Liquid-Crystalline Polymers with a Bicyclo[1.1.1]pentane Cage in the Backbone

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ABSTRACT: Two series of liquid-crystalline polymers were synthesized, both with mesogenic triads connected by aliphatic spacers varying in length from 4 to 10 carbons. The triads consisted of two residues of *p*-hydroxybenzoic acid attached to the central diacid, which was bicyclo[1.1.1]pentane-1,3-dicarboxylic acid in one series and terephthalic acid in the other. Properties of these polymers were studied by differential scanning calorimetry, thermogravimetric analysis, and polarizing microscopy. The replacement of the aromatic ring of the terephthalic acid by a bicyclopentane cage led to a very substantial depression of the liquid crystalline to isotropic transition and to a less substantive depression of the melting temperature. Thus, the temperature range of the mesogenic state was much narrower for the bicyclopentane polymers than for the terephthalic ones. Apparently, the bulky bicyclopentane cage may fit well into a crystalline lattice but has lesser tendency for forming parallel bands of molecules in the mesogenic state. This is probably a result of the free rotation around the backbone bonds attached to the bridgehead carbons of the bicyclopentane cage as compared to the rotation of the terephthalic residue that is restricted by extensive conjugation within the mesogenic groups.

Introduction

Development of high-performance thermoplastic materials with a long sequence of rigid and/or aromatic structures in the backbone has been recently pursued in many industrial and academic laboratories.[1-7] Polymers with rigid aromatic structure that show a high degree of molecular order in solution (lyotropic) or in the melt (thermotropic) and exhibit substantial anisotropy, while maintaining the mobility of fluids[8,9] are termed liquid-crystalline polymers, LCPs. Both these LCPs (i.e., lyotropic and thermotropic) form engineering materials of exceptional strength due to their anisotropic nature. Active research in the field of LCPs has been under way in many laboratories.[8,10]

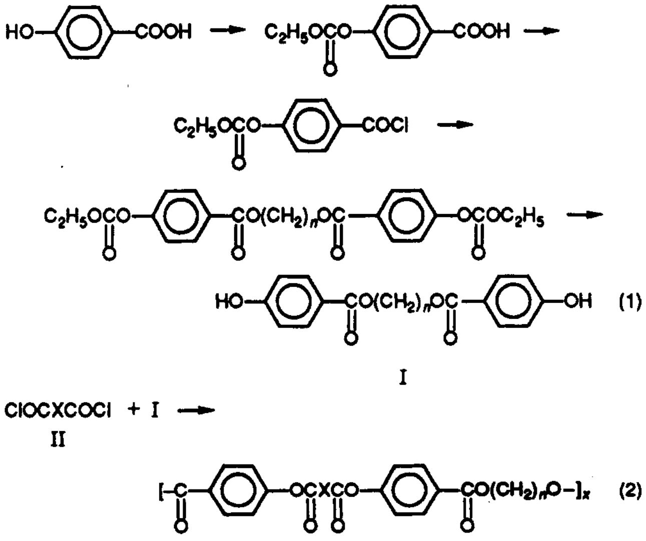
Fully aromatic main-chain LCPs are intractable due to their high melting points and decomposition before melting. Hence, less perfect structures having lower melting points and easier processability were developed in later studies. Lateral substitution on the aromatic mesogenic part,[1,3,8,11-20] insertion of kinks into rigid chains,[8,10] incorporation of aliphatic flexible spacers,[8,15,17-20] etc., were suggested as effective modifications for achieving this goal. These modifications were used either individually or in combination.

The overall mesogenic behavior reflects primarily the sterical properties of the polymer chains. Consequently, attention has been devoted to the study of these properties, mainly by varying the length and/or constitution of the spacer segments and, in lesser extent, by varying the constitution of rigid segments.[15,21] However, very little attention has been paid to interactive properties of the rigid segments. It is the aim of this paper to study the changes in the mesogenic behavior when a spatially similar but chemically quite different unit is introduced into the rigid segments instead of the *p*-phenylene moiety.

