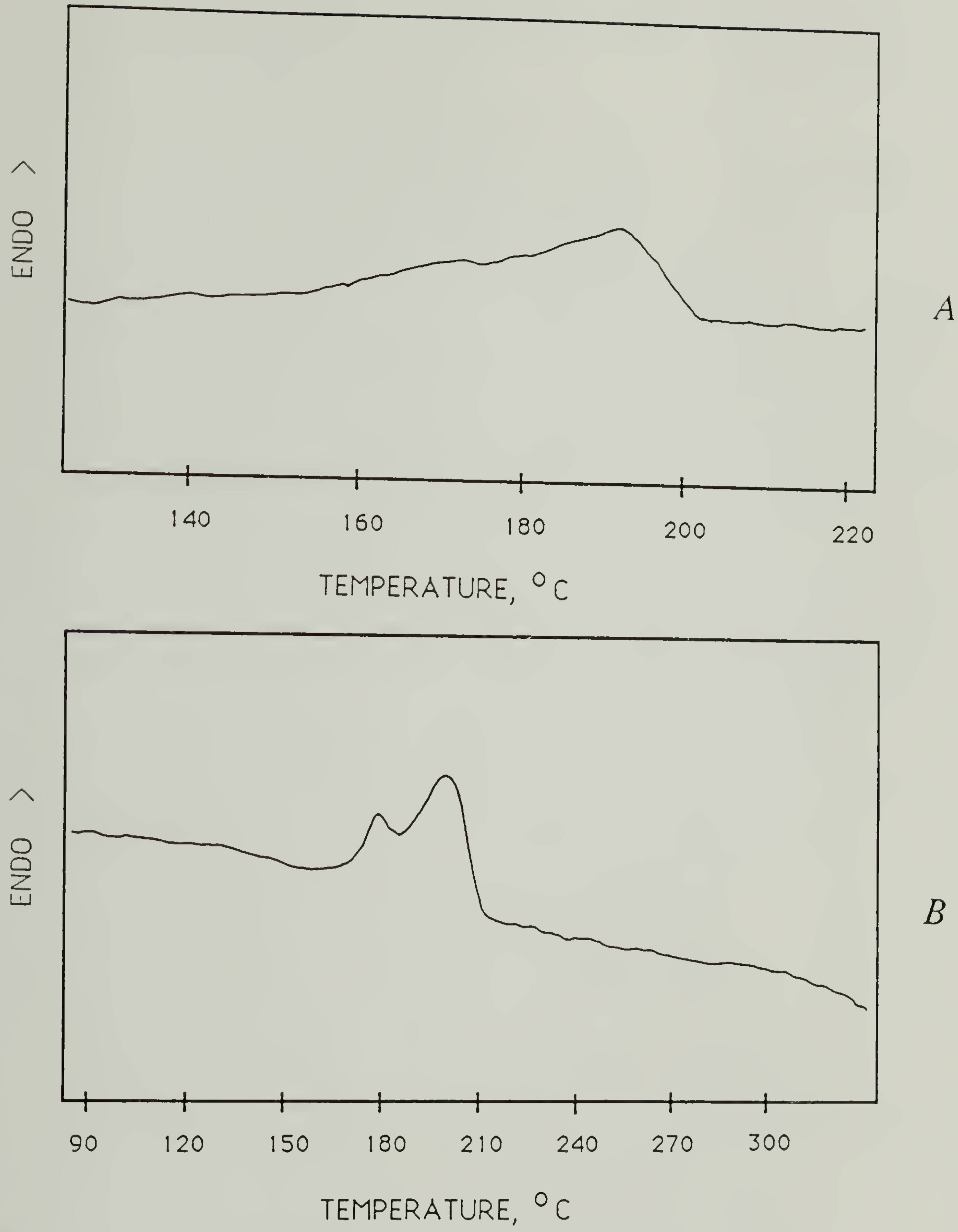

Figure 3.20 Differential scanning calorimetry of a hexanediol/*trans*-1,4-cyclohexanedimethanol/1,4-cyclohexanedicarboxylic acid polyester, with 87% of the -1,4-cyclohexanedicarboxylic acid in the *trans* form. *A*-first heating; *B*-second heating

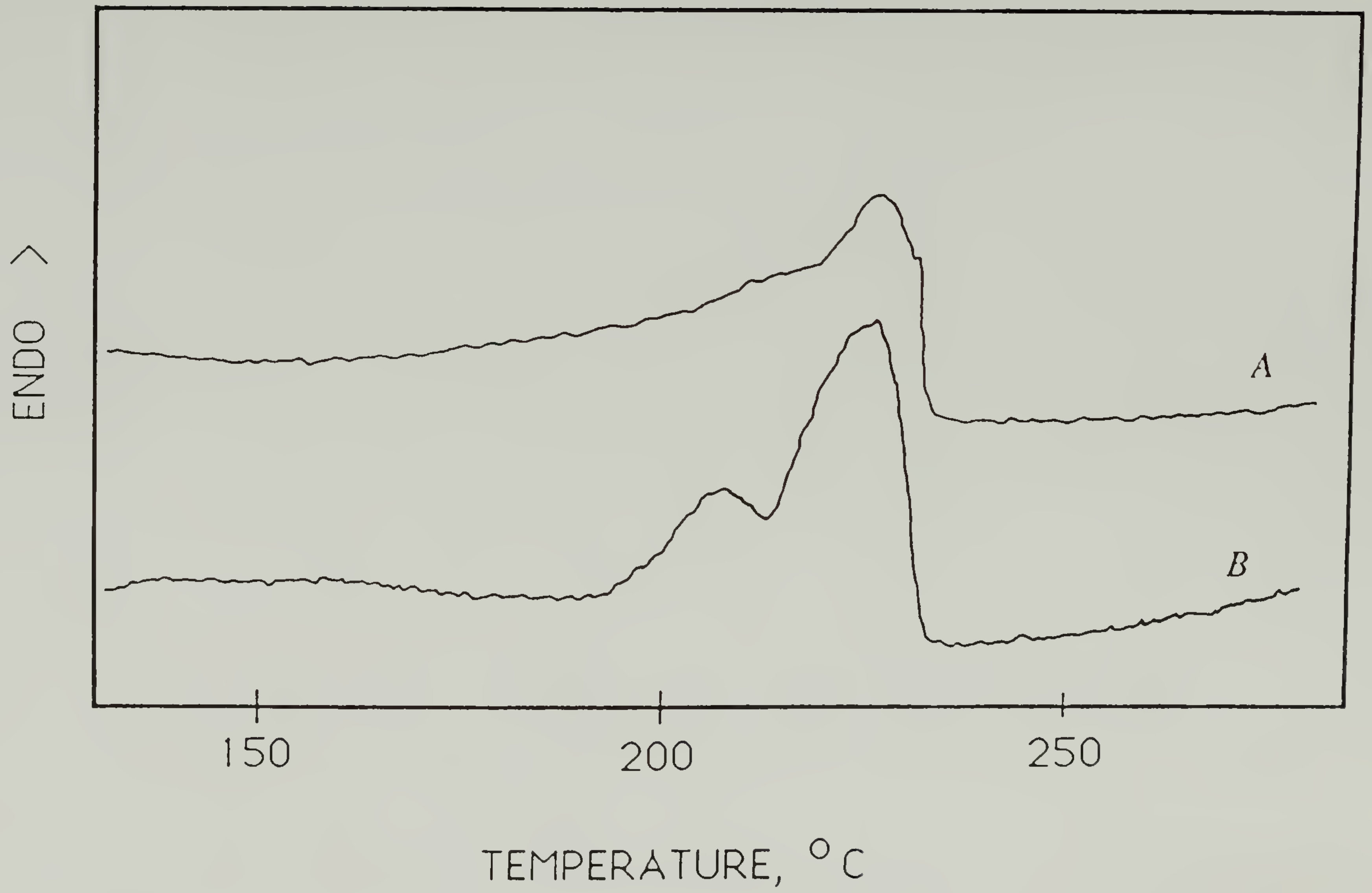

Figure 3.21 Differential scanning calorimetry of a hexanediol/*trans*-1,4-cyclohexanedimethanol/1,4-cyclohexanedicarboxylic acid polyester with 100% of the 1,4-cyclohexanedicarboxylic acid in the *trans* form. *A*-first heating; *B*-second heating

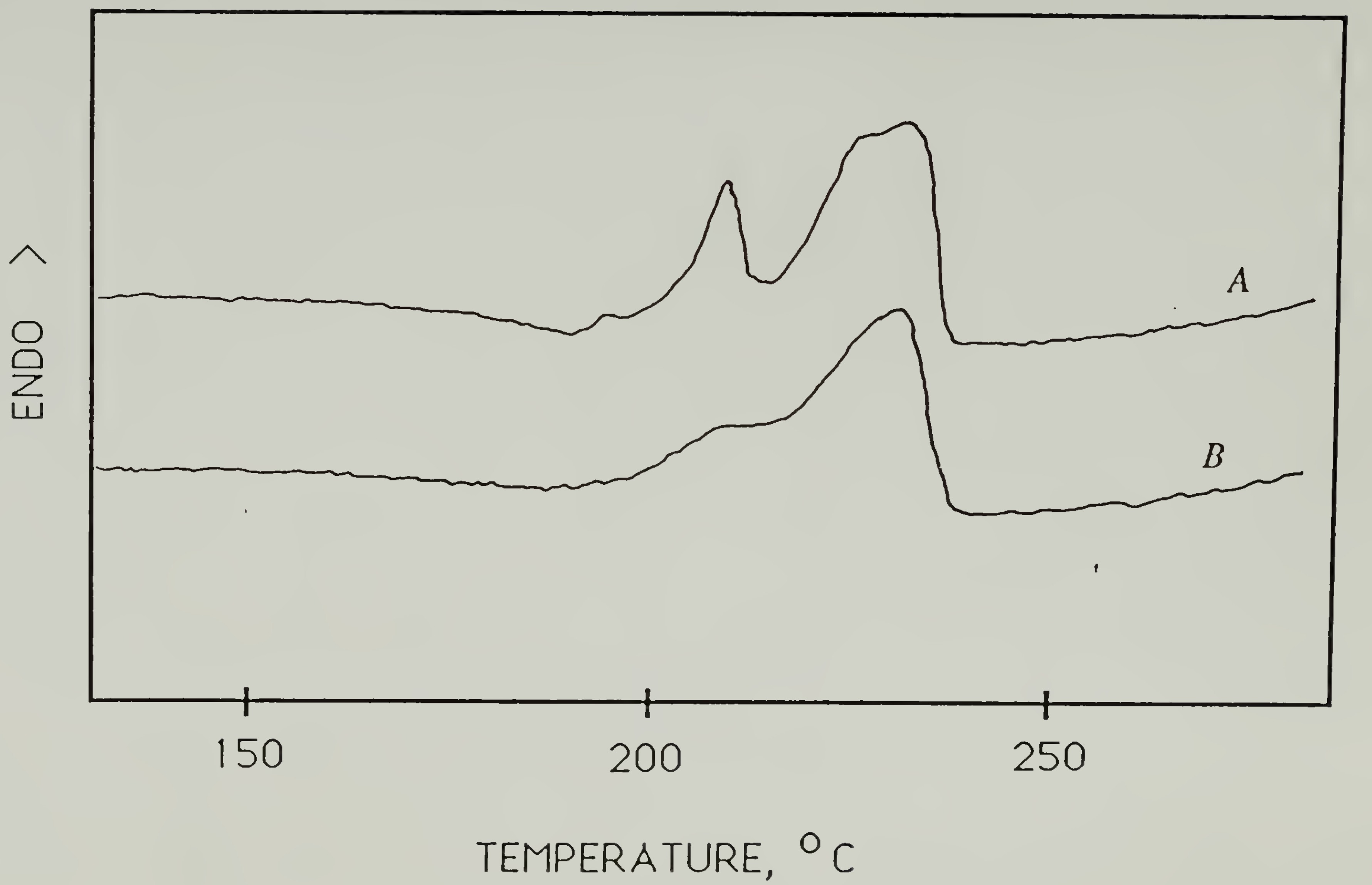

Figure 3.22 Differential scanning calorimetry of annealed hexanediol/*trans*-1,4-cyclohexanedimethanol/1,4-cyclohexanedicarboxylic acid polyester with 100% of the 1,4-cyclohexanedicarboxylic acid in the *trans* form. *A*-annealed at 197 °C; *B*-annealed at 207 °C

Post-polymerization isomerization attempts

Kwolek and co-workers have reported that for the first polymer in Figure 1.13 (5), polymer with 100% of the acid in the *trans* form is formed independent of the isomer content of the monomer feed, if the polymer is heat treated at temperatures greater than 250 °C. Attempts to reproduce that trend in CHDC/CHDM polymers failed, giving instead higher amounts of *cis* content in polymers heat treated at higher temperatures. This trend of higher *cis* contents for samples heat treated at higher temperatures is graphed as a van't Hoff plot in Figure 3.23. These samples were heat treated at the respective temperatures for 24 hours to assure equilibrium; DSC and NMR results indicate that equilibrium is reached in one hour at 242 °C. This increase in *cis* content at higher temperatures is the expected trend reasoning from Gibb's free energy equation, in that the entropically favored product is formed in greater amounts at higher temperatures.

The difference noted between this work and the work of Kwolek and co-workers is explained by the fact that the CHDC/CHDM homopolymers are completely molten at the temperatures at which isomerization proceeds. Kwolek's polymer is in a liquid crystalline or crystalline state at these temperatures, and as the *cis* component chemically isomerizes to the *trans* configuration, it becomes physically removed from further reaction by crystallization. This difference is also noted in isomer equilibration of the *cis* and *trans* compounds of the CHDC acid and the CHDC esters (5, 10). Higher temperatures in the range of 250-300 °C for the ester favor the *cis* isomer; higher temperatures in the acid favors the *trans* isomer, as only the *cis* isomer is molten in this temperature range. If, for a

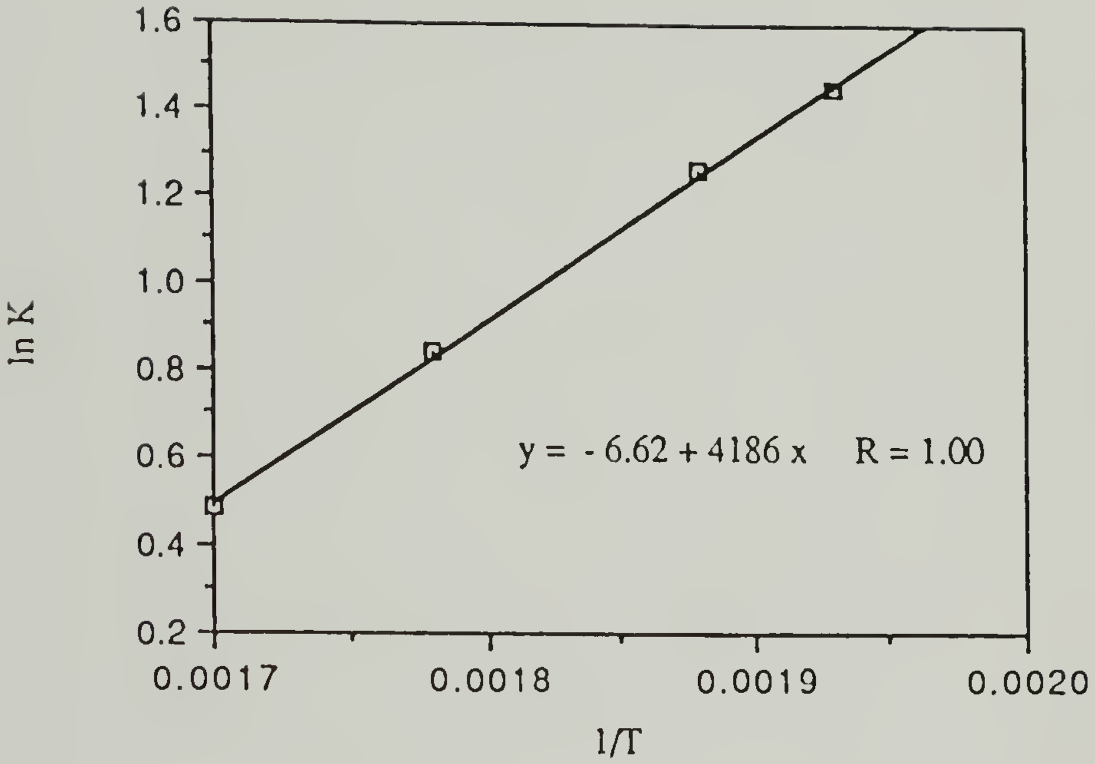

Figure 3.23 *Cis/trans* content versus temperature for *trans*-1,4-cyclohexanedicarboxylic acid-based polyesters. K=[*trans*]/[*cis*]

compound, the *trans* isomer is a solid above the isomerization temperature, equilibrium is pushed to high *trans* contents because of the essentially zero concentration of the solid *trans* isomer. This type of behavior is observed in the *trans* diacid and in Kwolek's polymers. If both components are molten above the isomerization temperature, as with the 1,4-cyclohexane dimethyl ester or the CHDC/CHDM polymers in this research, the *cis* component content increases with increasing temperature, as expected entropically. These trends also explain why problems with isomerization, as described in this research, exist only for the low melting polymers.

