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Semiflexible Liquid Crystalline Tetramers as Models of Structurally Analogous Copolymers

Peter A. Henderson and Corrie T. Imrie*

Department of Chemistry, School of Engineering and Physical Sciences, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, United Kingdom

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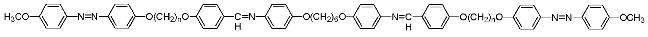
ABSTRACT: The synthesis and characterization of a series of liquid crystal tetramers is reported. These consist of molecules containing four liquid crystal units connected via three flexible alkyl spacers. The length of the central spacer is held at six methylene units, while that of the outer spacers is varied from three to twelve units. All the tetramers exhibit an enantiotropic nematic phase. The transitional properties exhibit a strong dependence on the length and parity of the outer flexible spacers. The properties of this series are compared to those of the corresponding series containing a pentamethylene central spacer. This change has a smaller than anticipated effect on the transitional properties and suggests that the four mesogenic units in the tetramer are not strongly correlated. The behavior of the tetramers is shown to strongly resemble that of a copolymer series containing differing lengths of spacers.

Introduction

Liquid crystal dimers consist of molecules containing two mesogenic units linked by a flexible spacer[1,2] and exhibit properties quite different from those of conventional low molar mass mesogens containing a single semirigid core. In addition to being of considerable interest in their own right, dimers have proved also to be valuable model compounds for semiflexible main-chain liquid crystal polymers.[3] In particular, the transitional behavior of dimers is strongly dependent on the length and parity of the flexible spacer in a manner strongly reminiscent of that seen for polymers. In other respects, however, the dimers behave quite differently from the polymers. For example, the tendency of a dimer to exhibit smectic behavior decreases on increasing the spacer length,[4] while quite the opposite is true for polymers,[3] although it should be noted that dimers do exhibit alternating smectic phases[5−7] which were first discovered for polymers.[8,9]

The question now arises as to how the properties of the dimers evolve into those of the polymers, and to begin to answer this, a number of liquid crystal trimers have been reported in which three liquid crystal groups are interconnected via two flexible spacers.[10−20] Again the transitional behavior is strongly dependent on the length and parity of the flexible spacers, resembling that seen for polymers. It is not yet clear whether the smectic properties of trimers are going to resemble those of dimers or polymers because the number of reported smectogenic trimers is very small.[13,14,16−19] It should be noted that, like the dimers, trimers exhibit highly unusual phase behavior including novel smectic phases.[21]

More recently we have reported the only examples of complete homologous series of liquid crystal tetramers, which consist of molecules containing four mesogenic units interconnected by three flexible spacers.[22,23] A small number of tetramers have also been reported by other authors.[24−26] To continue our investigation of both the novel mesomorphic phase behavior of oligomers and how transitional behavior evolves from low molar mass to polymeric systems, here we report the synthesis and characterization of a new series of liquid crystal tetramers in which the length of the central spacer is held at six methylene units while the lengths of the outer spacers are varied from 3 to 12 methylene units:



The tetramers are referred to using the acronym $n{-}p6p{-}n$ in which n denotes the number of methylene units in the outer flexible spacers. The properties of this series will be compared to those of a corresponding one but in which the central spacer contains an odd number of methylene units, the $n{-}p5p{-}n$ series.[23] The extent to which these materials can act as model compounds to understand the behavior of liquid crystal copolymers containing different lengths of spacers[27] will be discussed for the first time.

Experimental Section

The tetramers were prepared using the synthetic routes shown in Scheme 1 and are identical to those used to prepare the $n{-}p5p{-}n$ tetrameric series.[23]

1,6-Bis(4-aminophenyl-4′-oxy)hexane, 2. The synthesis of 1,6-bis(4-aminophenyl-4′-oxy)hexane is identical to that described for 1,5-bis(4-aminophenyl-4′-oxy)pentane,[23] and thus only representative spectroscopic data for it and its intermediates are provided.

