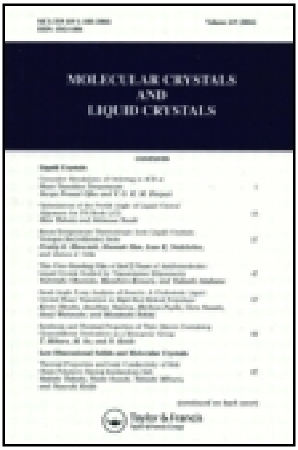

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THERMOTROPIC COPOLYESTERS CONTAINING THE BICYCLO[2.2.2]OCTANE RING SYSTEM

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Abstract A number of thermotropic copolyesters which contain the bicyclo[2.2.2]octane and bicyclo[2.2.2]-oct-2-ene ring systems have been synthesized. In order to decrease the melting temperatures to below the decomposition points, the following approaches were used: (1) sebacoyl flexible spacers; (2) ethylene glycol and 1,4-butanediol to form flexible spacer units; (3) trans-1,4-cyclohexylenedimethylene, 1,4-bicyclo[2.2.2]octylenedimethylene and 1,4-phenylenedimethylene semiflexible spacers; and (4) the lower symmetry bicyclo[2.2.2]oct-2-ene ring system as a replacement for the bicyclo[2.2.2]-octane ring system. The polycondensation of terephthaloyl chloride and bicyclo[2.2.2]oct-2-ene-1,4-diol resulted in the formation of a thermotropic homopolyester.

INTRODUCTION

A number of low molar mass liquid crystals have been synthesized which contain the bicyclo[2.2.2]octane and bicyclo[2.2.2]oct-2-ene ring systems.[1-7]

Although Watson[8] reported the syntheses and characterizations of homopolyesters and random copolyesters based on bicyclo[2.2.2]octane-1,4-dicarboxylic acid, no mention was made of liquid crystal properties for the polymers. Elmore[9] reported a polymer melt temperature above 385°C for poly(1,4-bicyclo-[2.2.2]octylene terephthalate).

Tamir and Smith[10] studied the thermal behavior of polymers containing bicyclo[2.2.2]octane and bicyclo-[3.2.2]nonane rings. In order to study the effect of structure on melting temperature, they synthesized polyesters from 1,4-bis(carboethoxy)bicyclo[2.2.2]octane, 1,4-bis(hydroxymethyl)bicyclo[2.2.2]octane, and 1,5-disubstituted bicyclo[3.2.2]nonane analogs. They reported that the lower symmetry of the bicyclo[3.2.2]nonane ring results in the production of lower melting polymers than obtained for the other ring systems. 1,4-Phenylene, trans-1,4-cyclohexylene, and 1,4-bicyclo[2.2.2]octylene rings were approximately equivalent in their effect on the melting temperature as long as only one bicyclo[2.2.2]-octane ring was present in each repeat unit. Two bicyclo[2.2.2]octane rings per repeat unit produced the highest melting polymers.

EXPERIMENTAL

SYNTHESIS

Bicyclo[2.2.2]octane-1,4-diol was synthesized according to the procedure described by Kopecky et.al.[11] with modifications. Bicyclo[2.2.2]oct-2-ene-1,4-diol was synthesized according to the procedure described by Harruna et.al.[12] Bicyclo[2.2.2]octane-1,4-dicarboxylic acid was prepared by the method of Wood.[13] 1,4-Bis-(hydroxymethyl)bicyclo[2.2.2]octane was prepared according to the method of Sukenik.[14] The diacid chlorides were prepared by a procedure described in the literature.[15] The other monomers were commercial products.

In a typical polymerization,[16,17] an equal number of moles of diacid chloride and diol in o-dichlorobenzene solution were heated under reflux in a nitrogen atmosphere for 8h. After cooling, the polymer was precipitated by hexane or acetone, collected by filtration, and dried in a vacuum oven at 100-120°C for 24h.

PHYSIOCHEMICAL CHARACTERIZATIONS

Inherent viscosities were determined at 30°C with a Cannon-Fenske viscometer at a concentration of 0.5 g/100mL in m-cresol or o-chlorophenol. Melting temperatures and glass transition temperatures were determined on either the DuPont 990 thermal analyzer and 910 differential scanning calorimeter or the Perkin Elmer DSC-4 differential scanning calorimeter under nitrogen. Polarizing optical microscopy was performed on a Leitz Laborlux 12 Pol Microscope with a Leitz 350 heating stage.