We have synthesized two series of polymers in which the rigid mesogenic triad consisted of an inflexible diacid esterified on both sides by *p*-hydroxybenzoic acid. These rigid triad segments were connected by aliphatic methylene spacers with a carbon chain length varying from 4 to 10. In the first series, the diacid was terephthalic acid (these polymers were already described by Ober et al.[17]); in the second series, it was replaced by bicyclo[1.1.1]pentane-1,3-dicarboxylic acid, which recently became available in research quantities.[22]

Experimental Part and Results

Polymer Synthesis. The polymers were prepared using the following reaction sequence.[17]



Compound II was either 1,3-bis(chlorocarbonyl)bicyclo[1.1.1]pentane (IIa) or terephthaloyl dichloride (IIb). In the first reaction of this sequence an excess of 4-(ethyloxy)benzoyl chloride was used and pyridine served as the HCl scavenger.[17]

Liquid-crystalline polyesters were prepared (reaction 2) from equimolar amounts of compound I and the respective acid chloride, IIa, or IIb in 1,1,2,2-tetrachloroethane and pyridine,

Table I
Intrinsic Viscosity of OPOC*n* Polymers in Chloroform at 25 °C

polymer	[η], mL/g	polymer	[η], mL/g
OPOC4	17.0	OPOC8	31.4
OPOC5	12.7	OPOC9	20.8
OPOC6	24.5	OPOC10	30.3
OPOC7	23.0	OPOC10[a]	24.2

[a] Melt polymerized.

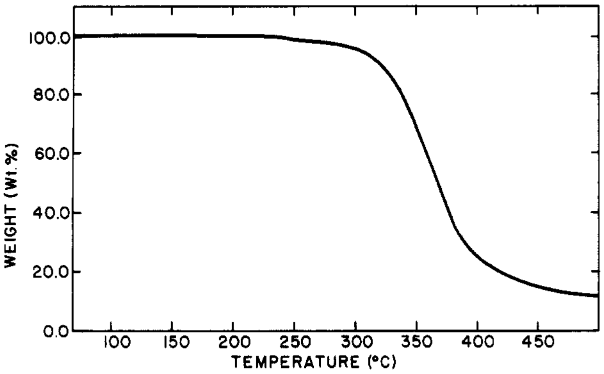


Figure 1. TGA scan of OPOC10.

pyridine being the catalyst, and the HCl scavenger. The two phenolic end groups were utilized for formation of rigid mesogenic segments. The reaction was allowed to proceed for 48 h at room temperature under dry nitrogen. The product obtained was washed with dilute HCl and water to eliminate pyridine and its hydrochloride, precipitated into excess methanol, filtered, and dried.

We have also attempted the melt polycondensation of equimolar quantities of the diacid chloride (IIa) and the bisphenol (I) leading to the polymer with a 1,10-decanediol spacer. The product was precipitated twice from chloroform into an excess of hexane and dried. The product had essentially the same properties as the same polymer obtained by the solution method, but its intrinsic viscosity was slightly lower, most probably, due to the stoichiometry that was disturbed by sublimation of the dichloride during the melting period.

In the following we will describe the polymers as OPOC*n* and OTOC*n* where O represents the oxybenzoate unit, T the terephthaloyl unit, P the bicyclopentane unit, C the hydrocarbon chain, and *n* the number of carbon atoms in this chain.

Polymer Characterization. Intrinsic viscosities [η] of the bicyclopentane series of polymers were measured in chloroform using the Ubbelohde viscometer with the photoelectric registration of the flow times. The intrinsic viscosities are presented in Table I. The polymers of the terephthaloyl series are not soluble in chloroform.

Thermal stability and phase behavior of the polymers was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) Using a Perkin-Elmer thermal analysis system (DSC7) equipped with a thermal analysis data station. Indium was used as a reference standard.