Data for 1,6-Bis(4-acetamidophenyl-4′-oxy)hexane, 1. Yield: 83%. Mp: 203−204 °C. IR (KBr): ν (cm^{-1}) 3307 (CONH); 2943, 2867 (CH$_2$); 1656 (CO), 1597, 1513 (Ar−H); 825 (*para*-substituted aromatic). **1** was not soluble in common organic solvents, and thus, a ^{1}H NMR spectrum was not obtained. Anal. Calcd: C, 68.7; H, 7.3; N, 7.3. Found: C, 68.9; H, 7.3; N, 7.0.

Data for 1,6-Bis(4-aminophenyl-4′-oxy)hexane, 2. Yield: 92%. Mp: 147 °C. ^{1}H NMR (CDCl$_3$): δ (ppm) 6.7 (m, 4H, ArH), 6.6 (m, 4H, ArH), 3.9 (t, 4H, OCH_2CH$_2$, J = 6.6 Hz), 3.3 (s, 4H, ArNH_2), 1.7 (m, 4H, CH$_2$CH_2CH$_2$CH$_2$CH_2CH$_2$), 1.5 (m, 4H, CH$_2$CH$_2$CH_2CH_2CH$_2$CH$_2$,). IR (KBr): ν (cm^{-1}) 3395, 3316 (aromatic NH$_2$); 824 (*para*-substituted aromatic).

The syntheses of the α-(4-methoxyazobenzene-4′-oxy)-ω-(4-formylphenyloxy)alkanes **4** and the α-bromo-ω-(4-methoxyazobenzene-4′-oxy)alkanes **3** have been described previously.[23]

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* To whom correspondence should be addressed. Phone: (44) 1224 272910. Fax: (44) 1224 272921. E-mail: c.t.imrie@abdn.ac.uk.

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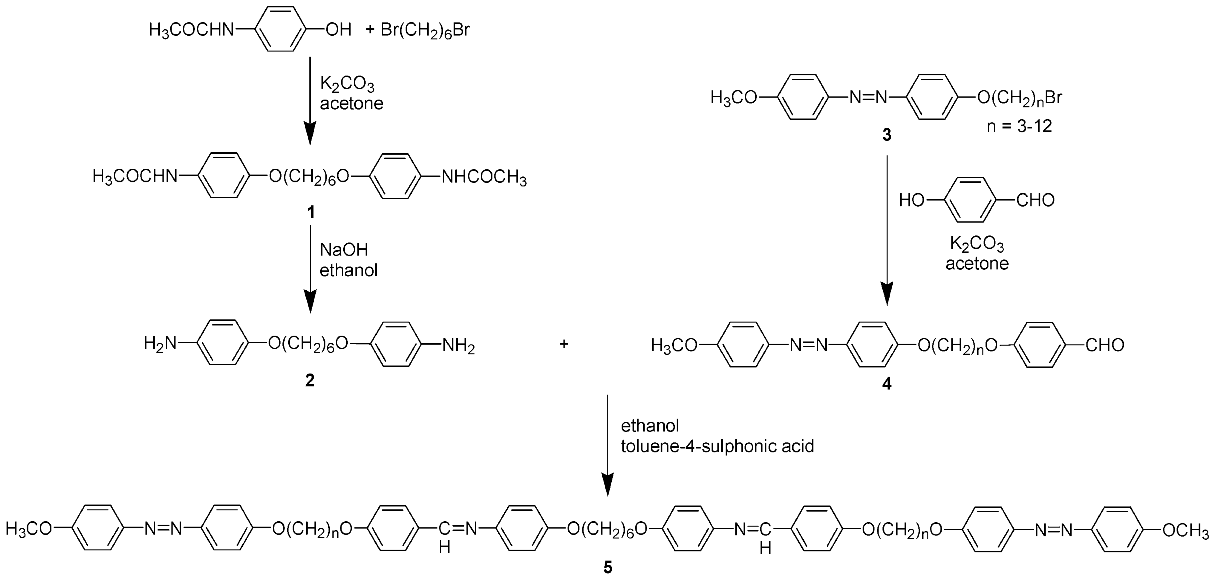
Scheme 1. Synthesis of the Liquid Crystal Tetramers