RESULTS AND DISCUSSION

HOMOPOLYESTERS

Initially our objectives were to demonstrate whether the 1,4-bicyclo[2.2.2]octylene ring was compatible with trans-1,4-cyclohexylene and 1,4-phenylene rings in thermotropic homopolyester systems. The structures of the homopolyesters which we synthesized are shown in Figure 1.

Initally we synthesized homopolyesters I-VI and found that none of these homopolyesters melted at a temperature below the decomposition temperature. The use of asymmetrically substituted phenyl rings in II, III, IV, and VI and the more flexible trans-1,4-cyclohexylene unit

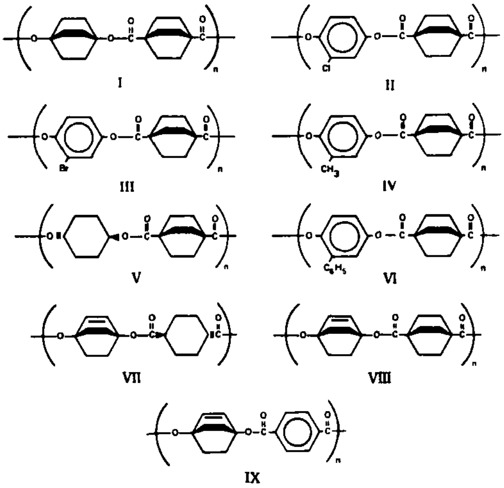

FIGURE 1. Homopolyesters

in V did not provide the necessary disorder to demonstrate thermotropic behavior.

Compared to the D_{3h} symmetry of the bicyclo[2.2.2]-octane ring system, the D_2 symmetry of bicyclo[2.2.2]oct-2-ene represents a reduction in symmetry. The use of the lower symmetry bicyclo[2.2.2]oct-2-ene ring in IX provided the necessary disorder to allow the demonstration of a transition to a birefringent fluid state at 258°C. The birefringence persisted up to the decomposition onset temperature of 298°C. The thermal properties of the thermotropic polymers are described in Table 1. The polarizing optical micrograph of IX at 296°C, shown in Figure 2, is characteristic of a nematic texture. VII and VIII showed no melting behavior below the decompostion temperatures.

TABLE 1. Physical Data for the Polyesters.

Polymer	Inherent Viscosity (dl/g) @30°C	DSC Transitions °C	Hot-Stage Polarizing Optical Microscopy Transitions, °C
IX	insoluble	190,234,265	227[a],258[b],298[c]
XI	0.90[e]	140,240,340	150[a],199[b],317[c]
XII	0.16[e]	237	175[a],242[b]
XIII	0.60[e]	127,255	166[a],208[b],345[c]
XV	0.28[e]	288,317[c]	229[a],254[b]
XVI	0.31[f]	157,210,255, 278,320,348[c]	280[a],317[b]
XVII	0.64[f]	195,250	280[a],320[b]
XXI	0.69[f]	173,272,331	178[a],219[b],272[c]
XXII	0.72[f]	270,297	246[a],293[b],321[c]
XXIV	0.78[f]	177,323[c]	147[a],263[b],326[c]
XXV	0.59[f]	151,274	195[a],240[b],316[c]
XXVI	0.57[f]	186	225[a],257[b],321[c]
XXVII	0.62[f]	150,220	152[a],221[b],295[c]
XXVIII	0.63[f]	193,270	203[a],290[b],300[d], 318[c]

[a] represents a softening temperature

[b] represents the transition to a birefringent fluid state

[c] represents a decomposition temperature

[d] is a clearing temperature

[e] in o-chlorophenol

[f] in m-cresol

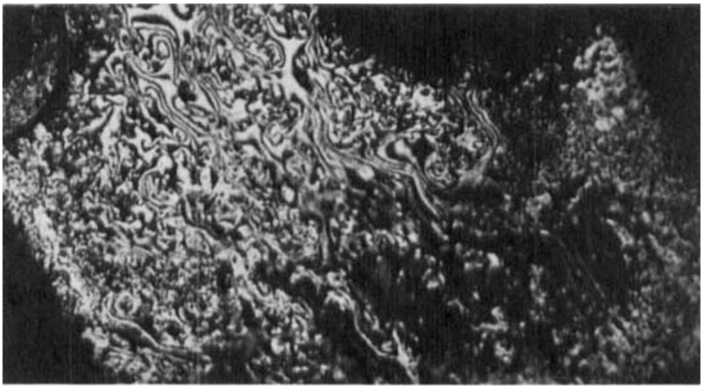

FIGURE 2. Photomicrograph of IX

COPOLYESTERS

Bicyclo[2.2.2]octane Copolymers

Since homopolyesters I, II, III, IV, V and VI did not melt below the corresponding decomposition temperatures, random copolyesters X-XV[16,17] (Figure 3) containing flexible spacer units were prepared by adding sebacoyl chloride to the polymerization recipes for homopolyesters I-VI. Copolyesters XVI-XVIII (Figure 3) were prepared by adding ethylene glycol, 1,4-butanediol, and 1,8-octanediol to the polymerization recipe for VI.