According to TGA results, the OTOC*n* polymers are thermally stable up to 300 °C. At this temperature starts the weight loss that reaches 10% at about 350 °C and 50% at 380–400 °C. The OPOC*n* polymers suffer a minor mass loss (3–7%) starting at 250 °C. The total decomposition starts at about 300 °C and reaches 10% at about 330 °C and 50% at about 380 °C. A typical TGA experiment is depicted in Figure 1. We ascribe the mass loss at 250 °C to decomposition of the bicyclopentane moiety. For this reason, we have limited our subsequent DSC experiments on OPOC*n* polymers to temperatures below 225 °C. The experiments on OTOC*n* polymers were done at temperatures below 300 °C, and only occasionally up to 325 °C.

DSC behavior is dramatically different between the OTOC*n* and OPOC*n* polymers as well as between the polymers with odd and even *n*. In the OTOC*n* polymers, two well-separated transition regions are observed. In the heating part of the DSC curve, a major endothermic transition (melting) is found; the corresponding enthalpies ΔH_m are 20 J/g and more. For polymers with even *n*, the melting temperature T_m decreases with an increase in *n*. For polymers with odd *n*, T_m is essentially independent of *n*; it is distinctly lower than that for polymers with even *n*.

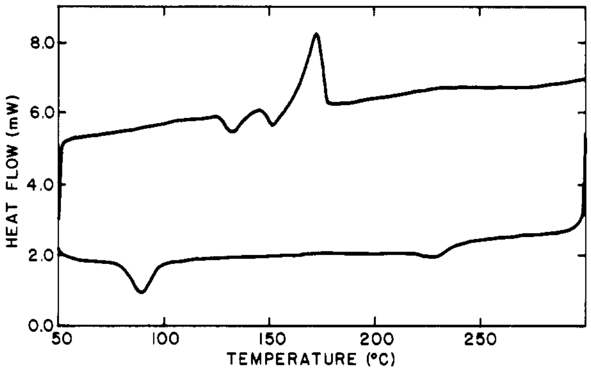


Figure 2. Heating and cooling DSC scan of OTOC9.

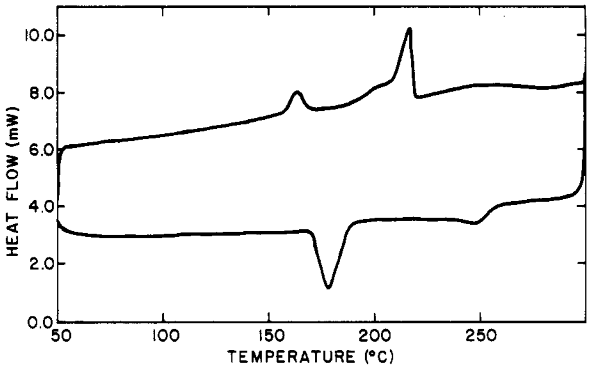


Figure 3. Heating and cooling DSC scan of OTOC10.

Table II
DSC Transition Temperatures and Enthalpies of OTOC*n* Polymers

polymer	T_m, °C	T_c, °C	T_t, °C	T_k, °C	ΔH_m, J/g	ΔH_c, J/g	ΔH_t, J/g	ΔH_k, J/g
OTOC4	290	243			29.7	13.5		
OTOC5	168	77		287		4.8	5.5	5.5
OTOC6	246	187	320	316	27.5	15.4		4.9
OTOC7	166	65	231	230	20.8	5.9	9.9	2.1
OTOC8	229	202	286	275	23.7	21.8	7.8	6.4
OTOC9	173	91	235	229	31.9	11.6	8.2	5.3
OTOC10	216	179	249	249	20.0	20.0	8.3	3.3

The liquid crystal to isotropic transition occurs at temperatures well above 200 °C and is very broad. For polymer OTOC$_4$, the transition was not reached within our experimental range of temperatures. Again, the transition temperature, T_t, decreases with increasing *n* for even *n*; it is lower and almost independent of *n* for odd *n*. However, the differences are not as large as they were for T_m. The transition enthalpies, ΔH_t, are difficult to measure for polymers with smaller *n* due to a rather high T_t. However, they seem to be lower than ΔH_t of polymers with larger *n*, for which ΔH_t levels off at about 8 J/g.