Other polyesters synthesized

Several other polyesters were synthesized in the course of this investigation and will be described briefly here.

The polyester from oxalyl chloride and 1,4-CHD was synthesized. This polymer exhibited no melting below 350 °C, and no solubility in known polyester solvents. The polymer of CHDC with 1,4-CHD in a 20:80 *cis/trans* ratio showed no melting below 300 °C, an observation which is consistent with Osman's data (6). Polymers with higher amounts of *cis* monomer were not synthesized in light of Osman's research.

An aromatic diol, the 4,4'-oxyethylenebiphenol was synthesized by J.Y. Jahdav in a separate research program. This diol, polymerized with CHDC, gave a 0.36 dL/g viscosity polymer that formed a nematic melt above 185 °C.

Analogous to the polymers described previously, in which BD was incorporated with 1,4-CHD in hopes of forming an isomorphic structure, adipoyl chloride was incorporated in polymers with CHDC. Two polymers were prepared, a two diacid/one diol polymer of 50:50 CHDC/adipoyl chloride with 1,4-CHD, and a two diacid/two diol polymer of 50:50 CHDC/adipoyl chloride and 50:50 1,4-CHD/CHDM. The first polymer showed only degradation at 280-290 °C. The second polymer melted at 215 °C with a nematic texture above this temperature that persisted until degradation at 300 °C.

Experimental

The following section gives experimental details for the preparation and characterization of the polymers described above, using specific examples where appropriate.

Equipment

Melting points were determined on a Fisher-Johns melting point apparatus and/or a Perkin Elmer DSC 2. Inherent viscosities (IV) were measured in a size 75 Ubbelohde viscometer at 30.0 °C at concentrations of 0.5 dL/g. Polyester viscosities were measured in 3:1 $CHCl_3$/trifluoroacetic acid. Nuclear magnetic resonance (NMR) spectra were obtained on Varian 200 or 300 MHz instruments with an internal tetramethylsilane (TMS) reference. Polarized optical microscopy (POM) was performed with a Leitz-Wetzler microscope at a magnification of 320X. Size exclusion chromatography (SEC) was performed on a Waters 201 Liquid Chromatograph with an ultrastyragel column. The molecular weight reference was polystyrene. X-ray diffraction patterns were obtained with a Statton camera with Ni filtered CuK α radiation (λ=1.542Å) at a sample to film distance of 51.6 mm. The sample holder was equipped with a heating element with an Omega thermocouple. Thermogravimetric analysis was performed on a Perkin Elmer TGS-2 with an S4 microprocessor. Elemental analyses were determined by the Microanalytical Lab at the University of Massachusetts.

Polymerization

Polyester solution polymerization. A typical polymerization was carried out as follows: All glassware was washed in a KOH/isopropanol bath, rinsed with 1 N HCl, 10% Na_2CO_3, several times with distilled water and dried at 125 °C for 16 h. The glassware was cooled in a glove box under a nitrogen atmosphere. The

CHDC was sublimed immediately prior to use. The CHDM was dried for 16 h under vacuum. CHDC (9.065 g, 4.336×10^{-2} mol) and CHDM (6.253 g, 4.336×10^{-2} mol) were weighed in a glove box into a 100-mL, 3-neck, round-bottom flask equipped with a gas inlet tube with stopcock, a septum-topped stopcock adapter and a ground glass stopper. The assembly was removed from the glove box and evacuated to 0.5 mm Hg three times with Ar purging between evacuations. The assembly was placed back in the glove box and the ground glass stopper replaced with a Friedrich condenser equipped with a Drierite® loaded drying tube. The assembly was removed from the glove box and connected to an Ar purge. Aldrich Gold Label anhydrous *o*-dichlorobenzene was transferred by cannula into the round-bottom flask. The Ar purge was continued and the sample heated to the boiling point of the solvent (179-180 °C). Reflux was continued for 16 h, with initial rapid HCl evolution which slowed dramatically after 2 h of reaction. The cooled sample formed a gel, which was removed and mixed with 100 mL of dichloromethane. This mixture was stirred into methanol and the resulting precipitate dried under vacuum. The dried polymer was redissolved in 100 mL of chloroform and reprecipitated into 600 mL of methanol. After drying under vacuum, 10.3 g (85% yield) of polymer was recovered. NMR analysis in $CDCl_3$ showed no isomerization from the all-*trans* configuration.

Polyester melt polymerization. A typical polymerization was performed as follows: The glassware and monomers were treated as for the polyester solution polymerization above. The monomers used were 0.058 g of 1,6- hexanediol (4.91×10^{-4} mol), 0.284 g CHDM (1.97×10^{-3} mol) and 0.514 g CHDC (2.456×10^{-3} mol). The sample was continually purged with Ar. The sample was heated to 110

°C for 2 h, and rapid HCl evolution was observed for the first 15 min of heating. The sample temperature was slowly raised to 220 °C at which point the sample melted, and HCl evolution occurred rapidly. The HCl evolution slowed to an imperceptible rate after 10 min. The temperature was raised to 245 °C and held there for 4 h. The sample was cooled, dissolved in dichloromethane and reprecipitated into methanol. After drying under vacuum, 0.497 g was recovered (73% yield). NMR analysis in $CDCl_3$ showed isomerization at the acid methine position of 23%.

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CHAPTER 4

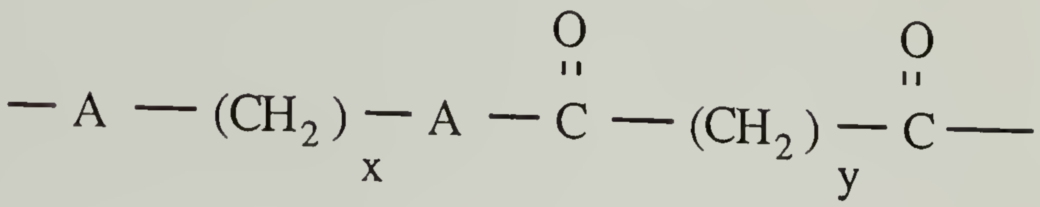
POLYAMIDE SYNTHESIS AND CHARACTERIZATION

Introduction

In pioneering work during the early days of polymer science, W.H. Carothers researched several aliphatic polymers for fiber-forming properties. Polyamides were eventually chosen for commercial development over polyesters because of their higher melting points and increased solvent resistance (1). Several polymers showing this trend for melting point are shown in Table 4.1. The much higher melting point of these polyamides as compared to polyesters is explained by the increased molecular attractive force due to hydrogen bonding. This hydrogen bonding originates in the interaction of the carbonyl group with the nitrogen-bonded hydrogen.

Also shown in Table 4.1 are examples of *N*-methylated aliphatic polyamides. For these polymers the melting point is markedly lower as compared to the non-*N*-methylated polyamides. Some of this decrease is explained by the steric hindrance

Table 4.1 Melting points of some aliphatic polyamides and polyesters



$$-A-(CH_2)_x-A-\overset{O}{\overset{\|}{C}}-(CH_2)_y-\overset{O}{\overset{\|}{C}}-$$

A	x	y	mp, °C	Reference
NH	4	2	287	2
NCH3	4	2	123	2
O	4	2	34	3
NH	6	4	265	4
NCH3	6	4	75	2
O	6	4	57	5
NH	6	8	228	6
O	6	8	78	7

to crystal packing, but the largest factor is the decreased ability of these polymers to hydrogen bond (8).

The only commercial liquid crystalline polyamide is Kevlar® (structure shown in Figure 1.6). For Kevlar®, analogous to the polyamides that Carothers examined, a primary diamine is used in the synthesis. The resulting aromatic, linear Kevlar®, degrades below a melting point and is only soluble in concentrated acid. However, if this polymer is *N*-alkylated or *N*-alkylarylated, solubility is increased and melting temperature is lowered. For example, the *N*-propyl derivative of Kevlar® is soluble in tetrahydrofuran and dimethylsulfoxide, and the *N*-9-methyleneanthracene derivative melts below 300 °C (9).

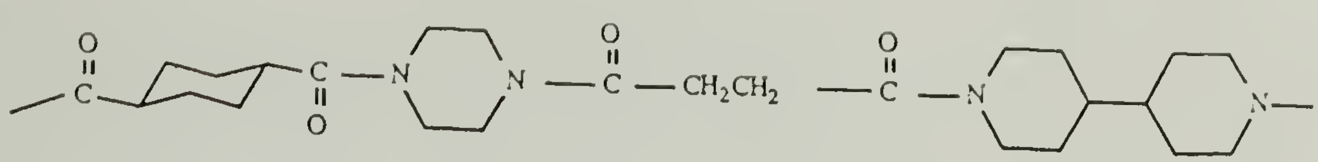
There are few examples of thermotropic polyamides (10). These examples use substituted mesogens and long flexible spacers. To obtain thermotropic liquid crystallinity in polyamides that do not have flexible spacers, a polymer must be synthesized with the above trends in mind. That is, a polyamide must be synthesized that does not have the ability to strongly hydrogen bond. The *N*-substituted analogs of Kevlar® were made by a post-polymerization reaction, chosen in part due to the decreased reactivity of the secondary aromatic diamines. In the research described in this dissertation, more reactive, non-aromatic diamines were used in polymer synthesis and the use of secondary diamines was possible. The structures of three diamines used in this research are shown in Figure 2.14, Column III.

The purification of the diamines was described in Chapter 2. Also described were liquid crystalline phases for carboxylated versions of these diamines. This Chapter will detail the synthesis and characterization of liquid crystalline polyamides. These polymers were synthesized in the hope of obtaining thermotropic or lyotropic (in organic solvents) polyamides.

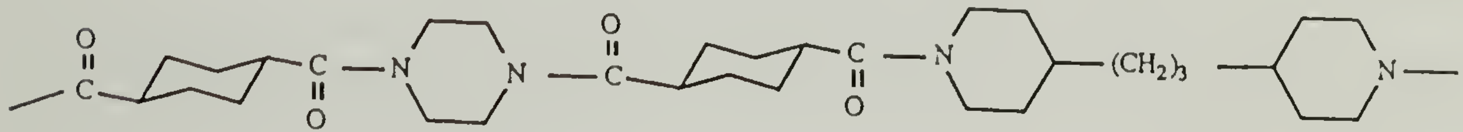
Polyamides based on *trans*-1,4-cyclohexanedicarboxylic acid, succinyl chloride, 4,4'- bipiperidine and piperazine

The first series of polyamides was made based on two diacids and two diamines as seen in Figure 4.1 *A*. With this combination a wide range of polymer compositions are obtainable, and it was hoped that copolymers could be formed that would have melting points below 300 °C. Table 4.2 shows the composition of the polymers made. These polymers were made interfacially, with a dichloromethane organic layer and a KOH acid acceptor in the aqueous phase as seen in Figure 4.2. Three of these polymers melted to birefringent fluids; the others degraded at temperatures of 280-300 °C. The three polymers that melted are the Table 4.2 polymers 1, 4 and 5.

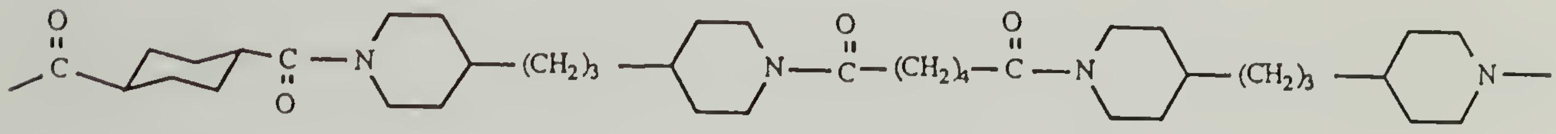
Polymer 4.2-1 melted at 220 °C, and polarized optical microscopy (POM) of this polymer melt revealed a birefringent fluid up to a degradation temperature of 280 °C. The differential scanning calorimetry (DSC) trace and POM photographs are shown in Figure 4.3. Polymer 4 in Table 4.2 melted to a nematic phase at 225 °C. The DSC and POM evaluations of this polymer are shown in Figure 4.4. Polymer 4.2-5 flowed at 210 °C, displaying a birefringent melt, with the DSC and POM of this polymer shown in Figure 4.5. These latter two polymers also



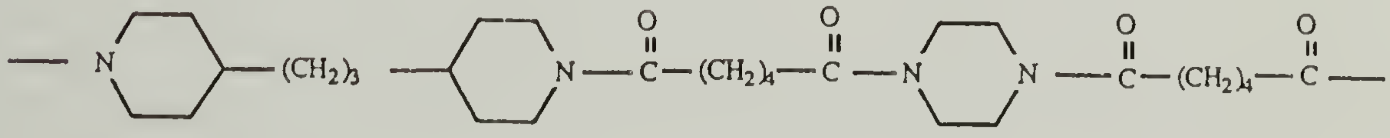
A



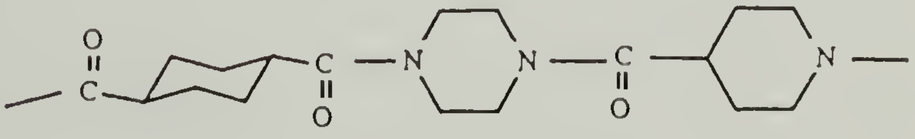
B



C



D



E

Figure 4.1 Polyamides synthesized in this research

Table 4.2 Composition of Series 4.1 *A* polyamides

Sample Number	Acid Component		Base component	
	% CHDC	% Succinyl Chloride	% Piperazine	% BP
4.2-1	-	100	100	-
4.2-2	50	50	100	-
4.2-3	-	100	-	100
4.2-4	50	50	-	100
4.2-5	50	50	50	50
4.2-6	-	100	50	50
4.2-7	100	-	100	-
4.2-8	100	-	50	50

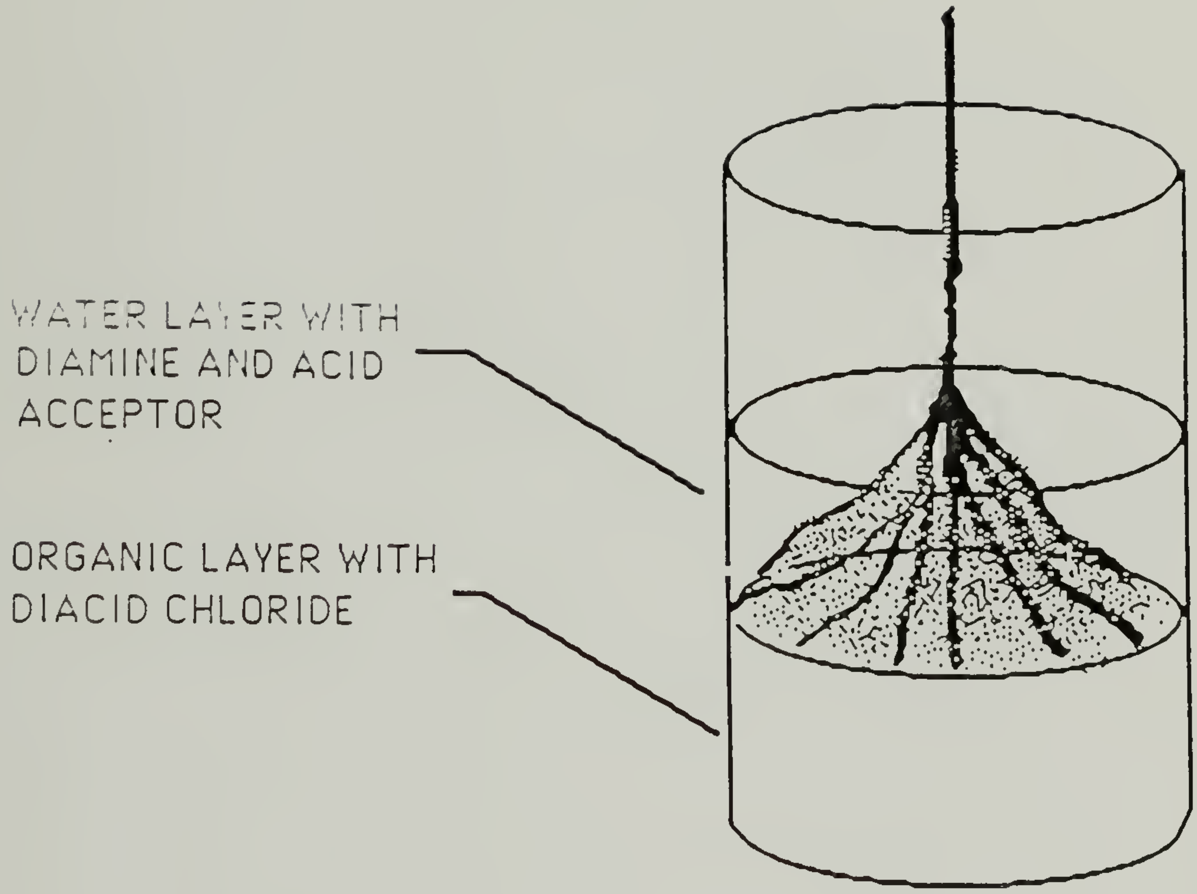


Figure 4.2 Interfacial synthesis of polyamides (*Ref. 11*)

