

Rapid Communications

Special Odd-Even Effect of Degree of Oligomerization on Properties of Cyclic Oligoesters^{*}

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Abstract We demonstrate here seven pure cyclic samples, which belongs to two series of oligoesters, cyclic oligo(trimethylene terephthalate)s (COTTs) and cyclic oligo(butylene terephthalate)s (COBTs), showing odd-even effect of degree of oligomerization (repeating units number) on properties. The pentamer of COTT and trimer of COBT show much lower melting temperature, and the trimer of COTT and trimer of COBT show significant lower refractive index, which can be ascribed to the low packing density of cyclic oligoesters with odd number of degree of oligomerization. Our results reveal the discrete property change as a function of cyclic size of oligomers, which can be used to design materials with special properties.

Keywords: Cyclic polymer; Oligomer; Odd-even effect; Refractive index.

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-015-1675-2>.

Recently, cyclic polymers have attracted great attentions due to their special topological structure with no chain end groups^[1–7]. However, most of the reported cyclic polymers show no supreme property over their linear counterparts except some solution properties (viscosity *etc.*)^[8–12]. This is due to the chain end groups' influence on the linear polymer properties (if not correlated to topology) can be neglected for polymers with relatively high molecular weights. As a result, the linear polymers show similar properties as cyclic polymers. Since the synthesis of linear polymers is much easier than that of cyclic polymers, finding where the cyclics show significant difference to linears is important for their applications.

We believe the cyclic polymers with low molecular weights, *i.e.*, cyclic oligomers, should be one of the key research directions due to the following reasons: 1) the difference between cyclic and linear oligomers should be significant, since the end-groups have significant influence on the properties of the latter^[13–18]; 2) by careful purification process, pure cyclic oligomers with different degree of oligomerization (cyclic ring size) can be obtained. This excludes the effect of molecular weights distribution, which exists in all traditional polymers. These pure cyclic oligomers can be looked as the perfect samples to reveal the structure-property relationship in cyclic polymers, besides their “endless” topological structure which excludes the influence of chain ends.

^{*} This work was financially supported by the National “973” Project (No. 2011CB606004), the National Natural Science Foundation of China (Nos. 21274099, 21234005 and 21474067), and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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Received April 7, 2015; Revised May 4, 2015; Accepted May 7, 2015

doi: 10.1007/s10118-015-1675-2

Up to now, some excellent works reported the difference in properties of cyclic oligomers and their linear counterparts, where poly(methylene)s and their cyclic homologues are thoroughly studied^[19–21]. However, most of them are focused on the crystalline properties (melting temperature and crystal structure), while other properties are untouched. In this paper, we would like to study other properties in addition to melting point from 7 pure cyclic oligoesters as presented in Fig. 1(a), among which 4 belongs to cyclic oligo(trimethylene terephthalate)s (COTTs) while the other 3 to cyclic oligo(butylenes terephthalate)s (COBTs), respectively. The results will greatly extend our knowledge on cyclic oligomers.

The synthetic route as in references provides a mixture of cyclic oligomers^[22, 23]. Careful column separation obtained pure cyclic oligoesters. Figure 1(b) is the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of the seven samples. The observed strong peaks can be assigned to $[M+Na]^+$, where M represents the corresponding cyclic oligomers. The small peaks around 500 Dalton are coming from the matrix. Clearly, no contamination of analogues is observed in any samples, indicating the high purity in all samples. This is also supported by the NMR results (Fig. S1), where the phenyl groups from different oligoesters have different chemical shifts. Detailed synthesis, purification process and characterization data are provided in Electronic Supplementary Material (Figs. S1–S11).