Copolyesters XI, XII, XIII, XV, XVI, and XVII formed birefringent fluid phases in the melt. The polarizing optical micrographs of XIII and XV (Figures 4 and 5) were particularly interesting. Observation of molten XIII between crossed polarizers at magnification X32 and above the melting point of 208°C shows the Schlieren texture characteristic of the nematic state and brillant blue, green, and red interference colors. Observation of molten XV between crossed polarizers at magnification X32 and 265°C shows a texture characteristic of the smectic B structure.

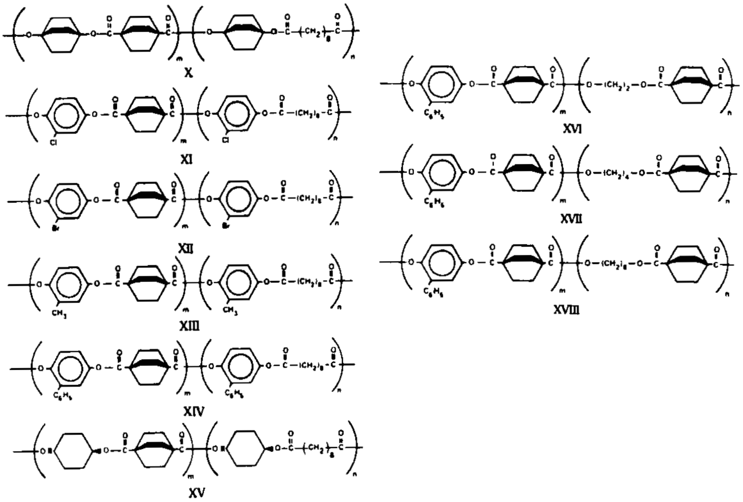

FIGURE 3. Copolyesters with Flexible Spacers

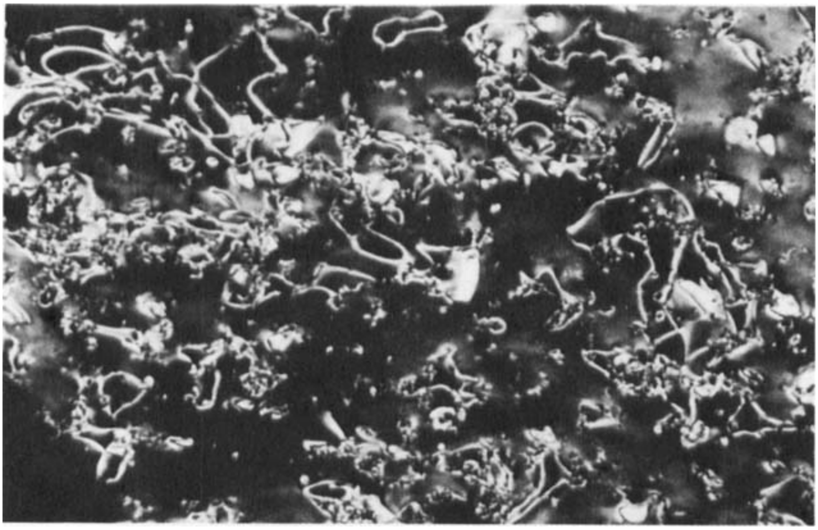

FIGURE 4. Photomicrograph of XIII

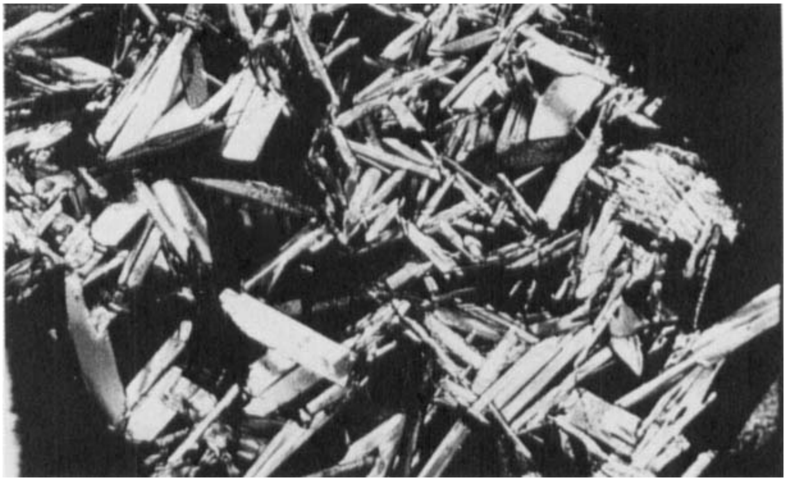

FIGURE 5. Photomicrograph of XV

Apparently the rigidity of the bicyclo[2.2.2] octane rings dominates the structure of X such that even the introduction of a flexible spacer does not result in the formation of a meltable composition. The results for copolyester XIV were inconclusive. Apparently the eight carbon spacer in XVIII prevented the formation of the nematic state because of the increased flexibility of the carbon chain.

Copolyesters XIX-XXI (Figure 6) were prepared by the polycondensation of trans-1,4-cyclohexanedicarbonyl chloride and a 3:2 molar mixture of bicyclo[2.2.2]octane-1,4-diol and trans-1,4-cyclohexanedimethanol, 1,4-bis(hydroxymethyl)bicyclo[2.2.2]octane or 1,4-benzenedimethanol. Copolyesters XXII-XXIV, (Figure 6) were prepared by the polycondensation of bicyclo[2.2.2]octane-1,4-dicarbonyl chloride with a 3:2 molar mixture of bicyclo[2.2.2]octane-1,4-diol and trans-1,4-cyclohexanedimethanol, 1,4-bis(hydroxymethyl)bicyclo[2.2.2]octane or 1,4-benzenedimethanol. Copolyesters XXI, XXII and XXIV formed birefringent fluid states in the melt.