***$n-p6p-n$* Series 5.** The synthesis of the $n-p6p-n$ series is identical to that of the $n-p5p-n$ series described elsewhere[23] except that the $n-p6p-n$ tetramers were purified by Soxhlet extraction using toluene as the solvent. Due to their insolubility in an appropriate solvent, no NMR data were obtained for the tetramers. Their IR spectra, however, were consistent with the proposed structures. Specifically the bands associated with the stretch and bend deformations of the N−H bond in the amine **2** and that associated with the carbonyl band in the aldehydes **4** are absent in the spectra of the products. A new band associated with the imine stretch is seen at approximately 1600 cm^{-1}. In addition, elemental analysis data are consistent with the proposed structures, and representative data are provided. Anal. Calcd for $3-p6p-3$: C, 73.5; H, 6.2; N, 8.0. Found: C, 73.7; H, 6.1; N, 7.7.

Characterization and Thermal Analysis. The tetramers and their intermediates were characterized using a combination of ^{1}H NMR spectroscopy (where suitable), using a Bruker AC−F 250 MHz spectrometer, FTIR spectroscopy using an ATI Mattson Genesis Series FTIR spectrometer, and elemental analysis carried out by Butterworth Laboratories. The thermal behavior of the materials was investigated by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 820 differential scanning calorimeter equipped with a TS0801RO sample robot and calibrated using indium and zinc standards. The heating profile in all cases was heat, cool, and reheat at 10° min^{-1} with a 3 min isotherm between heating and cooling. All samples were heated from 0 °C to 20−40 °C above their clearing temperatures. Thermal data were normally extracted from the second heating trace. Phase characterization was performed using polarizing light microscopy using an Olympus BH2 polarizing light microscope equipped with a Linkam TMS 92 hot stage.

Results and Discussion

The transition temperatures and associated entropy changes for the $n-p6p-n$ series are given in Table 1. The data listed were extracted from the reheat DSC traces, and several members of the series showed complex melt/crystallization behavior before the formation of the nematic phase. All the members of the series exhibit an enantiotropic nematic phase. The nematic phase was identified on the basis of the observation of characteristic schlieren textures containing both types of point singularity and which flashed when subjected to mechanical stress.

Table 1. Transition Temperatures and Associated Entropy Changes for the *$n-p6p-n$* Series

n	T_{CrN}/°C	T_{NI}/°C	$\Delta S_{CrN}/R$	$\Delta S_{NI}/R$
3	213	248	23.1	2.15
4	251	291	28.6	4.35
5	215	246	25.6	2.52
6	240	274	38.8	4.53
7	206	234	32.6	2.92
8	229	253	41.2	5.26
9	197	236	30.6	3.37
10	222	243	41.7	4.89
11	187	213	34.3	3.83
12	216	231	46.0	5.32

The dependence of the transition temperatures on the number of methylene units in the outer flexible spacers for the $n-p6p-n$ series is shown in Figure 1. Both the melting and clearing temperatures exhibit a pronounced odd−even effect as the outer spacer lengths are increased in which the even spacers exhibit the higher values. The magnitude of the alternation in the melting points is largely unchanged on increasing the spacer lengths, and similar behavior has been observed for liquid crystal tetramers,[22,23] trimers,[16,17] and dimers.[1,3] This is thought to indicate either that the change in the conformation statistical weights of the spacer on melting into a nematic phase is small for even-membered spacers but large for odd-membered spacers or that this alternation reflects the difficulty that the bent conformations of the odd-membered compounds experience in packing efficiently into a crystal lattice compared with the more elongated all even-membered tetramers. The magnitude of the odd−even effect seen for the nematic−

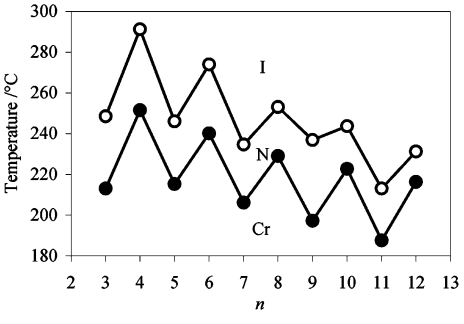


Figure 1. Dependence of the transition temperature on n, the number of methylene units in the two outer spacers, for the $n-p6p-n$ tetramer series: Cr−N (●), N−I (○).