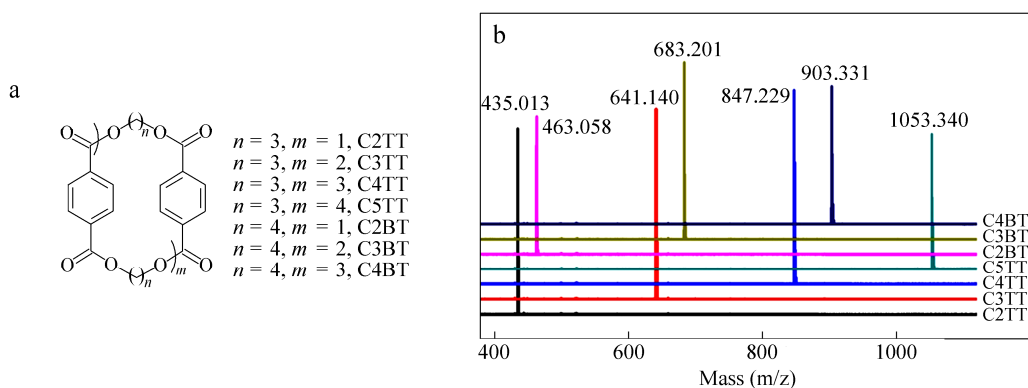


Fig. 1 (a) Structures of cyclic oligoesters, (b) MALDI-TOF mass spectra of cyclic oligoesters (The strong peaks are from $[M+Na]^+$, where M represents the corresponding cyclic oligomers.)

Interestingly, for COTTs, the chemical shifts from phenyl groups of oligomers with odd number of oligomerization degree are larger than those with even number ones. The difference becomes smaller with increasing oligomerization degree. This can be ascribed to the constrained topology of cyclic oligomers, while the stress is released with increasing ring size. Similar phenomena are observed in COBTs, though the difference is not so significant as in COTTs. Since there is one more flexible methylene group in repeating units of COBTs than in COTTs, it confirms that the restricted structure leads to this special property.

The thermal behavior of seven samples was measured by DSC. The curves are presented in Figs. S9–S11, and the results are summarized in Table 1. The properties from linear polymer analogues (PTT and PBT) are also added for comparison^[24–27]. For COTTs, the melting point of pentamer (C5TT, 152 °C) is much lower than the others (~250 °C), while in COBTs, the trimer (C3BT) shows much lower melting temperature (167 °C). Except for C3TT (trimer), the cyclic oligoesters show an odd-even effect of repeating number on the melting temperature. This is due to the relatively smaller enthalpy per repeating units in C5TT and C3BT.

Percec *et al.* reported the similar observations on their cyclic crown ethers, where the isotropization temperature and the associated enthalpy changes of these cyclics increased in an odd-even dependence with degree of oligomerization^[28]. They ascribed these to the conformation difference in the supramolecules, where even ones are packing better. We believe this can also be applied in our system. To prove this, the density of these cyclic oligoesters was measured, and the results are presented in Table 1. Clearly, in COTTs, the oligomers with odd number of repeating units (degree of oligomerization) have relatively lower density than those with

even number. Similar trend is observed in COBTs, confirming our assumption. In addition, all these cyclics have lower density than their linear polymer counterparts. This should come from their cyclic topology, which hinders the densely packing of atoms and surrenders the high density.

Table 1. Physical properties of cyclic oligoesters and linear polymer counterparts

Sample	T_m^a (°C)	ΔH_m^b (J·g ⁻¹)	T_g^c (°C)	n^d	ρ^e (g·cm ⁻³)
C2TT	251.1	92.7		1.591	1.248
C3TT	253.7	101.6		1.482	1.216
C4TT	255.4	104.6		—	1.284
C5TT	152.1	54.6	35.9	1.572	1.239
PTT ^f	230	146.0	45	1.638	1.332
C2BT	192.8	78.2		1.549	1.202
C3BT	166.7	60.9		1.467	1.173
C4BT	246.8	78.0		1.564	1.211
PBT ^f	226	145.5	26	1.619	1.310

^a Melting temperature; ^b melting enthalpy; ^c glass transition temperature obtained from DSC (heating rate: 10 K·min⁻¹) during the second heating step; ^d Measured refractive index of cyclic oligoesters at the sodium D line (589 nm); ^e Measured density at room temperature; ^f Linear polymer properties from references 24–27

The observed odd-even effect here is different to the traditional odd-even effect that observed in crystalline materials, where the odd numbers of C atoms in alkyl chain show large melting temperature difference compared to the adjacent even numbers analogues, or in chirality transfer in polymerization of liquid crystalline polymers, or in gel formation of low molar mass gelators^[29–35]. Considering the repeating units here, COBTs are one methylene group more than COTTs, and the dimer, trimer and tetramer of COBTs has lower melting temperature than the corresponding oligomers of COTTs with same degree of oligomerization, respectively. This is consistent with the observation that PTT has higher melting temperature and density than PBT, due to the relatively rigid backbone. With more methylene groups added in the repeating units, the melting temperature and density of the linear semi-aromatic crystalline polyesters decreased continuously^[24–27, 36]. The traditional odd-even effect is not applicable in these polyesters.

