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Polymer 41 (2000) 8283–8290

polymer

www.elsevier.nl/locate/polymer

Cyclic oligomers in saturated polyesters

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Received 15 December 1999; accepted 23 March 2000

Abstract

To get an in-depth understanding of the structure–property relationship in saturated polyester resins, the reactivity of various diols and diacids as well as reaction conditions were studied. Adipic acid (AA), phthalic anhydride (PA), isophthalic acid (IPA), terephthalic acid (TPA), 2-butyl-2-ethyl-1,3-propanediol (BEPD) and 2,2-dimethyl-1,3-propanediol (NPG) were addressed. It was found that in addition to linear oligomers with carboxyl and/or hydroxyl end groups cyclic oligomers were detected. Cyclic dimers of TPA and NPG are known to migrate to the coating surface causing "blooming". The understanding of this phenomenon and the monomers capable of forming cyclic dimers are the subject of this study, where we combined molecular modeling and analytical characterization. The probability of the formation of macrocyclic structures was shown to decrease in the order: BEPD–PA $>$ BEPD–AA $\geq$ BEPD–IPA $>$ BEPD–TPA. The temperature dependence was found to be small. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclic oligomers; Saturated polyesters; Molecular modeling

1. Introduction

Saturated polyesters are commercially important in coatings. The coated surfaces have to be mechanically strong, chemically inert and maintain a durable appearance. In general three to five different monomers are used to tailor-make the desired coating. This study was carried out to get an in-depth understanding of the structure–property relationship in saturated polyester resins. Basic parameters like reactivity of different diols and diacids and reaction conditions were studied. The studied raw materials were adipic acid (AA), phthalic anhydride (PA), isophthalic acid (IPA), terephthalic acid (TPA), 2-butyl-2-ethyl-1,3-propanediol (BEPD) and 2,2-dimethyl-1,3-propanediol (NPG). Polyesterifications were done with one diacid and one diol at a time, in order to distinguish the effect of each component. The effect of steric hindrances on polymer structure and molecular weight was clarified, as well as the differences of IPA and TPA as raw materials. The polymerization was followed by acid number titration and viscosity measurements. The polymerization was stopped when the desired acid number was reached. The molecular weight distribution was analyzed by gel permeation chromatography (GPC) and the end group distribution of oligomers by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI). The MALDI data indicated that in addition to linear oligomers with carboxyl and/or hydroxyl end groups, a fraction of cyclic oligomers was also formed [1]. The size and the amount of the cyclic components were characterized by GPC, GC–MS and MALDI-MS methods, and studied theoretically by molecular modeling. Cyclic dimers of TPA and NPG are known to migrate to the surface of coatings, causing a phenomenon called "blooming" [2,3]. Blooming is caused by crystallization of cyclic dimer at the coating surface, giving rise to an undesired whitish patina.

There are two main routes for the formation of cyclic structures. These can form in the beginning of the reaction when the chain ends of the same chain react with each other (ring closure reaction). Another way to produce cyclic structures is when the carboxylic acid group at the chain end reacts with an ester group of the same chain (back biting).

Schematically the routes are described as shown below (Schemes 1 and 2) (A is a carboxylic acid group, B an alcohol group and C an ester group).

In both schemes, the formation of macrocyclic structures strongly depends on the flexibility of the polyester chain.

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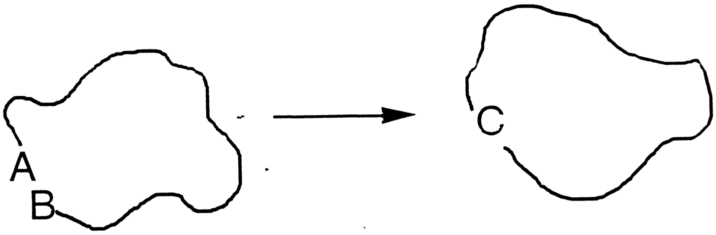
PII: S0032-3861(00)00257-3



Scheme 1.

Thus, the RIS Metropolis Monte Carlo (RMMC) [4] and molecular dynamics/mechanics (MD/MM) [5] methods are well suited for modeling of ring formation.