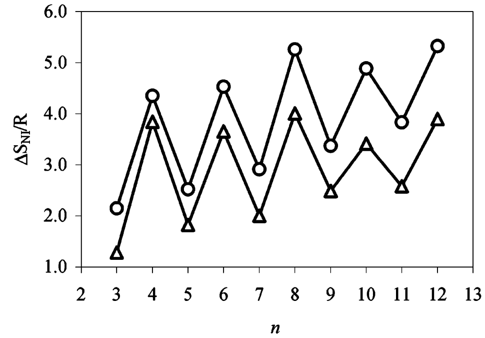


Figure 2. Dependence of the entropy change associated with the nematic−isotropic transition for the *n*−*p*6*p*−*n* (○) and *n*−*p*5*p*−*n* (△) series on the number of methylene units in the outer alkyl spacers.

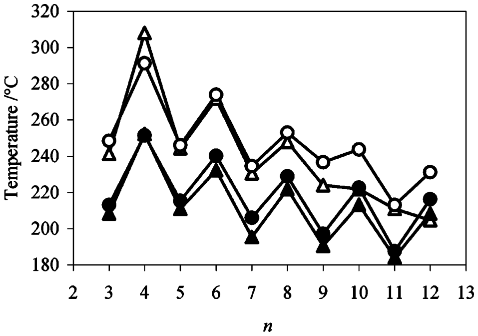


Figure 3. Comparison of the melting (filled symbols) and nematic−isotropic (open symbols) transition temperatures of the *n*−*p*6*p*−*n* (●, ○) and *n*−*p*5*p*−*n* (▲, △) series.

isotropic transition temperatures is attenuated on increasing *n*, with the temperatures for the even members falling more rapidly than those of the odd members. Similar behavior was seen for the *n*−*p*5*p*−*n* series[23] and other tetramers.[22]

The dependence of the entropy change associated with the nematic−isotropic transition on the number of methylene units in the outer spacers is shown in Figure 2. A pronounced odd−even effect is observed in which the values for the even members are typically 1.5−2 times larger than those of the odd members. The general trend is for the clearing entropy to increase upon increasing *n*, as is seen in dimers, trimers,[1−3] and polymeric systems,[28] although there is a less regular dependence on the value of $\Delta S_{NI}/R$ for both tetramer series when *n* is even. Unlike polymers, the entropy values are not scaled for the number of mesogenic units in the molecule, and it is not entirely clear to what extent this should be carried out for low oligomeric materials. Further speculation should await simulation studies on this class of oligomers.