To our astonishment, a glass transition was observed at about 36 °C in C5TT during DSC scanning, but not in the other cyclic oligomers with lower oligomerization degree. The glass transition is usually looked as the intrinsic properties of polymers, and believed to be associated with the polymer segment's movement^[37]. If the existence of glass transition is used to distinguish polymers and small molecules, and considering the cyclic topology in C5TT, it indicates 5 repeating units of TT is the thresholds for cyclic oligomers to display polymer's properties, which is smaller than we expected. These results would be of great helpful for us to understand the fundamentals in polymers.

What we are interested in here is the other properties of these cyclic oligoesters. The refractive indices of the cyclic oligomers were measured by ellipsometer, and the results are shown in Fig. 2, while the refractive index of C4TT can't be measured due to its low solubility. The measured refractive indices for these cyclics decrease slightly with increasing wavelength, and the corresponding refractive indices at sodium D line (589 nm) are summarized in Table 1. The odd-even effect of number of repeating units on properties is again observed. Specially, the trimer of COTT (C3TT) and the trimer of COBT (C3BT) exhibit much lower refractive index than other studied cyclic oligoesters. This can be partially explained by their lower density, since higher density will lead to larger refractive index as predicted by the Lorentz-Lorenz equation^[36]. As we know, such kind of significant difference in refractive index of cyclics has not been reported.

When compared to the linear polymer counterparts, all the cyclic oligoesters show relatively lower density and refractive indices. This is due to the cyclic topology of the oligoesters, which constrains the packing of atoms. The results are contrary to some of the reported cyclic polymers, where the density, melting temperature or glass transition temperature of cyclic polymers are higher than the linear counterparts^[2, 38, 39]. The reason may lie in the molecular weights of the previously reported polymers, which is not lower enough to display this

special behavior. This is supported by Semlyen's observation on their cyclic PDMS polymers, where they found the density, refractive indices and glass transition temperature of cyclics as a relationship to molecular weights have a sudden turn off at very low molecular weights range^[40, 41]. For polymers with high molecular weights, the constraint in the cyclic polymers can be released by the polymer segment's movement. This is why C5TT only shows slightly lower refractive index compared to C2TT.

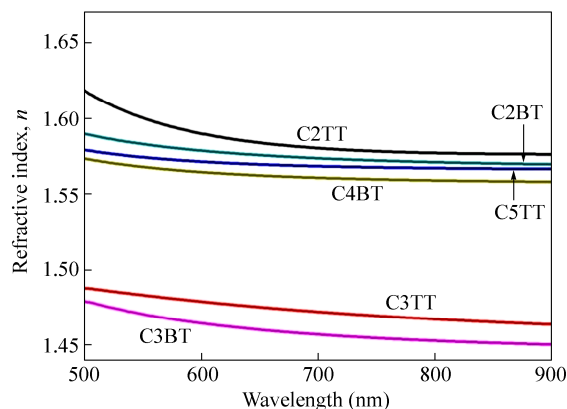


Fig. 2 Refractive indices of cyclic oligoesters as a function of wavelength

The above reported properties make the cyclic oligoesters useful for some applications. For example, the special lower refractive index of trimers of cyclic oligoesters compared to corresponding linear polymers can be used to design materials with ultralow refractive index, which is useful for anti-refraction and waveguide applications. In addition, since the ring size of these cyclic oligomers is comparable to the bioactive macrocycles (*i.e.*, cyclic peptides), their applications in biomaterials or as therapeutic agents sound promising.

In conclusion, the properties of two series of pure cyclic oligoesters with different degrees of oligomerization were studied, and the special odd-even effect of degree of oligomerization on properties was observed. Generally saying, the cyclic oligoesters with odd numbers of repeating units show lower density, melting temperature and refractive index compared to their adjacent even number analogues. The results indicate the constraint from the topological morphology can lead to big difference in properties, especially in those cyclic oligomers with odd number of repeating units when the ring size is not big enough. This special odd-even effect of degree of oligomerization may be a common rule in cyclic oligomers. In addition, the extrapolation of traditional polymer rules to oligomers may not be applicable. Further exploration on these cyclics will provide more interesting results.

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