The cooling scans for OTOC*n* polymers were much simpler than the heating scans. Typically, they just displayed two simple exothermic transitions, usually quite sharp. The isotropic liquid to liquid crystal transitions (T_k) were observed at temperatures only slightly lower than T_t; the enthalpies ΔH_k were of the order of 2–5 J/g. The liquid crystal to crystal transitions (T_c) occurred at temperatures that were lower than T_m by 30–60 °C for the even carbon polymers and by 80–100 °C for the odd ones. The enthalpies ΔH_c were essentially equal to the melting enthalpies for former polymers but much smaller for the latter ones. In Figures 2 and 3, typical DSC diagrams are presented for an odd and an even OTOC*n* polymer. The transition temperatures and enthalpies are listed in Table II.

The DSC behavior of OPOC*n* polymers is quite different. In the heating curves the two temperatures are so close to each

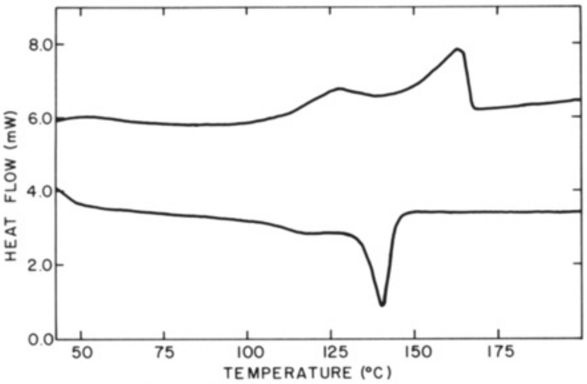


Figure 4. Heating and cooling DSC scan of OPOC10.

Table III
DSC Transition Temperatures and Enthalpies of OPOC*n* Polymers

polymer	T_m, °C	T_c, °C	T_t, °C	T_k, °C	ΔH_m, J/g	ΔH_c, J/g	ΔH_t, J/g
OPOC4	179	207			6.0		
OPOC5		83	141	117	16.4	2.9	1.1
OPOC6	192	170	209	192	49.6	27.0[a]	
OPOC7			144	124	28.2	3.9[a]	
OPOC8	189	162	200	189	37.0	19.2[a]	
OPOC9		74	143	118	31.0	14.7	4.7
OPOC10	127	117	163	140	44.3	35.6[a]	

[a] Combined values of $\Delta H_c + \Delta H_k$.

other that we were able to observe two separate maxima only for polymers with $n = 4$, 6, and 8. Even then, we were not able to calculate the transition enthalpies separately, only their sum, ΔH_s. For the remaining polymers, only a single transition was observed, with the DSC curve rising rather slowly but returning to the base line quite abruptly. We report the maximum value of this curve as T_t, but this assignment is not quite unambiguous.

On cooling, the polymers with $n = 6$, 8, 9, and 10 produce curves with two distinct exotherms; rather indistinct exotherms are displayed by OPOC5; OPOC4 does not exhibit any transition on cooling. Polymer OPOC7 is peculiar: a single exotherm possibly with two maxima, separated by about 2 °C. The temperature T_k is about 20 °C lower than T_t observed on heating; ΔH_k is about 4 J/g for most OPOC*n* series but is surprisingly high for OPOC10. The enthalpy ΔH_c is relatively low; this mirrors the behavior of OPOC*n* polymers on cooling. An example of the DSC diagram for the OPOC10 polymer is presented in Figure 4; the transition temperatures and enthalpies are listed in Table III.

The liquid-crystalline nature of the polymers was studied by using a polarizing microscope equipped with a Mettler FP80 hot stage; the magnification was 200×. All our polymers displayed thermotropic liquid crystallinity. All OTOC*n* polymers were enantiotropic: the liquid-crystalline phase can be observed during both the heating and cooling of the material. All OTOC*n* polymers (with the exception of OTOC9) showed the formation of nematic mesophase, i.e., threaded schlieren texture that is typical of optical phenomena for the nematic mesophase. OTOC9, on the other hand, showed a focal conic, broken fan type of texture typical of one of the smectic mesophases; OTOC9 might form a smectic mesophase due to the more flexible nature of the spacer of the odd carbon chain. Typical pictures of the OTOC*n* polymers in their liquid-crystalline phase are shown in Figures 5 and 6.