According to the Jacobson–Stockmayer theory [6–9], which is generally used to study macrocyclization, the equilibrium constant K_n for the cyclization reaction

$$-\mathrm{M}_y- \longrightarrow -\mathrm{M}_{y-n}- + \text{c-}\mathrm{M}_n$$

where $-\mathrm{M}_y-$ represents a linear, and c-M_n a macrocyclic chain, is given by

$$K_n = \left(\frac{3}{2\pi\langle r_n^2\rangle}\right)^{3/2}\frac{1}{2\mathrm{N_A}n} \qquad (1)$$

where $\mathrm{N_A}$ is Avogadro's number.

Since $\langle r_n^2\rangle \propto n$ and $K_n \propto n^{-5/2}$ the concentration of smaller rings is higher at equilibrium than is the concentration of larger rings. It is known that the Jacobson–Stockmayer theory underestimates the concentration of macrocyclic rings in the case of poly(ethylene terephthalate), while for aliphatic polyesters the number of rings is overestimated [9]. In both cases the dependence of K_n on n is predicted to be qualitatively correct and, therefore, the Jacobson–Stockmayer theory is used here only as a qualitative basis. Further, steric requirements for the reaction like the structure of the transition state are not taken into account by the Jacobson–Stockmayer theory.

2. Experimental

2.1. Polymerization

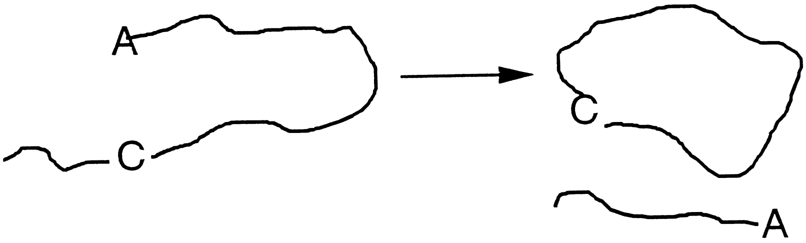
Polyesterifications were carried out in a 1 l oil-jacketed glass reactor supplied with a four-bladed mechanical stirrer, nitrogen inlet, 15 cm long vigreau column, condenser and temperature measurement unit. Oil was heated by using a Lauda K6 KP thermostat. The charge of the reactor was 1000 g, nitrogen flow about 5 l/h and stirring speed 260 rpm. Maximum reaction temperature was 238°C and maximum distillate temperature 99°C. Glycols and diacids were charged into the dried reactor and heating was started gradually to 238°C by controlling the distillation temperature. The acid value from ca. 1 g sample, dissolved in methanol/toluene solution (1:2), was determined by titration with 1 N KOH, using phenolphthalein as the indicator.

The initial polymerization progress of PA and BEPD was studied by frequent sampling in the beginning of the reaction. The oligomers were analyzed by GPC and MALDI in order to identify chain length and end groups.

2.2. Molecular weight

The molecular weight distribution was analyzed by GPC. Chromatographic measurements were carried out at room temperature with a Waters modular GPC system (Taunton, MA) equipped with a Waters 712 WISP injector, a Waters M510 pump and a Waters 410 refractive index detector. The column set consisted of Waters Ultrastyragel columns (7.8 mm I.D. × 300 mm) with pore volumes 10^4, 10^3, 500 and 100 Å. The molecular weight calibration was accomplished by using polystyrene standards from Polymer Laboratories (Church Stretton, UK). Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 ml/min. The samples were dissolved in THF and filtered through a 0.45 μm membrane. Concentration of the solutions was 0.1 wt%. The injection volume was 100 μl for the samples and 30 μl for the polystyrene standards. GPC fractionates molecules according to their conformational size, rather than molecular weight.

The fraction of cyclic dimer in a polymer sample was



Scheme 2.