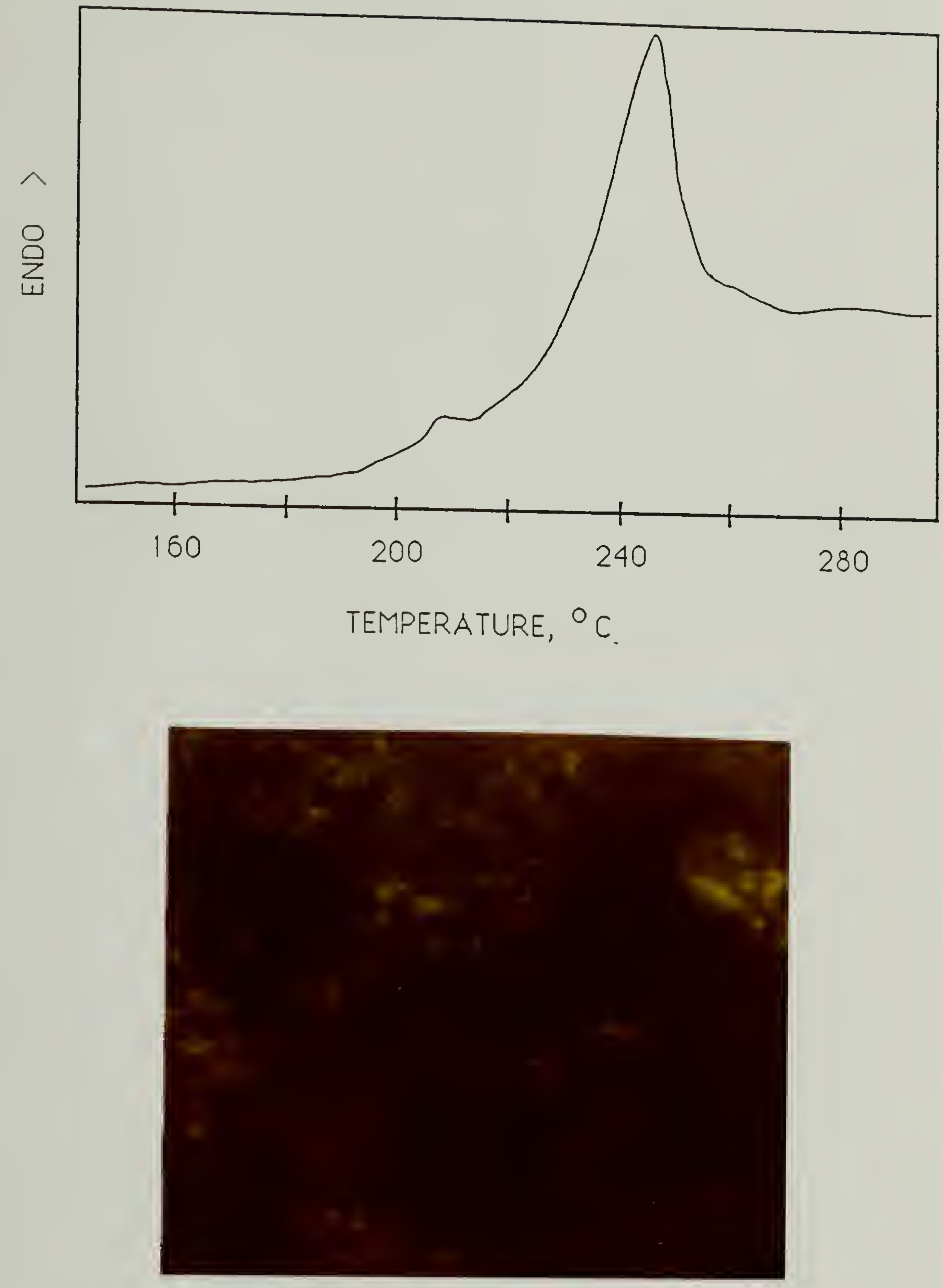


Figure 4.3 Differential scanning calorimetry and polarized optical microscopy of Table 4.2-1 polyamide

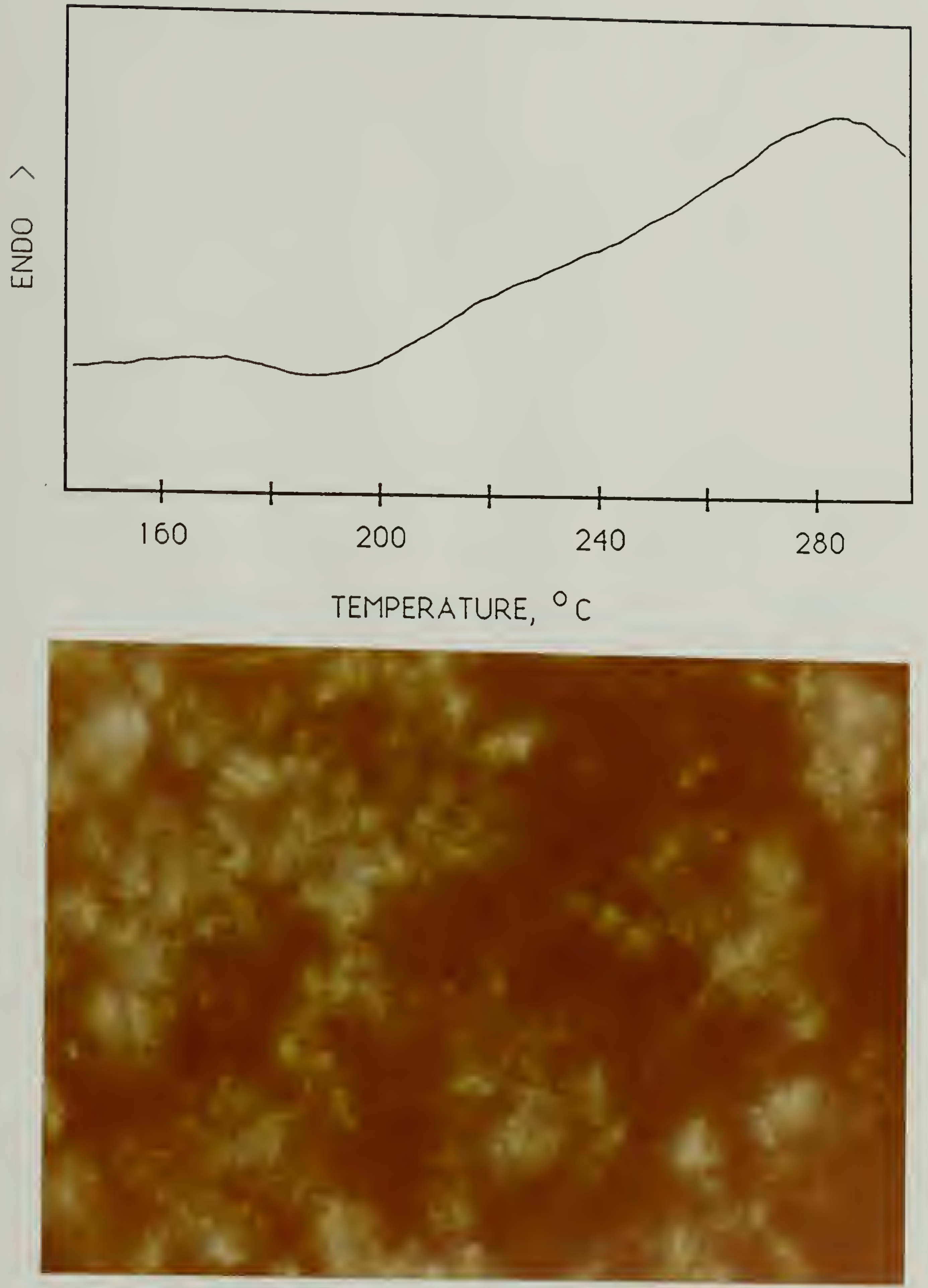
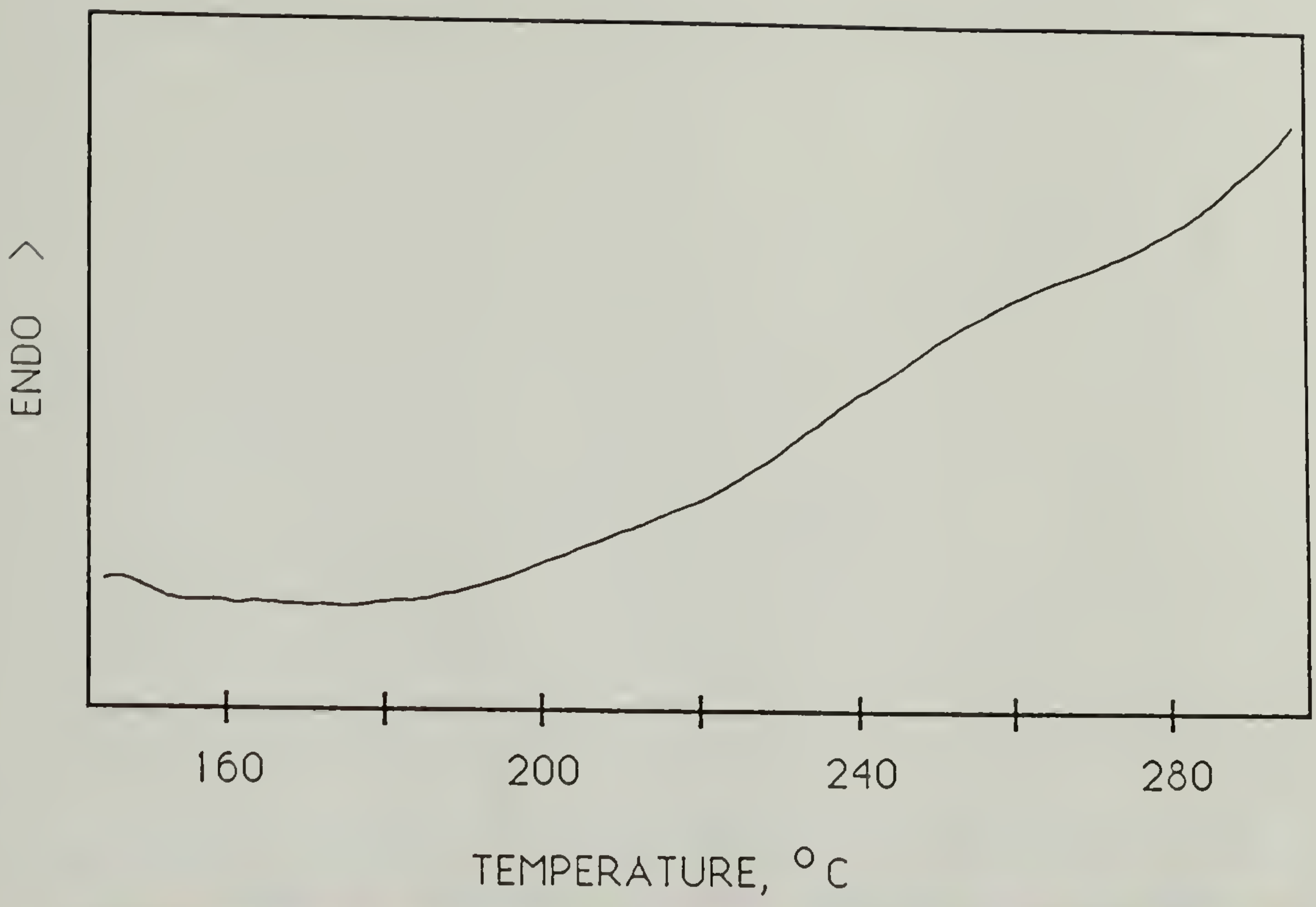


Figure 4.4 Differential scanning calorimetry and polarized optical microscopy of Table 4.2-4 polyamide



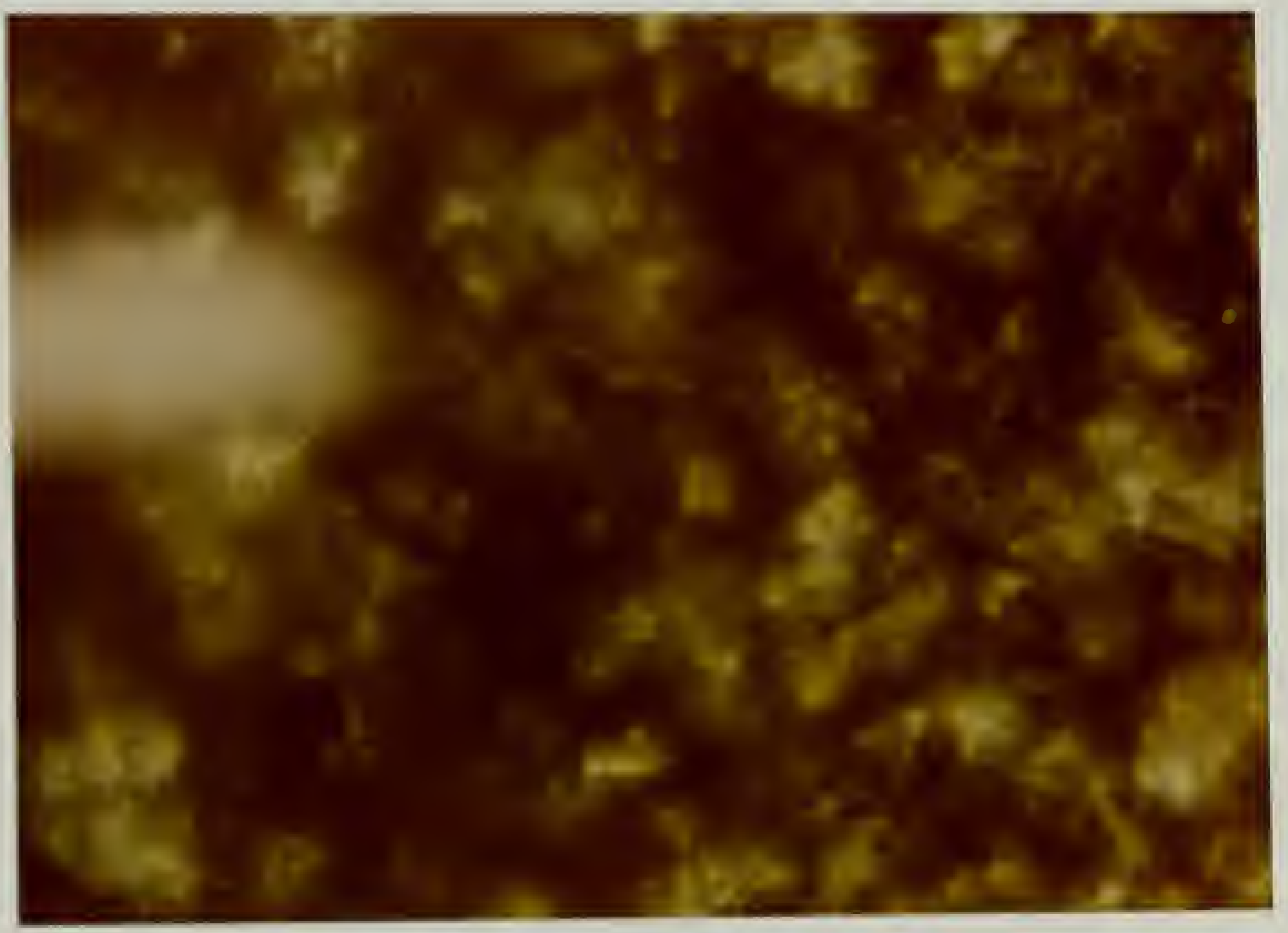


Figure 4.5 Differential scanning calorimetry and polarized optical microscopy of Table 4.2-5 polyamide

exhibited severe degradation between 280-300 °C, and no isotropization temperature was observed.

For many rigid rod polyamides synthesized interfacially, low molecular weights are observed due to low polymer solubility and the precipitation of the polymer at low degrees of conversion (12). The molecular weights of this series of polyamides were very low; the inherent viscosities of the three nematic polymers described above were 0.16, 0.13 and 0.07, respectively. For these polymers, a change of the organic phase in the interfacial polymerization did not lead to an increase in polymer molecular weight, and as the polymers were not soluble in organic solvents, a solution polymerization could not be performed.

Because the molecular weights of these polymers were so low, it was thought that the melting points were in the region of molecular weight dependence (13), and it was decided to resynthesize these polymers to obtain higher molecular weights. The molecular weight could be increased slightly by repurifying monomers and solvents, or to a larger extent by changing the reaction conditions. This method entailed slow removal of the organic solvent over a 6 to 12 hour period, with continual stirring. The resulting polymer was removed, washed several times with water, dried and dissolved in formic acid. The polymer was recovered by precipitation in water, and after extensive water washing the polymer was dried under vacuum. This method allowed for a higher monomer concentration near the end of the polymerization reaction and the removal of low molecular weight fractions by the dissolution and reprecipitation of the polymer.

For the polymers of this series, increases in molecular weight to a polymer with an inherent viscosity of 0.31 dL/g yielded a sample which did not melt below 300 °C, and showed no evidence of a nematic phase. Both the high and low molecular weight versions of these polymers showed no evidence of lyotropic phases in formic acid. Because the only examples of these polymers which showed liquid crystalline phases were of low molecular weight, further research with this series was not performed.