The OPOC*n* polymers were monotropic (with the exception of OPOC8, which appeared as enantiotropic): on heating, the two transitions overlapped and it was not possible to observe pure mesophase formation; it could be observed only upon cooling from the isotropic liquid. All the OPOC*n* polymers exhibited nematic mesophase texture. Pictures of the two OPOC*n* polymers in the liquid-crystalline phase are presented in Figures 7 and 8.

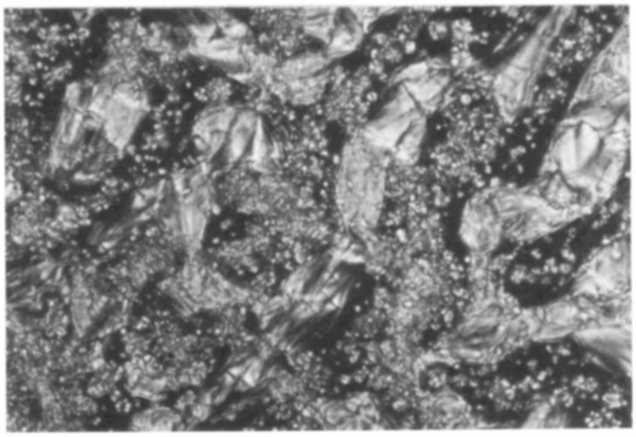


Figure 5. Polarizing micrograph of OTOC9.

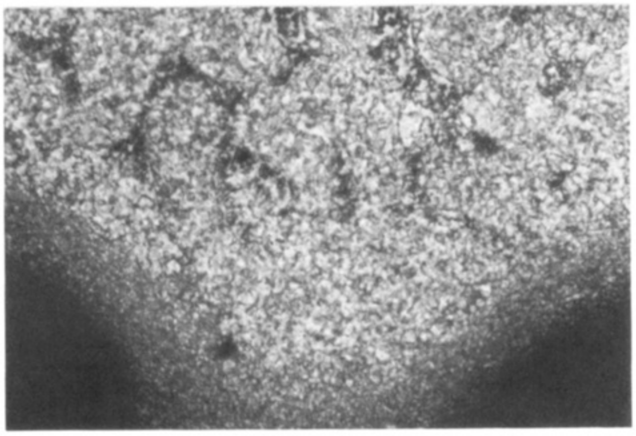


Figure 6. Polarizing micrograph of OTOC10.

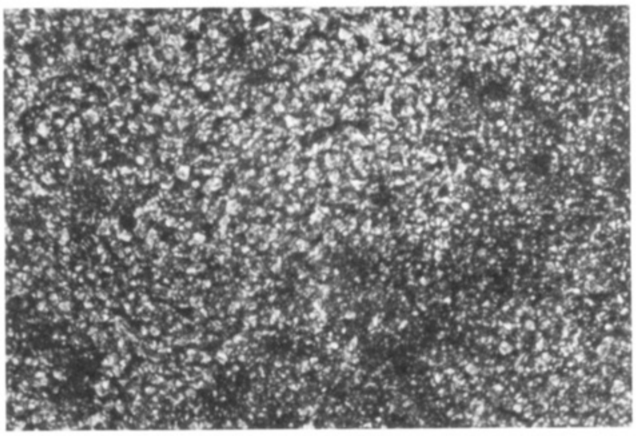


Figure 7. Polarizing micrograph of OPOC9.

In Tables IV and V we have collected the values of T_i, the temperature at which the last traces of the mesophase disappear upon heating, and of T_c, the temperature at which the mesophase appears first on cooling. The corresponding values obtained from the DSC measurements are also included in the tables. These values correspond to the edges of the transition peaks and are therefore higher than the T_i and T_k values, respectively. The latter values were measured in the center of the transition peak.