Table 1
Relative peak intensity and position of the cyclic MALDI peak. The relative intensity is the oligomer peak intensity to the maximum intensity peak

	BEPD–PA	BEPD–AA	BEPD–IPA	BEPD–TPA
Relative int. (%)	100	70	60	Low
Oligomer	Dimer	Dimer	Trimer	Tetramer

estimated from the integrated ratio of peak area to total area of the chromatogram. This technique is not absolute, but allows comparison of dimer content within a set of samples.

2.3. Oligomer composition

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI) is a relatively new technique, the first applications being published in the late 1980s. Mass spectrometric studies were performed with a Bruker Proflex time-of-flight mass spectrometer (Bruker Daltonics, Billerica, MA, USA), which was equipped with a nitrogen laser ($\lambda = 337$ nm). As matrix compound 2,5-dihydroxybenzoic acid (DHB) obtained from Aldrich (Steinheim, Germany) was used. The polyester samples were dissolved in tetrahydrofuran at the concentrations of 5.0–6.0 mg/ml. The spectrum was obtained with 100 laser pulses.

MALDI is suitable for analyzing molecular weight distribution (MWD) of low polydispersity samples, end group analysis and distinguishing linear and cyclic molecules. The preferred cyclic oligomer is taken from the relative intensity of cyclic oligomers.

GC–MS was used to identify the oligomers extracted from polyesters of high molecular weight.

2.4. Modeling

The Polymer software package by MSI was used for molecular modeling [4]. The calculations were run on a Silicon Graphics workstation Indigo^2 Impact 10000.

The molecular mechanics and molecular dynamics simulations were performed using the Discover 96.0/4.0.0 software by MSI. The MSI pcff force field as modified at VTT [10] was used in all calculations. The force field modifications were based on ab initio and density functional theory (DFT) calculations at the MP2/6-31G(d), B3-LYP/6-31G(d) and B-LYP/6-31G(d) levels of theory [10].

RIS Metropolis Monte Carlo (RMMC) calculations give the persistence lengths and the mean squared end-to-end distances of polymer chains [4], both of which are relevant properties in the analysis of the probability of ring closure reactions. The persistence length, which is the average projection of the end-to-end vector on the first bond [6,7], provides a measure of the rigidity of the polymer chain and, therefore, a measure of the distance over which the chain remembers its initial direction.

The RMMC calculations, in which for each case 200 conformations were saved (10^6 equilibration steps and 5×10^6 production steps where the properties were calculated after every 400 steps in the RMMC procedure), were performed at four temperatures (250, 300, 350 and 400 K).

In order to obtain information on the chain conformations and the distribution of certain types of atom–atom distances in each case, 100 structures were generated using high-temperature MD calculations with subsequent energy minimization. From these structures, pair correlation functions (pcf) were calculated [11].

3. Results and discussion

3.1. Experimental observations

MALDI was successfully used for end group analysis and also to identify the presence and relative intensity of cyclic oligomers. Polyesters polymerized under excess of diol exhibited a majority of diol end groups, but diacid end groups could not be avoided, even under a large excess of diol. Combination of IPA with PA and/or TPA with a diol can be analyzed, since IPA, TPA and PA have identical molecular weight in the polymer chain. On the other hand, they cannot be distinguished.

The existence of cyclic oligoesters has been confirmed by analytical methods, such as MALDI-MS, GC–MS and GPC. MS techniques are sensitive to molecules with a molecular weight between 200 and 1500. PA and AA showed maximum intensity for cyclic dimers, i.e. two acid and two diols, while the most common cyclic IPA oligomers are trimers. TPA formed both cyclic dimers and tetramers. The tetramers were dominating in MALDI data obtained from BEPD–TPA polyesters. A summary of the MALDI results is presented in Table 1.

GPC fractionates molecules according to their conformational size. Cyclic dimers have been observed in the GPC curves from AA-, PA- and TPA-containing polymers. The elution time in GPC is longer for cyclic dimers than for linear ones, indicating that they are smaller in size than their linear counterparts. This phenomenon is especially pronounced in dimers of PA and TPA with BEPD. AA has a lower molecular weight than phthalic acids but gives rise to a dimer larger in size. We have obtained some contradictory experimental data on TPA, where soluble oligomeric fractions have been extracted and analyzed by GC–MS. Both BEPD and NPG cyclic dimers with TPA have been detected in significant amounts. This contradiction between MALDI and GC–MS data is due to the polymer samples. Variations in polymers are due to different polymerization conditions, such as polymerization time and monomer availability. TPA has a high melting point and is subsequently available in low concentrations in the beginning and in larger concentrations at the end of the polyesterification.