Polyamides based on *trans*-1,4-cyclohexanedicarboxylic acid, piperazine and 4,4'-trimethylenedipiperidine

The data from the previous series of polyamides indicated that some degree of flexibility would be needed to obtain a high molecular weight thermotropic polyamide. The diamine monomer chosen to obtain this flexibility was 4,4'-trimethylenedipiperidine (TMP). Here, an advantage of aliphatic systems over aromatic systems in obtaining liquid crystallinity is seen, in that the presence of three methylene groups between rings does not necessarily lead to a nonlinear structure as shown in Figure 4.6. The nuclear magnetic resonance (NMR) spectrum of this monomer is also shown in Figure 4.6, revealing the preferred solution conformation of this monomer. The separation of the hydrogens on the carbon α to the nitrogen into axial and equatorial peaks show the existence of only one isomer. Because no known cyclohexane methine position is observed as a locked-in conformation singlet by NMR, the *trans* structure was assigned to this monomer, that is, the conformation shown in Figure 4.6. This assignment was later supported by the observation of a liquid crystalline phase in carboxylated TMP and in polyamides made from TMP.

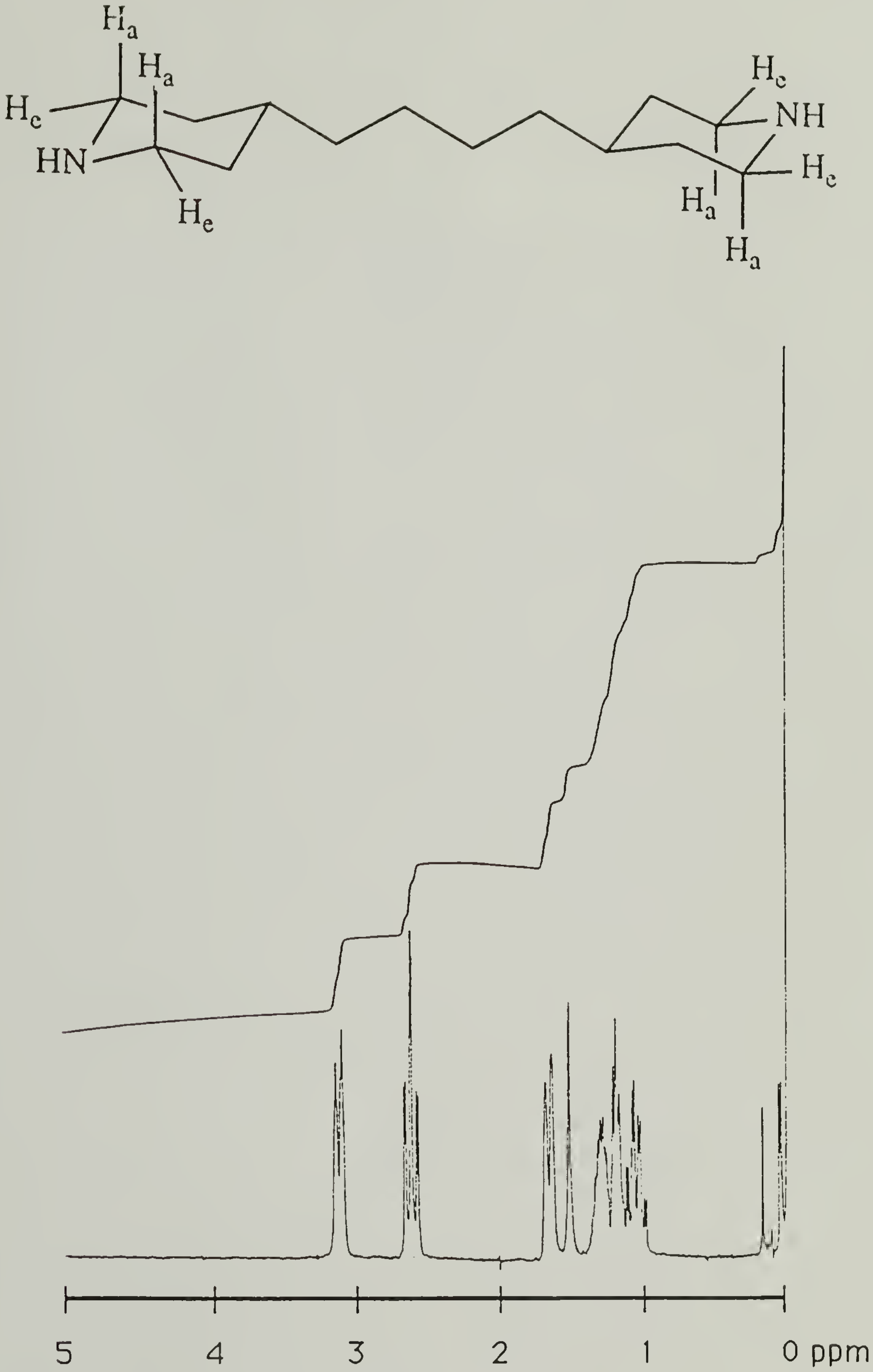


Figure 4.6 The structure and nuclear magnetic resonance spectrum of 4,4'-trimethylenedipiperidine

Polyamides were made with an acid component of pure *trans*-1,4-cyclohexanedicarboxylic acid (CHDC) and a base component of piperazine and TMP. As with the above series of polymers, these polymers were made in an interfacial system. The analysis of these polymers revealed that a large TMP content did not assure a polymer structure that would melt without degradation. The 45 mole percent TMP polymer, which is near the minimum melting point, did melt at 260 °C, but the melt was accompanied by severe degradation and clear observation by POM was not possible. The melting point versus composition curve for the polymer is shown in Figure 4.7. Here, in contrast to all the polyester series made, a nonlinear graph is observed. This behavior is explained by the non-isomorphic structures of TMP and piperazine, which are due to the three methylene groups between the piperidine rings of the TMP. In this system, as described for several polyester systems in Chapter 3, a solution-cast film of the polymer examined at room temperature displayed a nematic-like texture. Lyotropic phases were not observed in the formic acid solution.

A series with the same two diamines as above, but with a diacid component of 100% oxalyl chloride, was made with TMP molar contents of 10, 20 and 30%. These polymers degraded too rapidly to observe any structure in the melt or to observe a DSC melting transition. For example, thermogravimetric analysis (TGA) for the 10% TMP polymer showed 1.0% weight loss at 116 °C, 10% weight loss at 295 °C and 17% weight loss at 400 °C. No other oxalyl-based polymers were made in view of the low temperature degradation of this functionality (14).

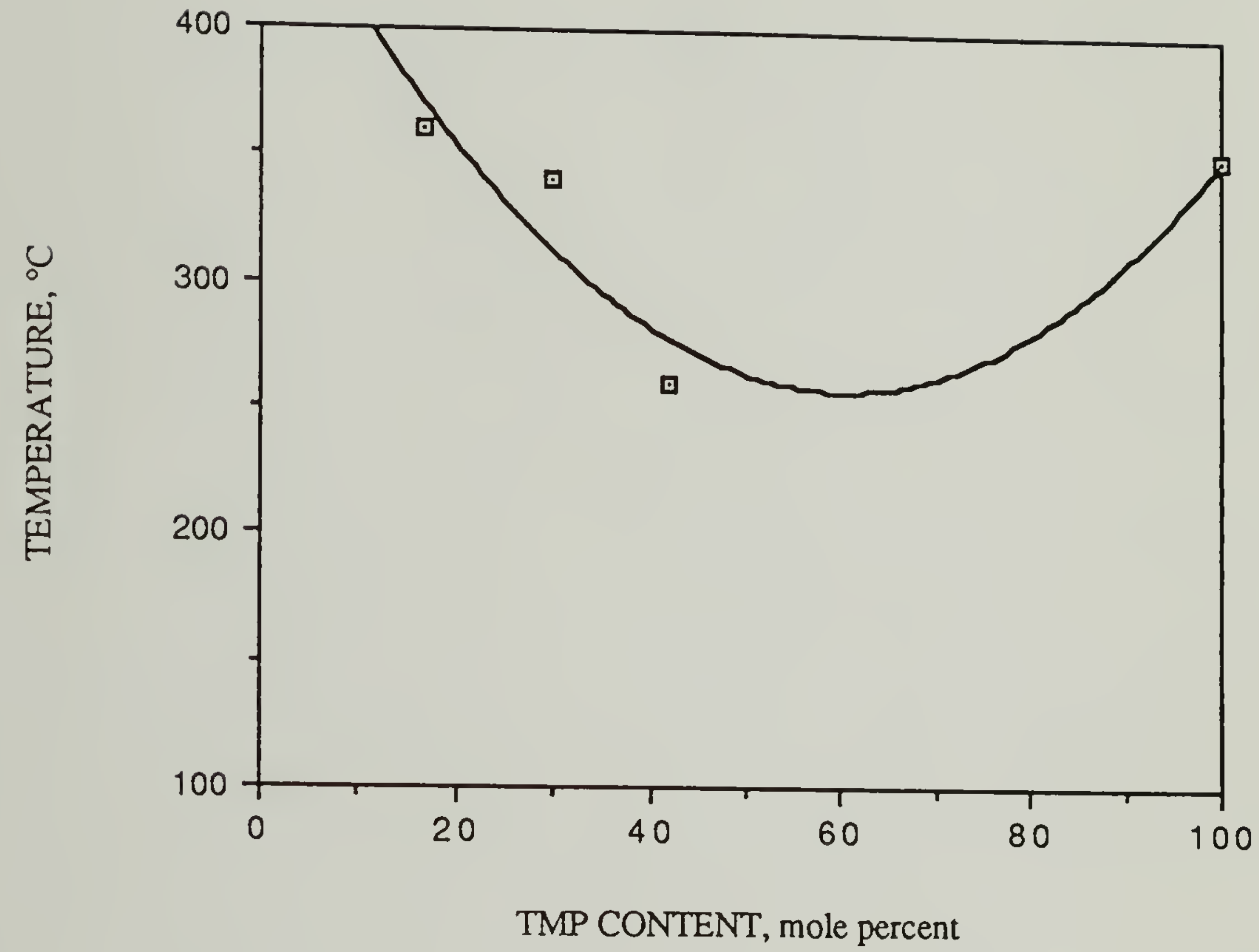


Figure 4.7 The melting point curve for 4.1 *B* polyamides

Polyamides based on *trans*-1,4-cyclohexanedicarboxylic acid, adipoyl chloride and 4,4'-trimethylenedipiperidine

Room temperature of the above TMP/CHDC polymer in a solution-cast film revealed a nematic-like texture. This observation was taken as evidence that the TMP was in a linear conformation and that TMP-based compounds could form liquid crystalline phases. Additional evidence for the linear structure was the existence of liquid crystalline phases in carboxylated TMP. A series was made to exploit this linear structure, in hopes that the three-methylene link between the piperidine rings would give some flexibility for lowering the melting point. Using the same rationale as described for the polyester series of Chapter 3 with isomorphic flexible spacers, adipoyl chloride was chosen to be copolymerized with TMP and CHDC. As seen in Figure 4.8 this monomer can adopt a conformation that is isomorphic with CHDC.

The two homopolymers were made, as well as the 25, 50 and 75 mole percent CHDC. The melting temperature versus composition curve is shown in Figure 4.9. The linear drop indicates isomorphic behavior, as noted in several series of polyesters described in Chapter 3.

The first two polymers made in this series were the 0 and 50 mole percent CHDC. The inherent viscosities of these two polymers were 0.91 and 0.51 dL/g as measured in formic acid. The POM and DSC analyses of these two polymers are shown in Figures 4.10 and 4.11. For the 0 mole percent CHDC polymer (Figure 4.10), the POM revealed a schlieren texture. However the DSC results indicated that the thermal transition into the region above 110 °C is not a nematic transition,

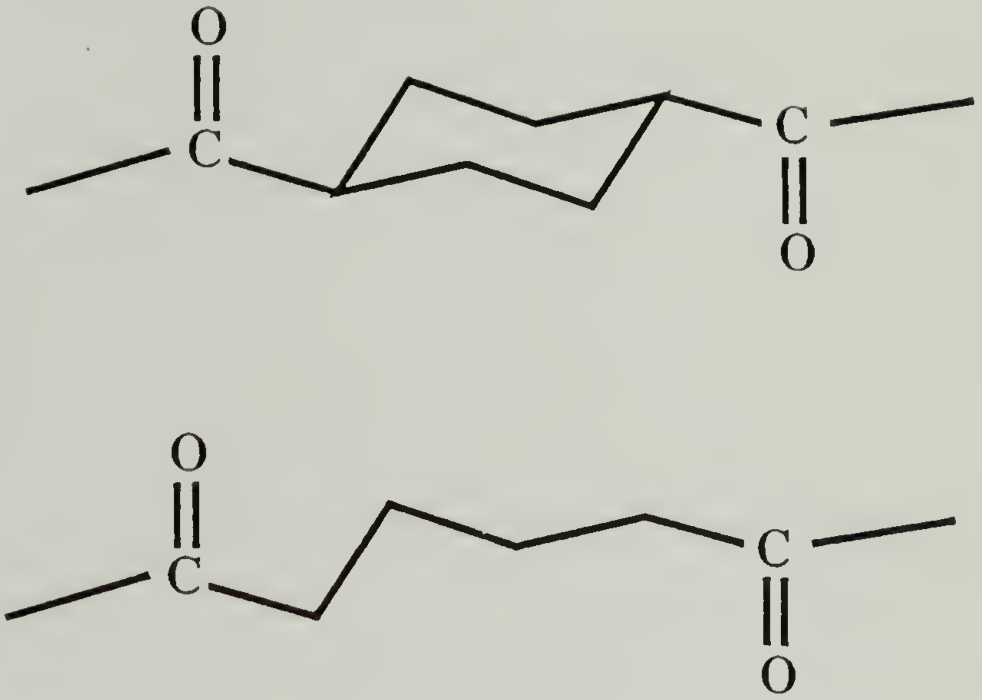


Figure 4.8 Isomorphic structures of *trans*-1,4-cyclohexanedicarboxylic acid and adipoyl chloride

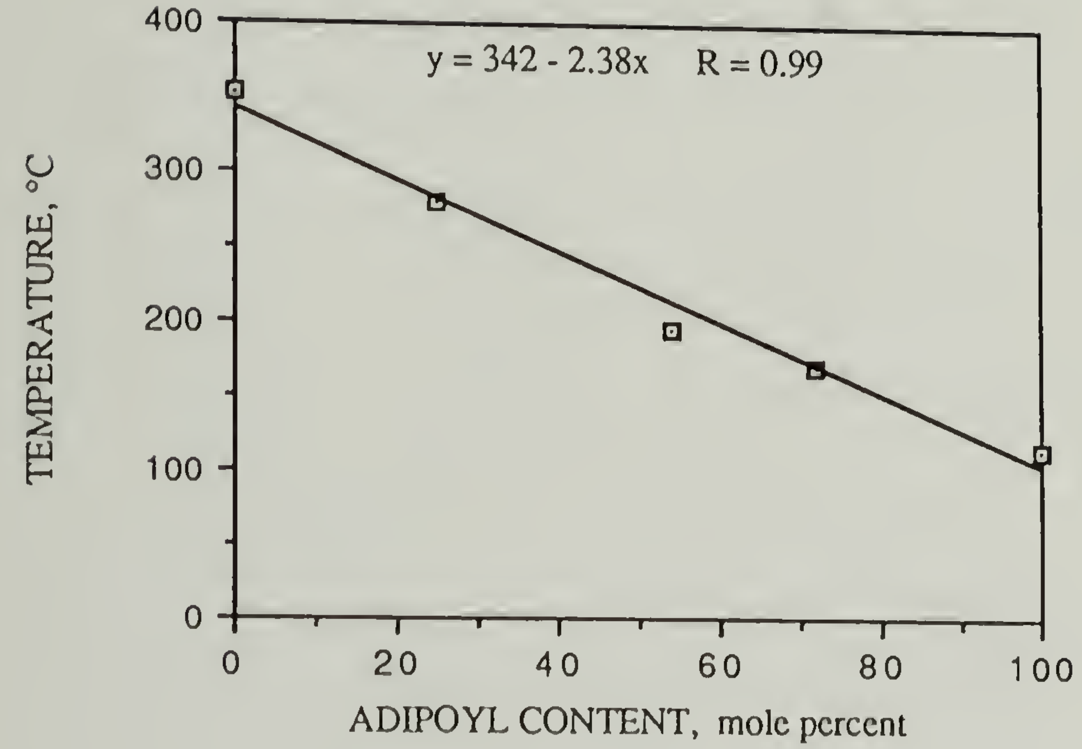
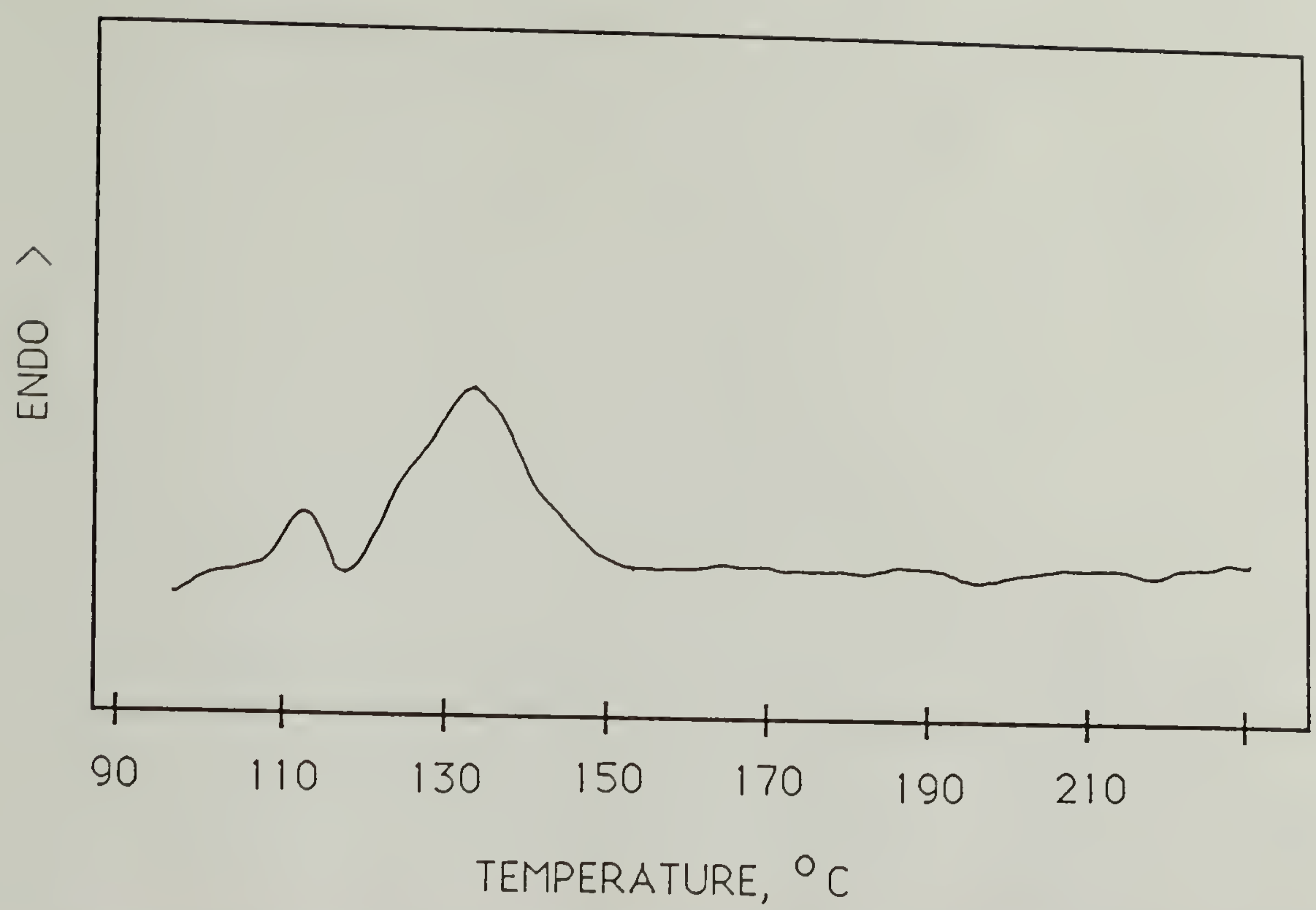