Discussion

Extensive literature exists that describes the relationship of the liquid-crystalline behavior to the structure of the mesogenic unit and to the length and type of the spacer unit. Several aspects of this relation recognized in general are as follows: (1) The coplanarity and the colinearity of the mesogenic part influence the effective molecular alignment and in turn the molecular packing.[15] These factors, therefore, affect the mesophase stability. (2) The conformation of the mesogenic repeat unit is dependent to some extent on the terminal atoms such as ether oxygen,

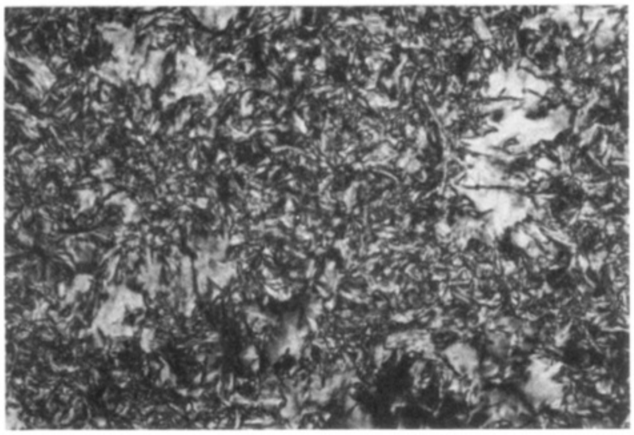


Figure 8. Polarizing micrograph of OPOC10.

Table IV
T_i and T_c Temperatures for OTOC*n* Polymers Determined by Polarizing Microscopy and DSC

polymer	T_i[a]	T_i[b]	T_c[a]	T_c[b]
OTOC4	393[c]			
OTOC5	315	264	298	308
OTOC6	338		330	322
OTOC7	293	279	249	249
OTOC8	315	312	293	286
OTOC9	270	269	236	243
OTOC10	281	279	260	260

[a] Polarizing microscopy. [b] DSC. [c] With decomposition.

Table V
T_i and T_c Temperatures for OPOC*n* Polymers Determined by Polarizing Microscopy and DSC

polymer	T_i[a]	T_i[b]	T_c[a]	T_c[b]
OPOC4	255	255	220	
OPOC5	176	157	112	125
OPOC6	210	216	187	199
OPOC7	150	156	125	131
OPOC8	225	205	194	199
OPOC9	147	151	120	126
OPOC10	183	168	167	147

[a] Polarizing microscopy. [b] DSC.

carbonyl carbon, etc., of the phenyl unit.[15] It is assumed that the terminal carbonyl groups are in resonance interaction with neighboring phenyl rings, adding to the length of the mesogen. (3) Longer mesogenic units lead to polymers with higher mesophase to isotropic transitions.[15] (4) Substituents on the basic mesogenic units interfere with molecular packing and lower the transition temperature.[15,19] (5) Polymers that have an even number of atoms in the backbone of the spacer exhibit substantially higher transition temperature than their homologues with an odd number of atoms.[10,15,17–19] This effect seems to suggest that the spacer part of the polymer backbone is to a large extent in its most extended conformation: in this conformation the even spacers retain their colinearity with mesogens, while the odd spacers do not.

In the present study we are comparing two families of polymers that both have a triad mesogen without substituents of essentially the same length and same linearity. The spacer segments are the same in both families. The major difference is the replacement of the planar *p*-phenylene ring of the terephthaloyl residue by the rigid but bulky three-dimensional cage of the bicyclopentane. It is possibly even more important that the aromatic *p*-phenylene group contributes significantly to the coplanarity of the parts of the mesogen, while the bicyclopentane cage allows for free rotation of its bridgehead substituents.