We have seen in Figures 1 and 2 that both the nematic−isotropic transition temperatures and associated entropy changes of the *n*−*p*6*p*−*n* series depend critically on the length and parity of the spacer in a manner strongly resembling that seen for the transitional properties of dimers,[1,3] trimers,[16,17] and semiflexible main-chain liquid crystal polymers.[28] In dimers such behavior is most often attributed to the dependence of the molecular shape on the parity of the spacer considered in the all-trans conformation. Thus, in an even-membered dimer the mesogenic units are antiparallel, whereas in an odd-membered dimer they are inclined at some angle with respect to each other. This more linear structure for even-membered dimers is then considered to be more compatible with the molecular organization found in the nematic phase than that of the bent odd-membered dimers, and it is this greater compatibility which results in, for example, the higher values of $\Delta S_{NI}/R$ found for the even members. This interpretation, however, completely neglects the flexibility of the spacer, and a more realistic interpretation of the dependence of the transitional properties on the parity of the spacer must certainly include a wide range of conformations and not just the all-trans conformation. Such a model has been developed[3] and shows that in the isotropic phase approximately half the conformers of an even-membered dimer are essentially linear compared to only 10% of the conformers of an odd-membered dimer. At the transition to the nematic phase the synergy that exists between conformational and orientational order ensures that for even-membered dimers many of the bent conformers are converted to a linear form, enhancing the orientational order of the nematic phase. This increases $\Delta S_{NI}/R$ relative to what would be expected for a monomer. For an odd-membered dimer, however, the difference in free energy between the bent and linear conformers is too large for the orientational order of the nematic phase to convert bent into linear conformers. Thus, odd-membered dimers exhibit smaller values of $\Delta S_{NI}/R$ than even-membered dimers. For tetramers we now have three spacers to consider, one of which is always even for this particular series. It would seem reasonable to assume that this model would also successfully predict the transitional properties of the tetramers. The odd−even effect shown by the nematic−isotropic transition temperatures attenuates on increasing *n* (see Figure 1), whereas that shown by $\Delta S_{NI}/R$ does not (see Figure 2). This is also archetypal behavior for dimers and presumably reflects that on increasing the spacer length the greater number of available conformations means that the average shapes of the molecules, and hence the interaction strength parameters between them, become more similar. Thus, the alternation in T_{NI} attenuates, but there will still be a marked difference in the conformational distributions of the spacers, giving rise to the odd−even effect seen for $\Delta S_{NI}/R$.

Comparison of the *n*−*p*5*p*−*n* and *n*−*p*6*p*−*n* Tetrameric Series. Figure 3 compares the melting and nematic−isotropic transition temperatures of the *n*−*p*5*p*−*n* and *n*−*p*6*p*−*n* series. The melting points of the *n*−*p*6*p*−*n* series are higher than those of the corresponding members of the *n*−*p*5*p*−*n* series with the exception of the butyl homologue for which the melting points are essentially the same. For the remaining homologues, the difference in melting points, however, is small and on average is just 7 °C. Similar behavior is seen for the nematic−isotropic transition temperatures (see Figure 3), and the *n*−*p*6*p*−*n* series exhibits higher values than the corresponding member of the *n*−*p*5*p*−*n* series. The differences are, however, rather small for the lower homologues but tend to increase on increasing the length of the outer flexible spacers. The T_{NI} for 4−*p*6*p*−4 is lower than expected, and this may be attributed to the onset of decomposition at these high temperatures. The increasing difference between the nematic−isotropic transition temperatures of these two series on increasing the length of the spacers reflects that the odd−even effect observed for T_{NI} for the *n*−*p*5*p*−*n* series is attenuated more rapidly than that seen for the *n*−*p*6*p*−*n* series.

A comparison of the entropy changes associated with the nematic−isotropic transition for the $n-p5p-n$ and $n-p6p-n$ series is shown in Figure 2. The $n-p6p-n$ series exhibits higher values of $\Delta S_{NI}/R$ than the corresponding member of the $n-p5p-n$ series. The values of $\Delta S_{NI}/R$ for the two series are considerably larger than those exhibited by conventional low molar mass mesogens and fit the emerging trend that $\Delta S_{NI}/R$ increases on passing from the monomer to the dimer, trimer, and tetramer.[16,22] It has been argued that for oligomers these values should be scaled according to the number of mesogenic groups, and indeed such a scaling is routinely performed when data are analyzed for semiflexible main-chain liquid crystal polymers. Thus, the scaled values of $\Delta S_{NI}/R$ for $6-p6p-6$ (i.e., $[\Delta S_{NI}/R]/4 = 1.13$) and for $5-p5p-5$ (0.46) are comparable in magnitude to those of trimers containing two hexamethylene or pentamethylene spacers, respectively.[16,29]