Figure 4.9 The melting point curve for 4.1 *C* polyamides



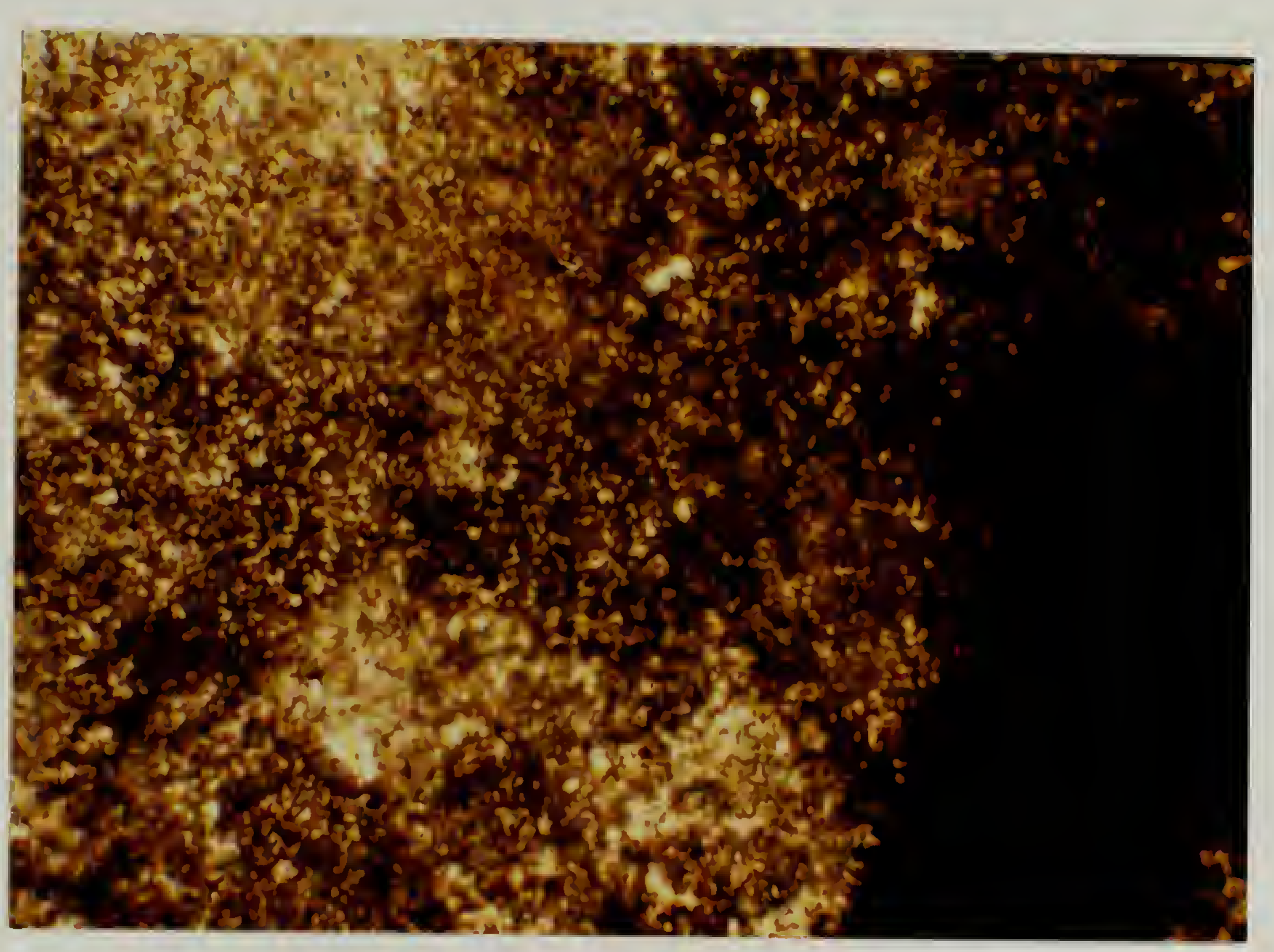
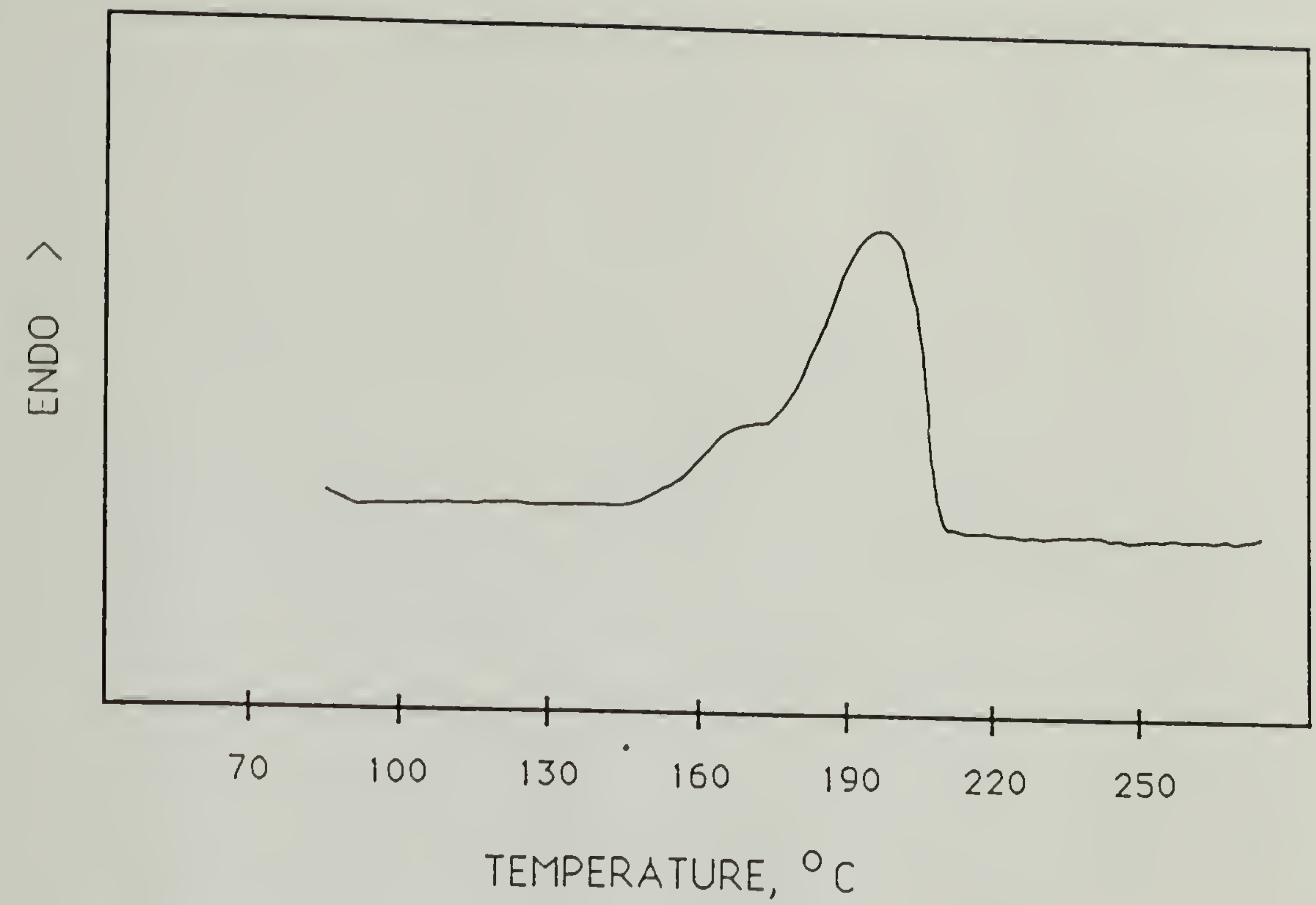


Figure 4.10 Differential scanning calorimetry and polarized optical microscopy of the 4,4'-trimethylenedipiperidine/ adipoyl chloride homopolymer



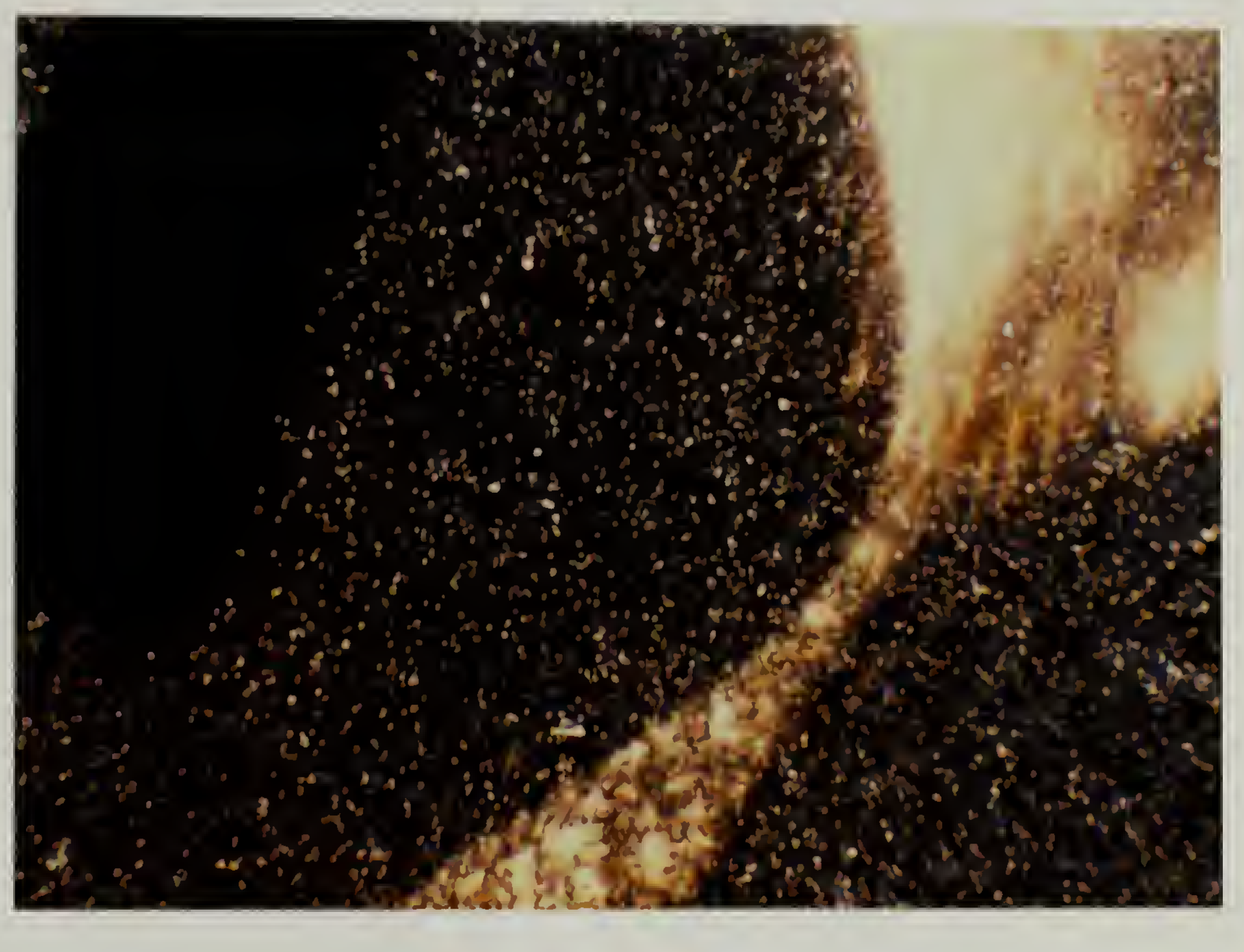


Figure 4.11 Differential scanning calorimetry and polarized optical microscopy of the 4,4'-trimethylenedipiperidine/ adipoyl chloride/ *trans*-1,4-cyclohexanedicarboxylic acid copolymer

because the higher thermal transition (into an isotropic melt) is of a larger ΔH (see Chapter 1). The X-ray examination of this polymer (Figure 4.12) shows a more complex pattern than expected for a nematic phase.

The 50 mole percent CHDC polymer exhibited similar behavior. DSC analysis (Figure 4.11) showed results similar to those for the previous polymer except that the peaks were not as clearly resolved. The sample showed a schlieren texture in the temperature range just below the isotropization peak.

This series was completed with the preparation of two additional polymers, the 25:75 and the 75:25 molar ratio. The molecular weights of these two polymers were higher than the preceding polymers, as indicated by the inherent viscosities of 2.18 and 1.35 dL/g. The DSC traces of these two polymers are shown in Figure 4.13. The peaks observed are sharp melting peaks, and optical flow birefringence above this temperature was not observed.

A repeat synthesis of the 0 mole percent CHDC polymer to obtain a higher molecular weight polymer was successful. However, this polymer did not display observable liquid crystalline phases by POM. Annealing the polymer at 130 °C for 24 hours did not change this observation. On the basis of the failure to observe liquid crystalline phases in this high molecular weight sample, and of the DSC and X-ray results of the lower molecular weight sample of this polymer, the phase was identified as smectic. As the molecular weight increases, the higher viscosity hinders the orientation and formation of a liquid crystalline phase.

It is not surprising that the TMP/adipoyl chloride polymer structure results in smectic phases. The TMP has a great enough axial length to be a mesogen, and the adipoyl group acts as a flexible spacer connecting these mesogens.