It is therefore not surprising that the temperatures of the thermal transitions of the OPOC*n* polymers are much lower than those of the corresponding OTOC*n* polymers. Somewhat less expected is the fact that the mesophase to isotropic transition temperature is lowered much more than the melting transition. Consequently, the temperature range for the stable mesophase becomes quite narrow; through optical observation, the transition even may be classified as a monotropic one. In this context it is significant that the total transition enthalpy (sum of ΔH_m and ΔH_t) is higher for OPOC*n* polymers than for the OTOC*n* ones. Seemingly, the bicyclopentane cage does not prevent an efficient packing in the crystalline lattice, it may even contribute to the stability of the lattice by some sterical interlocking. However, after melting, the coplanarity of the mesogen is lost and the mesogenic tendency is reduced.

Clausen et al. recently prepared and characterized[21] a family of main-chain LC polyesters that were analogues of the polymers reported in this paper; they contained a *trans*-1,4-cyclohexane ring in the mesogenic triad unit instead of a bicyclopentane cage. The replacement of the aromatic ring by the *trans*-1,4-*trans*-cyclohexane ring depressed the melting transitions of the polymers by about the same degree as its replacement by the bicyclopentane cage. However, the depression of the mesophase to isotropic transition temperatures T_i was much less pronounced than its depression by the bicyclopentane cage. This difference may be related to easier rotation of the bicyclopentane cage as compared to the *trans*-1,4-cyclohexane ring.

The odd–even effect on polymer properties was similar in OPOC*n* and OTOC*n* polymers. Not only are the transition temperatures much lower for the polymers with an odd number of atoms in the spacer than for the even ones, but the gap between the temperatures of melting and crystallization was much larger for polymers with an odd carbon chain spacer than for even ones. Apparently, the successful packing of chains into a lattice is more difficult for odd polymers. Also on heating, these polymers (i.e., polymers with an odd carbon chain spacer) display much more complex (structured) melting behavior than do the even polymers, suggesting that for the former ones several lattices are possible that differ only slightly in energy.

Conclusions

A family of liquid-crystalline polymers was prepared that contained bicyclo[1.1.1]pentane-1,3-dicarboxylic acid in the middle of the triad mesogenic repeat unit and a series of linear flexible polymethylene spacers. Properties of these polymers were compared with analogous polymers containing terephthalic acid. The inclusion of the bicyclopentane cage in the mesogenic unit led to the lowering of transition temperatures, most probably due to the freer rotation of the cage and to the ensuing loss of coplanarity of all parts of the mesogen.

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Registry No. [I (n = 4)](IIa) (copolymer), 131865-31-1; [I (n = 4)](IIa) (SRU), 131865-38-8; [I (n = 5)](IIa) (copolymer), 131865-32-2; [I (n = 5)](IIa) (SRU), 131865-39-9; [I (n = 6)](IIa) (copolymer), 131865-33-3; [I (n = 6)](IIa) (SRU), 131865-40-2; [I (n = 7)](IIa) (copolymer), 131865-34-4; [I (n = 7)](IIa) (SRU), 131865-41-3; [I (n = 8)](IIa) (copolymer), 131865-35-5; [I (n = 8)](IIa) (SRU), 131903-87-2; [I (n = 9)](IIa) (copolymer), 131865-36-6; [I (n = 9)](IIa) (SRU), 131865-42-4; [I (n = 10)](IIa) (copolymer), 131865-37-7; [I (n = 10)](IIa) (SRU), 131865-43-5; [I (n = 4)](IIb) (copolymer), 81565-45-9; [I (n = 4)](IIb) (SRU), 78666-29-2; [I (n = 5)](IIb) (copolymer), 81565-46-0; [I (n = 5)](IIb) (SRU), 78666-30-5; [I (n = 6)](IIb) (copolymer), 81565-47-1; [I (n = 6)](IIb) (SRU), 81565-81-3; [I (n = 7)](IIb) (copolymer), 81565-48-2; [I (n = 7)](IIb) (SRU), 81565-82-4; [I (n = 8)](IIb) (copolymer), 81565-49-3; [I (n = 8)](IIb) (SRU), 81565-83-5; [I (n = 9)](IIb) (copolymer), 81565-51-7; [I (n = 9)](IIb) (SRU), 81565-84-6; [I (n = 10)](IIb) (copolymer), 81565-52-8; [I (n = 10)](IIb) (SRU), 81565-85-7.