It is interesting to note that both the $n-p5p-n$ and $n-p6p-n$ series are exclusively nematogenic and increasing the spacer length has not resulted in smectic phase formation. This is similar to the behavior observed for liquid crystal trimers[16] and symmetric dimers[4] but quite unlike that of semiflexible main-chain polymers for which increasing the spacer length enhances smectic behavior.[30,31] Although we are at an early stage in the development of the empirical rules relating molecular structure to properties in both trimers and tetramers, these data do suggest that the driving force for smectic phase formation must differ between liquid crystal oligomers and polymers. Presumably for the polymers the driving force must be an entropic one to disentangle the polymer chains. The situation is somewhat different for other liquid crystal tetramers for which smectic phase stability does not simply increase or decrease on increasing the length of the outer spacers, but for these tetramers the driving force for smectic phase formation was believed to be a specific interaction between the unlike mesogenic groups in the tetramer.[22] For the $n-p5p-n$ and $n-p6p-n$ series such specific interactions do not exist.

We have seen that for a given value of n passing from an odd- to an even-membered central spacer only slightly increases the nematic−isotropic transition temperature and entropy but that this difference increases on increasing n. This is rather surprising behavior as it might have been expected, and particularly for small values of n, that varying the central spacer would give the dramatic alternation in transitional properties seen on varying the spacer length in liquid crystal dimers. The physical significance of this observation is not clear, and the generality of this behavior must be established for a greater number of compounds.

Tetramers as Model Compounds for Copolymers. As we have noted already it might have been expected, a priori, that varying the central spacer in a tetramer would give rise to an alternation in the clearing temperature and entropy at least of a magnitude similar to that observed on varying the spacer in a liquid crystal dimer.[2,3] This appears not to be the case, however, and only a rather small difference in clearing temperature is observed (see Figure 3). We will now consider whether this surprising behavior is consistent with that seen for semiflexible main-chain liquid crystal polymers; i.e., to what extent can the tetramers be used as model compounds for the polymers? Specifically, the tetramers having three identical spacers, $5-p5p-5$ and $6-p6p-6$, may be considered as model compounds for homopolymers, while those having differing spacers, $5-p6p-5$ and $6-p5p-6$, may serve as model compounds for 2:1 copolymers (see Figure 4).

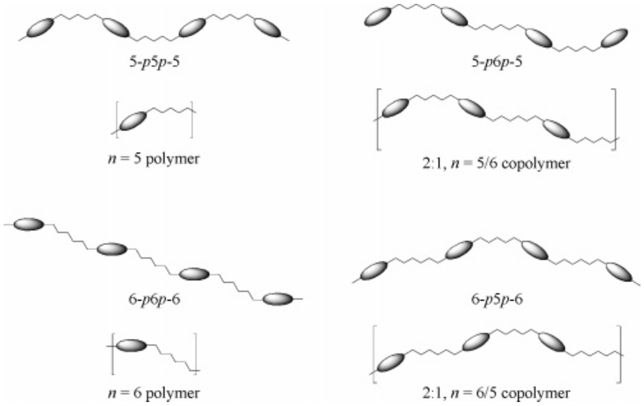


Figure 4. Schematic representations of odd- and even-membered tetramers and the polymers they resemble.

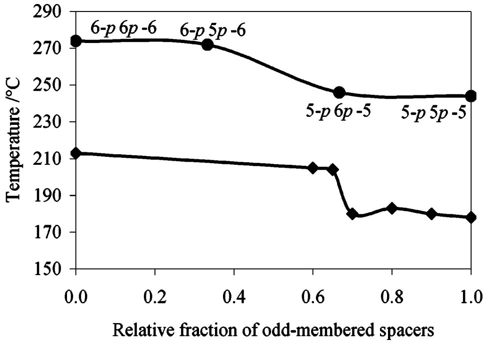
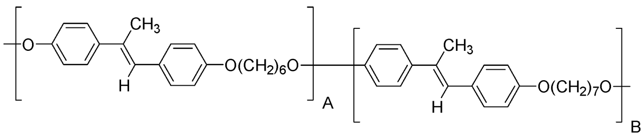


Figure 5. Dependence of the clearing temperature on the relative fraction of odd-membered spacers in (◆) copolymers[27] and (●) tetramers.