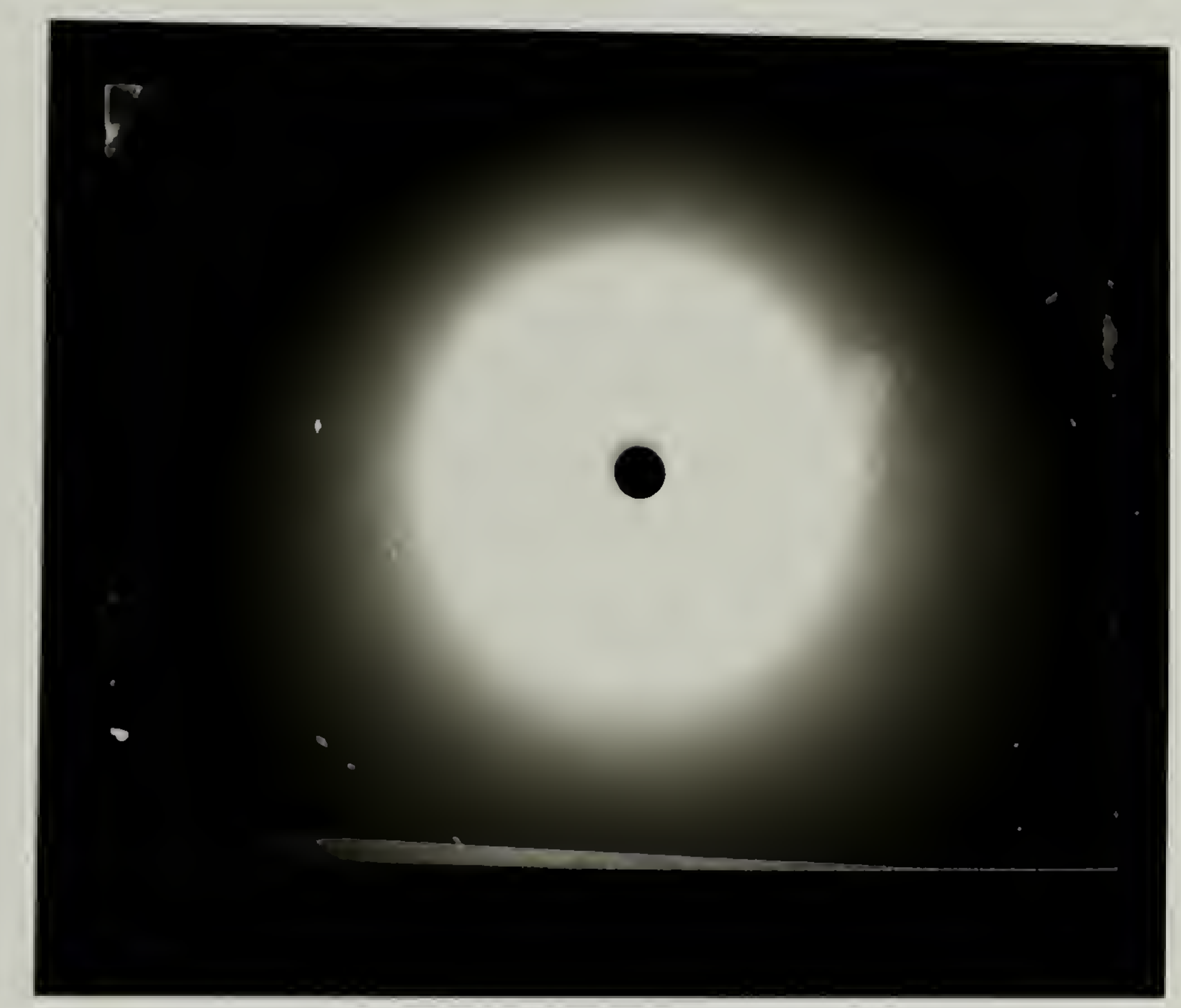


Figure 4.12 X-ray analysis of the 4,4'-trimethylenedipiperidine/ adipoyl chloride homopolymer at 115 °C

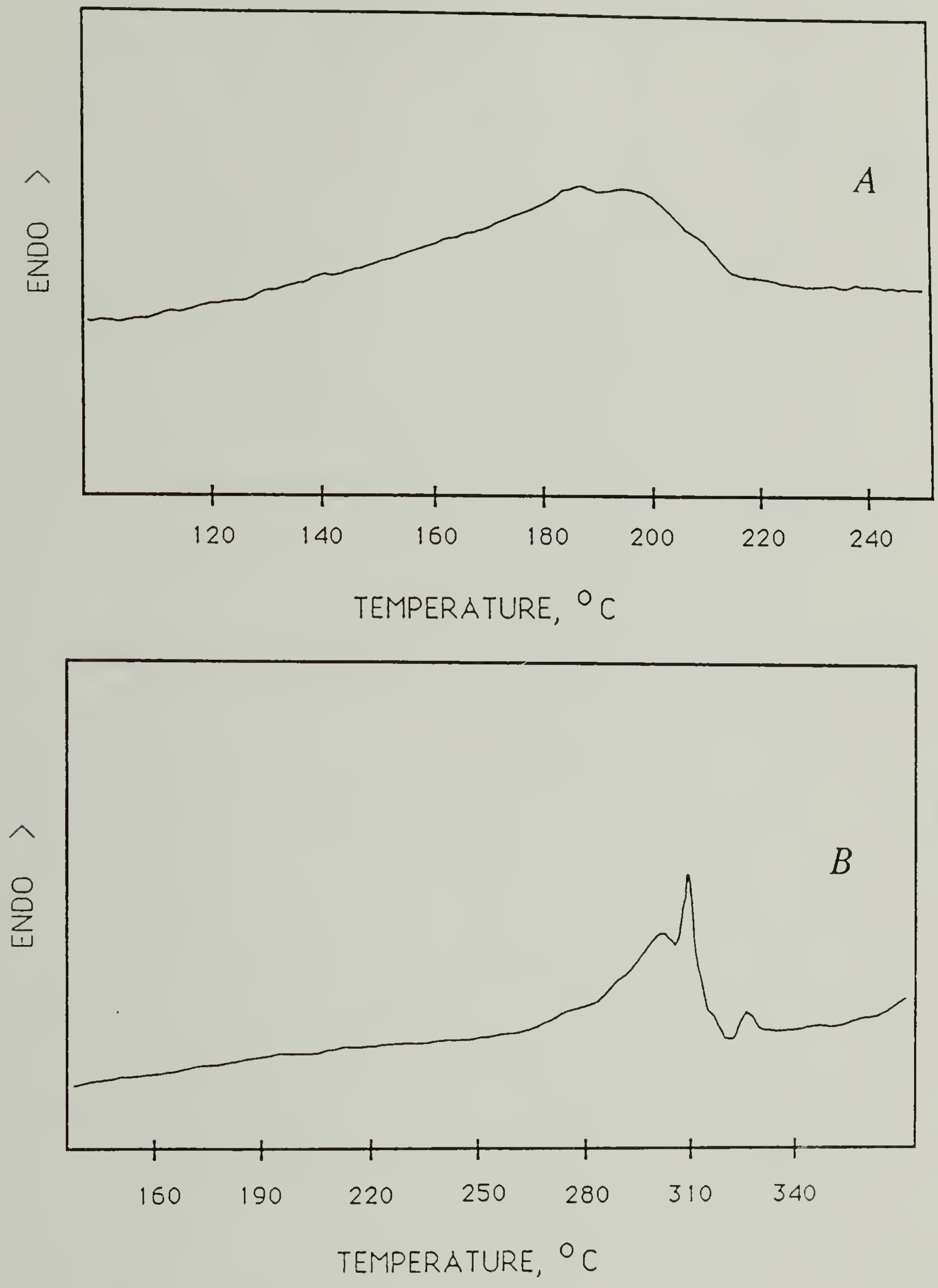


Figure 4.13 Differential scanning calorimetry of higher molecular weight versions of the 4,4'-trimethylenedipiperidine/ adipoyl chloride/ *trans*-1,4- cyclohexanedicarboxylic acid copolymers.
A-75% adipoyl, *B*-25% adipoyl

Structures with this mesogen/flexible spacer arrangement are known to possess smectic phases (15).

There are two physical properties of these polymers that deserve mention. First, when the polymers were even slightly wet with formic acid, they were very elastic and could be stretched up to 10 times the original length. Second, the polymers were very adhesive to aluminum and glass. If a polymer wet with a slight amount of water or formic acid was put into a container, the dried polymer could not be removed from the container.

An analogous series of copolyamides was made with piperazine in place of TMP. The greater rigidity of the piperazine led to polymers that degraded without melting.

Polyamides based on adipoyl chloride, piperazine and 4,4'-trimethylenedipiperidine

The TMP adipoyl chloride polymer, described above, displays a liquid crystalline phase, and it was decided to prepare an analogous series based on an acid component of only adipoyl chloride, and using two diamine components, TMP and piperazine. As with the previous series, it was hoped that the melting temperature could be varied from the 110 °C melting point of the homopolymer to the piperazine/adipoyl chloride melting point of 355 °C (16). It was not expected that the series would exhibit a linear drop in melting point with composition because the polyamide series 4.1 *B* based on piperazine and TMP did not show isomorphic behavior.

Four copolymers, in addition to the TMP/adipoyl chloride homopolymer, were made by varying the ratio of TMP to piperazine. These polymers were made by interfacial synthesis. The melting points of these polymers were measured and a fairly linear decrease was seen with increasing amounts of TMP, as shown in Figure 4.14. None of these polymers showed any evidence of liquid crystalline phases, either by DSC or POM. The lower melting point 75 mole percent TMP polymer was annealed at 150 °C and the resulting sample showed no change by POM. These polymers were soluble in dichloromethane and methanol, but no lyotropic phases were observed.

The linearity of the decrease is surprising in light of the different sizes of TMP and of piperazine. Upon melting, the polymer series 4.1 *B*, based on the same two diamines, did not show a linear drop, but instead exhibited a minimum melting point (Figure 4.7). Detailed analysis by X-ray diffraction and infrared could elucidate the crystal structure of the polymer, particularly of the three non-ring methylenes in TMP, but such an analysis was beyond the scope of this research.

As with the previous polymer system, these polymers were elastomeric when slightly wet with water or formic acid and were very effective at adhering to glass or aluminum.

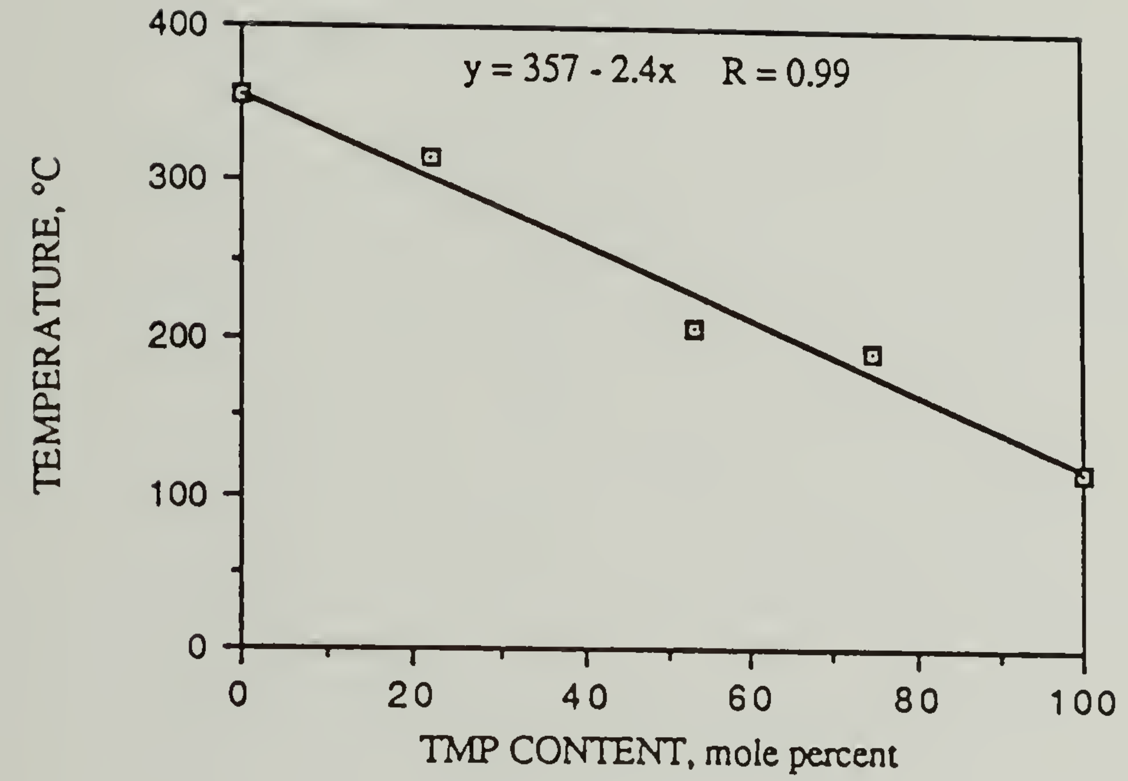


Figure 4.14 The melting point curve for 4.1 *D* polyamides

Attempted ring closure and polymerization of isonipecotic acid

Isonipecotic acid (INPA) has the structure shown in Figure 2.14, Column IV. A polymer prepared from INPA would have a structure that is similar to the polyamides made from the AA BB condensation reactions in this research, that is, a 1,4-cyclohexane backbone that contains a secondary nitrogen. The most convenient method for the polymerization of this compound would be to prepare the bicyclic compound and perform a ring-opening polymerization. This compound has not previously been cyclized and the failed synthesis has been attributed to Bredt's rule (17). Bredt's rule would disallow the normal resonance structure for an amide and would lead to a less stable molecule as compared to a bicyclic lactam with the nitrogen not in the bridgehead (for example 2-azabicyclo[2.2.2]octan-3-one). However, it would not account for the formation of this product being impossible insofar as [2.2.1] ring systems are known for compounds that have no possible resonance stability (18, 19).

Two methods were used to form the lactam. The INPA was heated in a distillation setup to remove reaction water. High vacuum was applied to the resulting low molecular weight polymer and the catalysts antimony trioxide and zinc oxide were used in cracking attempts. A very small amount of material distilled over, and that which did was unreacted INPA. The remaining low molecular weight polymer did not melt and was not found to be soluble in any solvents.

The ethyl ester of INPA was prepared and this compound was treated as the acid derivative above. Again, no bicyclic product was formed.

Polymers of INPA with piperazine and CHDC were prepared via the reaction of the salt. These polymers were insoluble and infusible materials.

Experimental

The following section gives experimental details for the preparation and characterization of the polymers described above, using specific examples where appropriate.

Equipment

Melting points were determined on a Fisher-Johns melting point apparatus and/or a Perkin Elmer DSC 2. Inherent viscosities (IV) were measured in a size 75 Ubbelohde viscometer at 30.0 °C at concentrations of 0.5 dL/g. Polyamide viscosities were measured in formic acid. Nuclear magnetic resonance (NMR) spectra were performed on Varian XL 200 or 300 MHz instruments with an internal tetramethylsilane (TMS) reference. Polarized optical microscopy (POM) was performed with a Leitz-Wetzler microscope at a magnification of 320X. Thermogravimetric analysis was performed on a Perkin Elmer TGS-2 with an S4 microprocessor. X-ray diffraction patterns were obtained with a Statton camera using Ni filtered CuK α radiation (λ=1.542Å), at a sample to film distance of 51.6

mm. The sample holder was equipped with a heater with an Omega thermocouple. Elemental analyses were determined by the Microanalytical Lab at the University of Massachusetts.

Polymerization

Polyamide interfacial polymerization I. A typical polymerization was performed as follows: TMP was sublimed immediately prior to use. 0.612 g (2.91 x 10^{-3} mol) was dissolved in 20 mL of water and 0.366 g of KOH (6.52 x 10^{-3} mol) was added. The CHDC was sublimed, and 0.602 g (2.88 x 10^{-3} mol) dissolved in 20 mL of sieve-dried dichloromethane. The aqueous layer was slowly poured on top of the dichloromethane layer. A small amount of film formed at the interface and was removed. The mixture was stirred and film collected at the top of both layers over a 2 h period. The film was washed several times with water and dried under vacuum. 0.77 g (77%) of polymer was collected.

Polyamide interfacial polymerization II. A typical polymerization was performed as follows: CHDC was sublimed immediately prior to use. Adipoyl chloride was distilled immediately prior to use. 0.143 g (6.84 x 10^{-4} mol) of CHDC and 0.31 mL (2.1 x 10^{-3} mol) of adipoyl chloride were dissolved in 20 mL of sieve-dried CH_2Cl_2. 0.601 g (2.86 x 10^{-3} mol) of TMP and 0.32 g (5.7 x 10^{-3} mol) of KOH were dissolved in 50 mL of water. The aqueous layer was mixed with the organic layer and stirred vigorously for 12 h under a positive nitrogen atmosphere vented to an exhaust hood. The resulting polymer was removed from the beaker by filtration, and washed several times with water. The polymer was dried and then dissolved in formic acid. The formic acid solution was precipitated into a five-fold excess of water, and the precipitated polymer washed with water until there was no residual formic acid (by smell). The polymer was dried in a vacuum oven, yielding 0.164 g (18% yield) with an inherent viscosity of 2.18 dL/g in formic acid.