Bicyclo[2.2.2]oct-2-ene Copolymers

Copolyesters XXV-XXVII (Figure 6) were prepared by the polycondensation of trans-1,4-cyclohexanedicarbonyl chloride with a 3:2 molar mixture of bicyclo[2.2.2]oct-2-ene-1,4-diol and trans-1,4-cyclohexanedimethanol, 1,4-bis(hydroxymethyl)bicyclo[2.2.2]octane, or 1,4-benzenedimethanol. Copolyesters XXVIII-XXX (Figure 6) were prepared by the polycondensation of bicyclo[2.2.2]octane-1,4-dicarbonyl chloride with a 3:2 molar mixture of bicyclo[2.2.2]oct-2-ene-1,4-diol and trans-1,4-cyclohexanedimethanol, 1,4-bis(hydroxymethyl)bicyclo[2.2.2]octane or 1,4-benzenedimethanol.

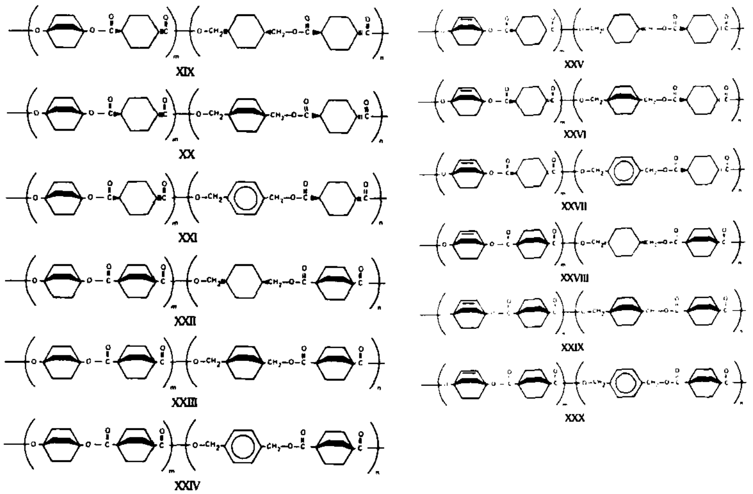

FIGURE 6. Copolyesters with Semiflexible Spacers

Copolyesters XXV, XXVI, XXVII and XXVIII formed birefringent fluid states in the melt. The large number of rigid rings per repeat units for copolyesters XXIX and XXX would appear to offer an explanation for the high melting temperatures for these systems(they undergo decomposition without melting). However the behavior of copolyesters XXIX and XXX is at variance with that of thermotropic copolyester XXIV with three bicyclo[2.2.2]-octane rings per two repeat units. Ultimately a study of the relative amounts of the copolyester units in these systems must be undertaken in order to explain this apparent discrepancy.

Acknowledgement

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