Percec and co-workers[27] have reported the thermal behavior of a series of copolymers containing odd- and even-membered spacers differing by only one methylene unit and expressed the dependence of the clearing temperature in terms of the relative fraction of odd-membered spacers, given by $B/(A + B)$. Although the mesogenic units in the tetramers and copolymers are not identical, we can assume that the interaction strength parameters between the mesogenic units within each system will be similar, the similarity in transitional behaviors serving to highlight the possible generality of the result. The clearing temperatures do not show a linear dependence on the relative amount of the odd-membered spacers (see Figure 5). Instead, the clearing temperature is rather insensitive to increasing the amounts of the odd-membered spacer up to ca. 0.6, at which point the clearing temperature falls. Further increases in the amount of odd-membered spacers have essentially no effect on the clearing temperature. The authors did not comment on this rather unexpected result.



The dependence of the clearing temperatures of the tetramers on the relative fraction of odd-membered

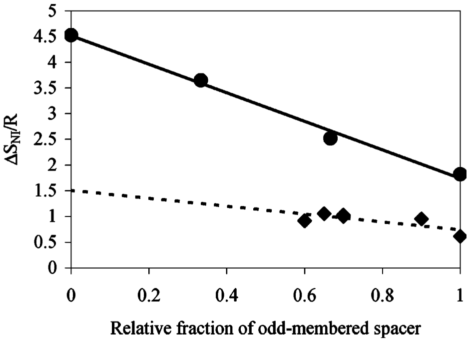


Figure 6. Dependence of the clearing entropy on the relative fraction of odd-membered spacers in the (◆) copolymers and (●) tetramers.

spacers is also shown in Figure 5. As seen for the polymers, the clearing temperature does not show a linear dependence on the relative fraction of odd-membered spacers. Instead and as we have seen already, 5−*p*6*p*−5 and 5−*p*5*p*−5 exhibit rather similar clearing temperatures as do 6−*p*6*p*−6 and 6−*p*5*p*−6, with the latter showing the higher clearing temperatures. Thus, the tetramers are showing behavior very similar to that of the polymers. This strongly suggests that orientationally the four mesogenic units are not strongly correlated and thus varying the length of the central spacer does not give rise to the expected pronounced odd−even effect in the clearing temperature. A small alternation in clearing temperatures has also been reported for an incomplete series of tetramers.[24] It appears, therefore, that the two outer spacers play a larger role in the odd−even effect seen in the clearing temperatures than does the central spacer. This suggests that the length and parity of the spacer having the major compositional fraction determines the transition temperatures and that the orientational motions of the four mesogenic units are not strongly correlated along the length of the tetramer.

The dependence of the clearing entropies for the tetramers on the relative fraction of odd-membered spacers is shown in Figure 6. We now have an apparent linear dependence of the clearing entropy on the relative fraction of the odd-membered spacer. The corresponding data for the polymers are also shown in Figure 6, expressed as the entropy change per repeat unit. The copolymers also appear to show a linear dependence of the clearing entropy on composition. The value for the all-even-membered $n = 6$ homopolymer is not included as the melting and clearing transition peaks could not be resolved in the DSC trace and the authors also noted that the rather low molecular weight of the even-membered polymer may mean that the estimated clearing entropy lay in the molecular weight dependent regime.[27] The molecular significance of the dependence of the clearing entropy on spacer lengths for both the tetramer and polymer is unclear, although it appears that both types of spacer contribute equally. A wider range of the *n*−*pxp*−*n* family of tetramers and of analogous copolymers should now be investigated to test the generality of these observations and to enhance our understanding of liquid crystalline phase formation and behavior in polymeric and oligomeric systems.

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