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CHAPTER 5

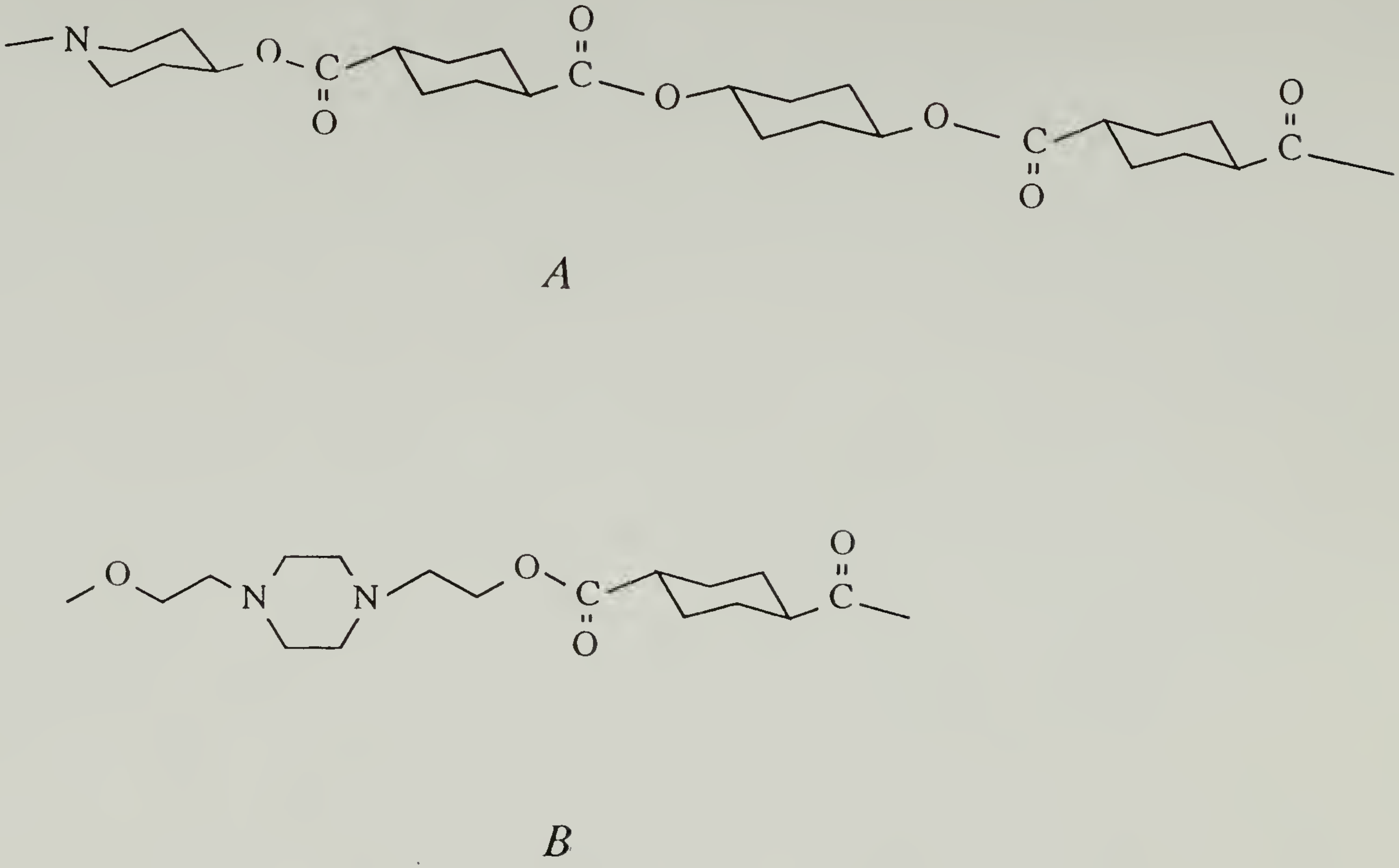
POLYESTERAMIDE AND POLYESTERAMINE SYNTHESIS AND CHARACTERIZATION

Polyesteramide synthesis and characterization

In contrast to the work done with liquid crystalline polyesters and polyamides, there have been relatively few reports of liquid crystallinity in polyesteramides (1-4). This trend is not difficult to understand. As noted in Chapter 1, the bulk of research has been directed toward preparing either thermotropic polyesters or lyotropic polyamides. From the viewpoint of incorporating an amide link in a thermotropic polyester, the increased hydrogen bonding from the amide linkage leads to a higher melting polymer than observed for liquid crystalline polyesters and results in polymers which degrade below a melting point. From the viewpoint of incorporating an ester link in a lyotropic polyamide, the ester bond may increase solubility, but the preferred acid solvents for liquid crystalline polyamides attack the ester bond and result in a badly degraded polymer.

As mentioned in Chapter 4, a favorable method for lowering the melting point in polyamides is to use secondary diamines in the polymer synthesis, so that the resulting polyamide has a decreased tendency to hydrogen bond. To take advantage of this method of melting point lowering in polyesteramide synthesis, an alcohol amine molecule, with a secondary amine functionality can be used. 4-Hydroxypiperidine (4-HP), shown in Figure 2.14, Column V, is such a monomer. Like other monomers used in this research, 4-HP is a six-membered alicyclic with 1,4-functionality. This monomer can be thought of as an analog to two other monomers used in this work, the 1,4-cyclohexanediol used for polyester synthesis and piperazine used for polyamide synthesis. If a copolymer was made via the reaction of 1,4-cyclohexanediol and piperazine, with a diacid chloride, a blocky polymer would result due to the greater nucleophilicity of the amine functionality (5). In contrast, incorporating both functional groups in one molecule, as with 4-HP, gives a convenient method for the synthesis of polyesteramides that cannot be blocky. In addition, the difference in reactivity of the two functionalities in the molecule provides a method for obtaining frustrated chain packing with only one dibasic monomer.

A series of polyesteramides was made with 4-HP, *trans*-1,4-cyclohexanediol (1,4-CHD) and *trans*-1,4-cyclohexanediacid chloride (CHDC) as shown in Figure 5.1 *A*. The ratio of 4-HP to 1,4-CHD was varied in these polymers from 0-100 mole percent. As expected, the polymer high (>50 mole percent) in 1,4-CHD degraded without melting. Polymers with 50-100 mole percent of the 4-HP monomer melted to liquid crystalline phases. The polymer melting point versus the mole percent of 4-HP is graphed in Figure 5.2. As seen, the polymer melting point curve is not linear, indicating normal melting point depression behavior. The


A

B

Figure 5.1 Polyesteramides and polyesteramines synthesized in this research

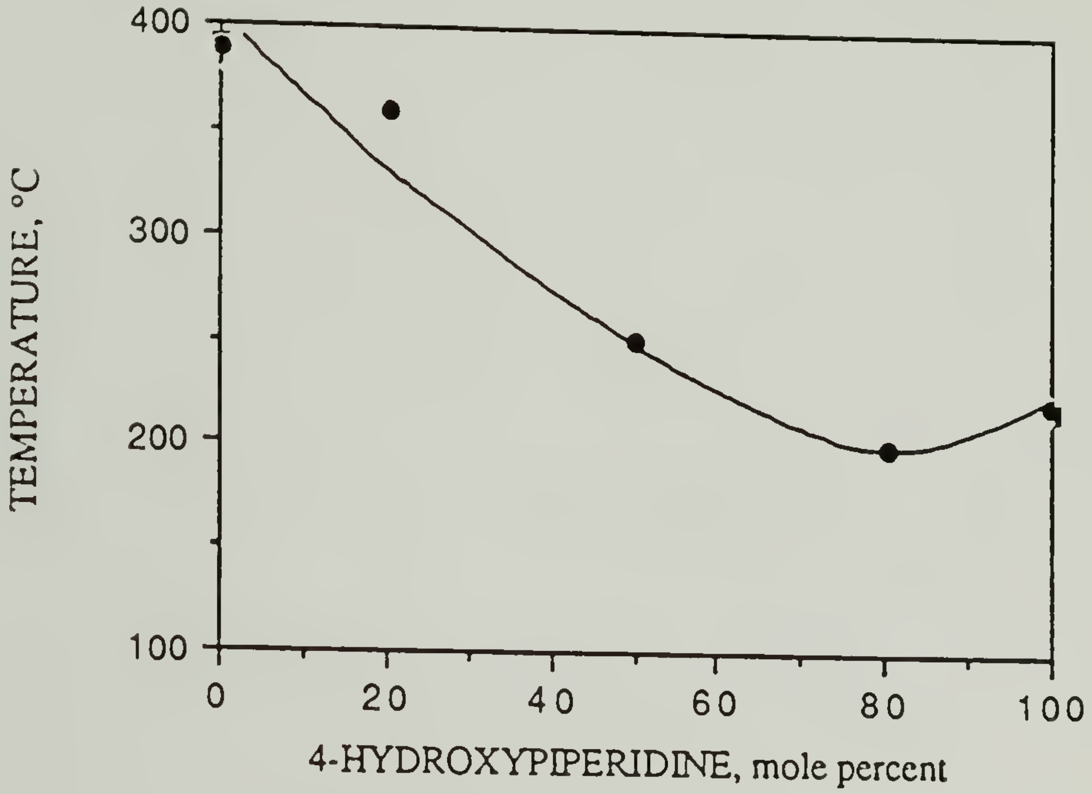


Figure 5.2 Melting point versus composition for Series 5.1 *A* polyesteramide

observation that the minimum melting composition is near the melting point of the 4-HP homopolymer is explained by the dissymmetry of the 4-HP monomer.

The 4-HP/CHDC polymer melted at 220 °C, the 80 mole percent 4-HP polymer melted at 200 °C and the 50 mole percent 4- HP polymer melted at 250 °C. The polarized optical microscopy (POM) of these three polymers showed all melting to birefringent fluids, as seen in two examples in Figure 5.3. These polymers were examined at heating rates of up to 20 °C per minute, but even at this rapid heating rate, degradation was apparent at the melting point, and proceeded so quickly that observation of an isotropization temperature was not possible.

Thermogravimetric analysis of the homopolymer showed very rapid degradation, with 1.0% weight loss at 227 °C, 20.0% weight loss at 300 °C and 61.5% weight loss at 400 °C. Although these polymers offer a system with very low thermal transition into liquid crystalline phase, the rapid degradation of such polymers (6) precludes not only a useful product, but also full characterization.

Attempted synthesis of polyesteramines based on 1,4-bis(2-hydroxyethyl) piperazine

A monomer that was an interesting possibility for the preparation of copolymers was 1,4-bis(2-hydroxyethyl)piperazine (BHEP). This diol (structure shown in Figure 5.4) would, of course, lead to the preparation of polyesters. It was hoped that these polyesters would gain rigidity from the piperazine ring. In addition, the piperazine would offer the possibility of cocrystallization with polyamides synthesized in this research. The presence of two methylene groups on

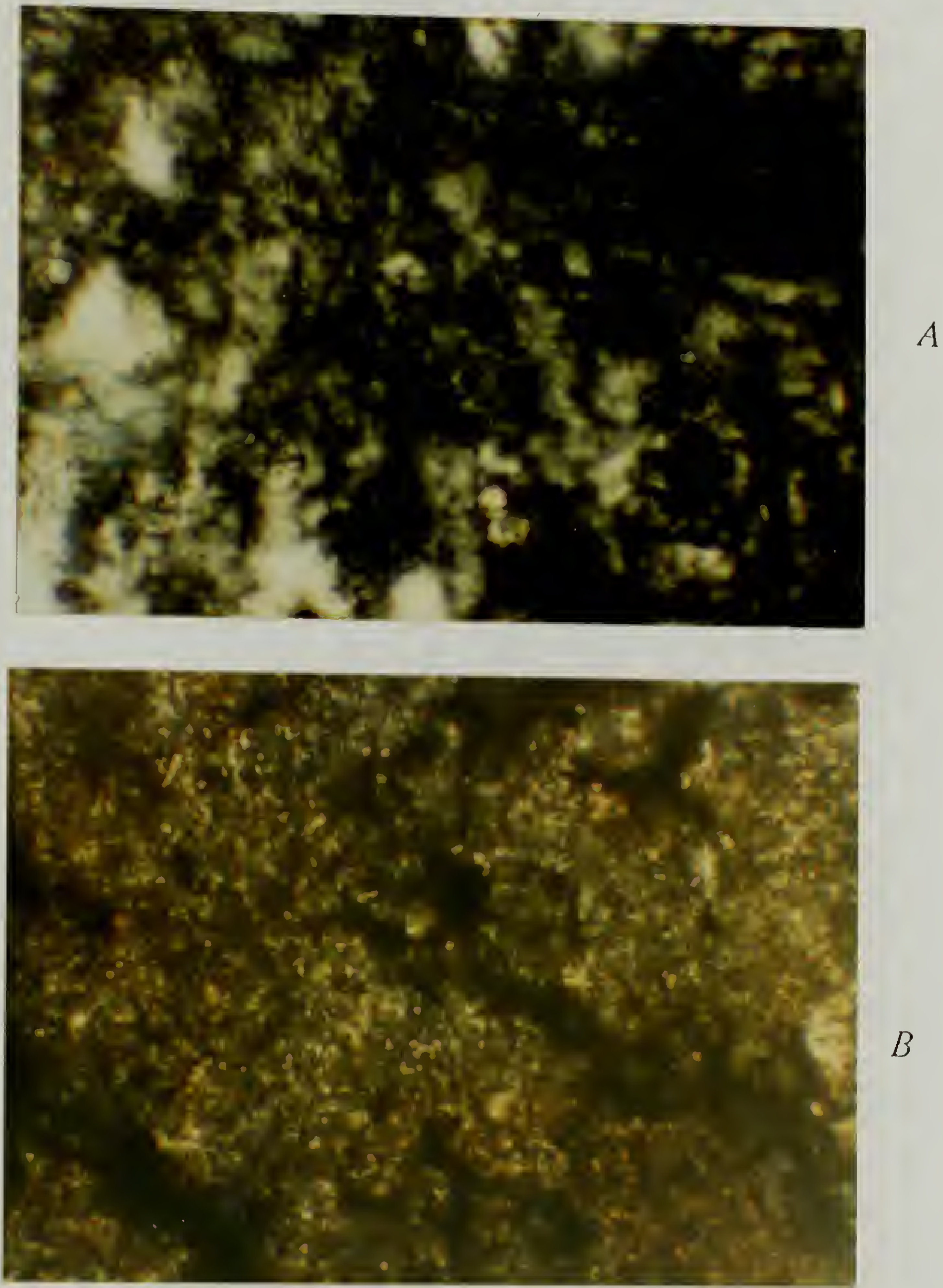


Figure 5.3 Polarized optical microscopy of Series 5.1 A polymers. *A*-100% 4-HP at 220 °C; *B*-80% 4-HP at 260 °C

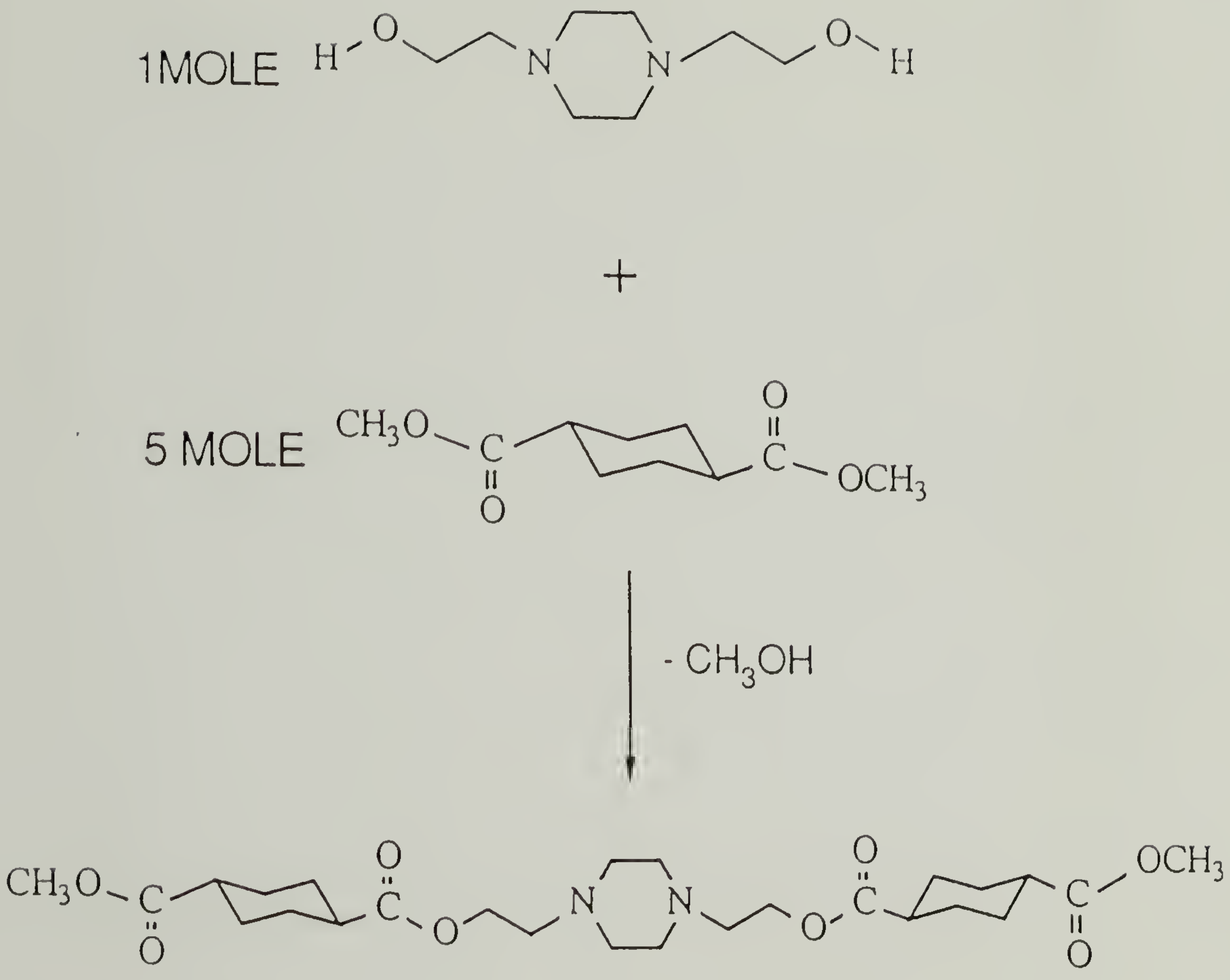


Figure 5.4 Synthesis of BHEP-di-CHDC methyl ester

each side of the piperazine ring would give a flexible polymer structure and would lead to a lower melting polymer.

Before any copolymers of BHEP, piperazine and a diacid component were made, the BHEP/CHDC homopolymer was synthesized as seen in Figure 5.1 *B*. It was not expected that a BHEP/CHDC homopolymer would be liquid crystalline (compare poly(ethylene terephthalate)). Attempts to prepare high molecular weight polymers from this monomer were unsuccessful, yielding in all cases a badly degraded product at reaction temperatures as low as 90 °C. Lower reaction temperatures yielded very low molecular weight compounds.

BHEP was endcapped with the methyl ester derivative of CHDC to obtain the "trimer" of molecular weight 510. Nuclear magnetic resonance and elemental analysis of this compound (shown in Figure 5.4) confirmed the structure. This low molecular weight compound exhibited multiple peaks on heating in differential scanning calorimetry (DSC) and POM revealed a liquid crystalline phase as shown in Figure 5.5. This trimer molecule was used in polymerization attempts with both piperazine and 1,4-cyclohexanediol, but only badly degraded product was formed. No attempts succeeded at preparing high molecular weight versions of any polymers based on BHEP. Once again the presence of the amine functionality in a polyester is seen to lower the thermal stability significantly (6).

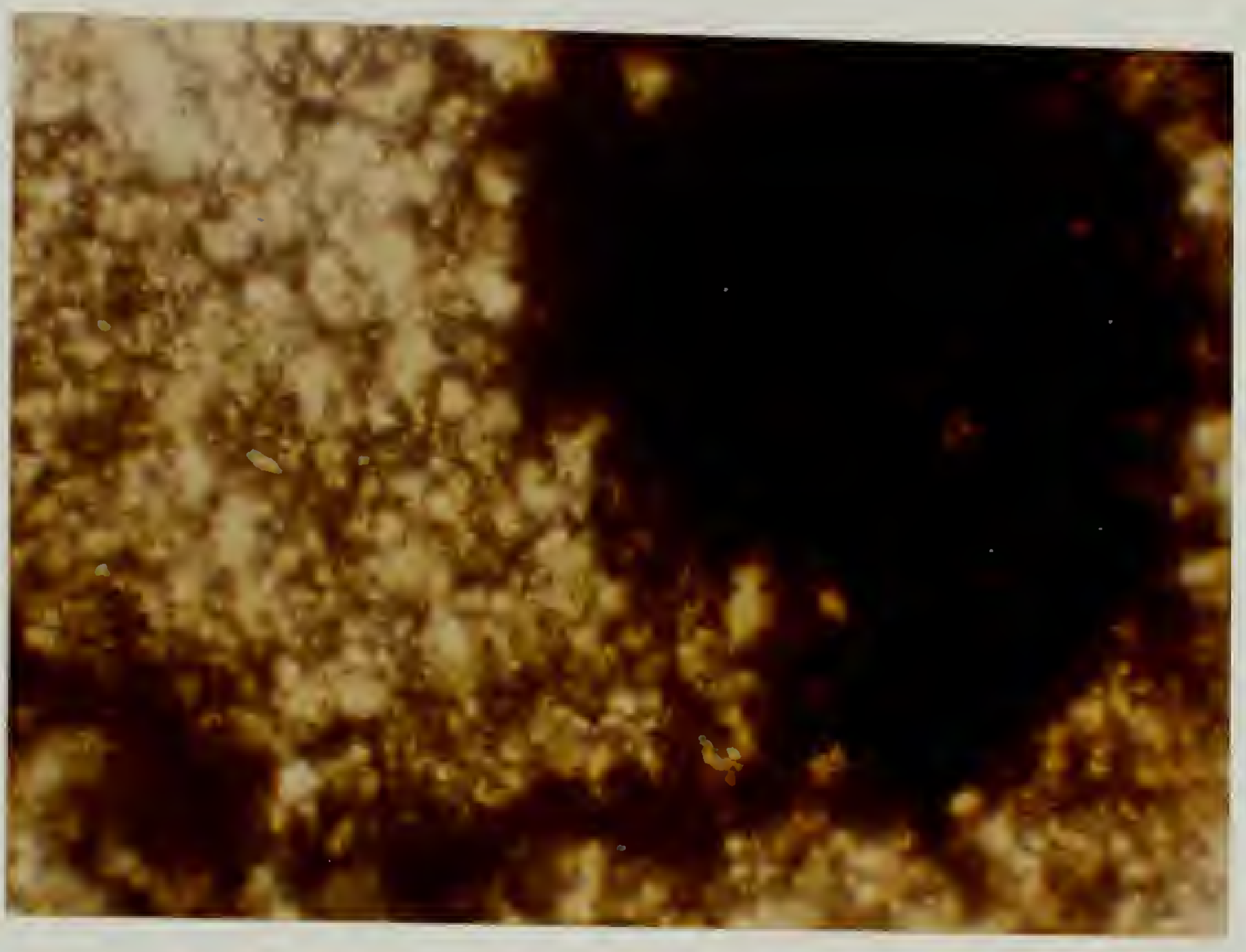


Figure 5.5 Polarized optical microscopy of BHEP-di-CHDC methyl ester at 85°C

Experimental

The following section gives experimental details for the preparation and characterization of the polymers described above, using specific examples where appropriate.

Equipment

Melting points were determined on a Fisher-Johns melting point apparatus and/or a Perkin Elmer DSC 2. Nuclear magnetic resonance (NMR) spectra were performed on Varian XL 200 or 300 MHz instruments with an internal tetramethylsilane (TMS) reference. Polarized optical microscopy (POM) was performed with a Leitz-Wetzler microscope at a magnification of 320X. Thermogravimetric analysis was performed on a Perkin Elmer TGS-2 with an S4 microprocessor. Elemental analyses were determined by the Microanalytical Lab at the University of Massachusetts.

Polymerization

Polyesteramide polymerization. A typical polymerization was carried out as follows: All glassware was washed in a KOH/isopropanol bath, rinsed with 1N HCl, 10% Na_2CO_3, several times with distilled water, and dried at 125 °C for 16 h. The glassware was cooled in a glove box under a nitrogen atmosphere. The CHDC was sublimed immediately prior to use. The 4-HP was vacuum distilled and stored under an Ar atmosphere. CHDC (0.542 g, 2.59 x 10^{-3} mol) and 4-HP (0.262 g, 2.59 x 10^{-3} mol) were weighed in a glove box into a 100-mL, 3-neck, round-bottom flask equipped with a gas inlet tube with a stopcock, a septum topped with stopcock adapter and a ground glass stopper. The assembly was removed from the glove box and evacuated to 0.5 mm Hg three times with Ar purging between evacuations. The assembly was placed back in the glove box and the ground glass stopper replaced with a Friedrich condenser equipped with a Drierite® loaded drying tube. The assembly was removed from the glove box and connected to an Ar purge. Aldrich Gold Label anhydrous *o*-dichlorobenzene was transferred by cannula into the round-bottom flask. The Ar purge was continued and the sample was heated in a 90 °C oil bath. The temperature of the oil bath was slowly raised. Complete solvation occurred at 140 °C, accompanied by rapid acid evolution, noted by litmus. Heating was continued for 4 h, and the initial rapid HCl evolution slowed dramatically after 2 h of reaction. The cooled solution was slightly cloudy. The polymer was collected by precipitation into toluene and dried under vacuum, yielding 0.39 g (63% yield).

Preparation of BHEP-di-CHDC methyl ester (See Figure 5.4). The preparation of this compound was performed as follows: BHEP was purified by recrystallization from toluene. The CHDC methyl ester, received from Eastman, was observed by NMR to be > 95% *trans* isomer. The CHDC methyl ester (30.4 g, 1.52 x 10^{-1} mol) was melted in a 250-mL, 3-neck, round-bottom flask under an Ar atmosphere. To this melt, the BHEP (5.23 g, 3.00 x 10^{-2} mol) was added. 0.5 mL of H_2SO_4 was added and heating continued for 22 h. Some sublimation was noted, and toluene was added to reflux and wash the sublimed crystal back into the melt. After the reaction was run for 22 h, 1.9 mL of distillate (in addition to the toluene) had been collected in the Barrett trap (theoretical amount of methanol = 2.4 mL). This slightly brown liquid was cooled to a slightly amber solid in a sublimator. Sublimation was continued over a 72 h period, and the sublimed material was the unreacted CHDC-methyl ester. 15.3 g were collected (83% of the theoretical unreacted CHDC-methyl ester). The remaining material was washed with ethanol, and the ethanol-soluble material discarded. The solid was dried and recrystallized from cyclohexane three times. Final yield was 0.24 g (1.6%).

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Conclusions

Processing from a liquid crystalline state is the best method of obtaining a high performance polymer. With the proper structure, near-perfect alignment of rigid polymer chains is obtained. In these systems modulus values are obtained which are very close to theoretical limits (1). In addition, the rigid, liquid crystalline polymer has non-entangled polymeric chains, resulting in very low viscosity melts or solutions. This low viscosity makes the mechanical aspects of processing easy (2). However, because of very low ΔS on melting or solvation, these polymers require strong acid solvents or very high temperatures for processing. The ideal polymer would maintain the rigidity and low viscosity of conventional liquid crystalline polymers, but would possess a lower melting point or solubility in common organic solvents. The research described in this dissertation was begun in order to investigate *trans*-1,4-cyclohexane as a possible mesogen to obtain this ideal duality.

Previous research described in the literature reported several mixed aromatic/cyclohexane liquid crystalline polymers. Several of these are shown in Figures 1.13 and 1.15. Three liquid crystalline polymers with only cyclohexane mesogens were also reported. A lyotropic polyamide was reported by Morgan (3), but this polymer was so rigid and so strongly hydrogen-bonded that it required the same strong acid solvents as aromatic liquid crystalline polyamides. Two non-aromatic thermotropic polyesters have also been described (4, 5), but these were poorly characterized; one case reported a 50% weight loss at a temperature 2 °C higher than the crystal to nematic temperature (4) and the other was a very low molecular weight polymer (5).

The most rigid, cyclohexane-based polymers synthesized in this research behave as do many linear all-aromatic, liquid crystalline homopolymers, in that melting is only observed with degradation, and solubility is limited to an amount lower than that necessary for ordering into a lyotropic solution. But by the technique of copolymerization, a number of well-characterized polymers were synthesized which possessed a liquid crystalline state. These polymers did not require a substituted mesogen or a flexible spacer but obtained the necessary melting point depression by frustrated chain packing due to copolymerization and the thermodynamic advantages of the cyclohexane mesogen.

In all cases of the polyesters, copolymers in a series displayed a linear decrease in melting point with increasing amount of the more flexible or less linear monomer. This linearity in melting point indicated isomorphic behavior. This type of behavior has been noted in non-liquid crystalline cyclohexane polymers (6), but apparently has never been reported with liquid crystalline systems. Isomorphism is equivalent to cocrystallinity which translates to superior mechanical performance. Isomorphism in these systems is not limited to one cyclohexane monomer with a different cyclohexane monomer, but is also observed in systems with a cyclohexane monomer and a flexible aliphatic spacer that can adopt the same conformation as the cyclohexane monomer. Incorporation of these flexible spacers (1,4-butanediol with *trans*-1,4-cyclohexanediol, 1,6-hexanediol with *trans*-1,4-cyclohexane-dimethanol and adipoyl chloride with *trans*-1,4-cyclohexanediacid chloride) gave a linear drop in polymer melting point with increasing amount of the flexible spacer and in some cases still showed liquid crystalline phases. Under favorable conditions the bulk processed polymer would have high crystallinity and alignment and would possess the mechanical properties of a liquid crystalline polymer that has no flexible links.

Linearity in cyclohexane compounds is limited to one of the two isomeric forms as seen in Figure 2.4. For *trans*-1,4-cyclohexanediacid chloride (CHDC) the hydrogen at the stereochemical center is acidic and can be exchanged at high temperatures, leading to a mixture of two isomeric forms. Only for polymers in an isotropic state is isomerization observed, as is evident in this research and that of Kwolek (7). Small amounts of isomerization had profound effects on the subsequent thermal behavior of these polymers as described in Chapter 3. The exact significance of these two endothermic peaks (see Figure 3.15) remains to be fully understood. The lower temperature transition is not a transition to a liquid crystalline phase as is evident by X-ray analysis. In that analysis crystallinity in the sample is observed at a temperature above the first transition. It is possible that the transition is a crystal/crystal transition or the melting of a separate crystalline structure. This second possibility could involve the crystal structures shown in Figure 3.17. An advantage of this hypothesis is that it provides a possible explanation of how a small amount (5-10%) of isomerization can cause the existence of two peaks of relatively equivalent size, in that the *A-D* form would be isomorphic with, and possibly encourage the formation of, the *B-C* form.

A number of polyamides were made that displayed nematic melts for low molecular weight samples, but did not melt below a degradation temperature for higher molecular weight samples. Several polyamide series were made with flexible spacers, and while many of these polyamides dissolved in chloroform or dichloromethane, they did not display lyotropic phases. The 4,4'-trimethylene-dipiperidine-based polymer displayed a thermotropic smectic phase in polymers with greater than 50% adipoyl chloride, but this phase was difficult to observe in high molecular weight samples.

One observation made for the monomers used for the polymer synthesis in this research is of note. Liquid crystalline phases were observed in carboxylated derivatives of the diamines shown in Figure 2.8. The rationale for the existence of these nematic phases is the schematic of Figure 2.13. Liquid crystalline phases are not observed in the purified versions of these diamines free of CO_2 or in nonlinear carboxylated diamines.

Recommendations for future work

The key problem with cyclohexane-based liquid crystalline polymers is the isomerization of the CHDC component. Several methods are available for hindering this isomerization: the use of a 1,1,4,4-tetrasubstituted CHDC, the use of CHDAA (structure shown in Figure 2.7) and the use of aromatic diacids with cyclohexanediols. This last method departs from the use of an all-cyclohexane based liquid crystalline polymer, but this combination of two different mesogens may allow for further melting point depression. The same flexible diols that were used in the all-cyclohexane polymers could be incorporated into these polymers. It is possible that isomorphic behavior would be observed in this mixed system as it was with the all-cyclohexane systems.

An interesting extension of this work would be the use of several monomers in a polymer, similar to the two diacid/two diol polymers described at the end of Chapter 3. Further addition of monomers would lead to a more random structure and a polymer with even further melting point depression.

Polyesteramides synthesized in this research degraded at temperatures below 300 °C. However, many structures showed nematic textures. An examination of the reason for the extensive degradation could lead to a method for decreasing the degradation and possibly yield useful polymers.

The presence of nonlinear cyclohexane in small amounts does not lead to a loss of liquid crystallinity. Polymer could be prepared with small amounts (~5%) of the *cis*-1,4-isomer. These polymers could be processed by conventional methods with the possibility of obtaining biaxial orientation due to kinks in the polymer backbone.

Several monomers described in Chapter 2 deserve further research. CHDI and derivatives can be used to prepare a large number of polyurethanes and polyamides, many of which have promise as liquid crystals. The dihalo-derivatives of CHDM, described as intermediates in the preparation of CHDAA, could be used in carbon-coupling reactions to prepare all-hydrocarbon, main chain liquid crystalline polymers. These polymers could be prepared with 1,6-hexanedibromide or -diiodide as comonomers, and the same melting point depression would be expected as that seen for several polymer series described in this research.

The research described in this dissertation has shown that cyclohexane-based mesogens are useful in preparing liquid crystalline polymers. In the interest of preparing a large number of polymers, none were prepared in a sufficient quantity to undertake mechanical evaluation. One obstacle to the preparation of a large quantity of any of these polymers is the isolation of the desired isomeric monomer. An additional problem is the isomerization of CHDC at high temperatures, which does not allow a melt polymerization to be done. However, the mechanical examination of the polymers would be of utmost interest, and would warrant the difficulty associated with preparing large batches. In particular, a polymer with 1,4-CHD and a diacid monomer other than CHDC (which could not isomerize) would be interesting. As noted above, such a polymer could be prepared with 1,4-butanediol as a comonomer, in hopes of observing a linear melting point depression.

An additional advantage for preparing liquid crystalline polyesters from cyclohexanediols is the lower toxicity of these cyclohexanediols as compared to hydroquinone and other phenolic alcohols. The cyclohexanediols are also less corrosive, and this fact coupled with the possibility of avoiding the preparation of the acetate derivative prior to polymerization (and the subsequent evolution of acetic acid during polymerization) could lead to less expensive equipment being needed for industrial preparation of these polymers.

As has been shown for several polymers in this research, liquid crystalline phases can exist for polymers that have no aromaticity. One interesting extension of this work would be the preparation of the exact cyclohexane analogs of the commercial liquid crystalline polymers, either by polymerization of the monomer analogs or by hydrogenation of the polymers. By estimation from all known polymers, the melting points of the cyclohexane polymers should be lower than aromatic ones. However, a comparison of mechanical properties should yield little or no difference and illustrate clearly that the existence of high mechanical performance is not synonymous with aromaticity.

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