The route of cyclization was studied by frequent sampling, especially in the early stages of a BEPD–PA polymerization. At first the major component was

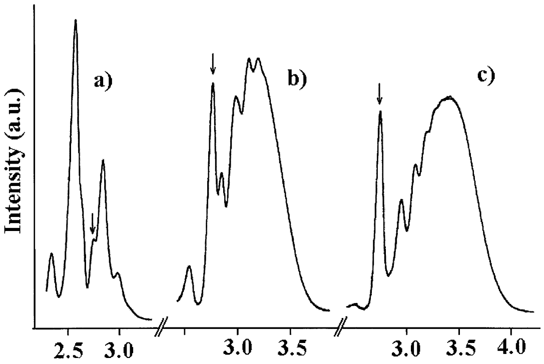


Fig. 1. Progress of molecular weight in BEPD–PA as a function of time. The GPC curves are obtained from samples taken at (a) 20 min; (b) 1 h; and (c) 5.5 h after start. The cyclic dimer peak is indicated with an arrow. The *x*-axis values are expressed as logarithm of the molecular weight.

BEPD–PA pair with a small amount of linear dimer and traces of cyclic dimer. As the polymerization progressed the average molecular weight changed, but the peak for cyclic dimer remained. In the final product it was the strongest of the oligomeric peaks, see Fig. 1.

The cyclic oligomers are undesirable in polyesters because they migrate and cause hazy surface deposits. The migration occurs when the polymer coating is exposed to temperatures above its glass transition temperature. Cyclic compounds generally lack functionality and subsequently, cannot react once they have been formed during the polymerization.

A rough estimate of the concentration of cyclic dimers in our polyesters was obtained from the ratio of the integrated dimer peak area to the total area of the gel permeation chromatogram; Table 2.

It is evident that the tendency for ring formation follows the order BEPD–PA > NPG–PA > BEPD–TPA > NPG–TPA > BEPD–AA. Corresponding peaks from IPA-containing polymers were not observed, indicating that IPA does not form detectable amounts of cyclic dimer. NPG–AA polyester was not prepared. According to MALDI data, cyclic trimers are formed in IPA-containing polymers.

Cyclic dimers of PA, TPA and IPA with ethanediol (ED) have been described in the literature [12]. In the same study, NPG was tested and the presence of cyclic dimers with TPA were reported. The most common cyclic oligomer containing TPA and ethanediol was the tetramer, but trimer and dimer were also formed. Of the above-mentioned monomers, the cyclic oligomer content decreased in the order ED–IPA > ED–PA > NPG–TPA > ED–TPA.

Table 3
The RMMC calculated square roots of the mean squared end-to-end distances $\langle r^2 \rangle^{1/2}$ (Å) at different temperatures for AA, PA, IPA and TPA with BEPD

n	Temperature (K)			
	250	300	350	400
(BEPD–AA)$_n$				
4	23.2 ± 2.2	22.9 ± 2.1	22.8 ± 2.1	22.5 ± 2.0
6	29.0 ± 2.7	28.7 ± 2.6	28.6 ± 2.5	28.1 ± 2.4
8	33.9 ± 3.3	33.4 ± 3.1	33.2 ± 3.0	32.8 ± 2.9
(BEPD–PA)$_n$				
4	15.8 ± 1.7	15.9 ± 1.7	16.0 ± 1.7	16.0 ± 1.6
6	20.5 ± 2.2	20.7 ± 2.1	20.6 ± 2.0	20.5 ± 1.9
8	23.9 ± 2.6	23.8 ± 2.5	23.8 ± 2.4	23.7 ± 2.3
(BEPD–IPA)$_n$				
4	27.4 ± 2.6	26.2 ± 2.5	25.8 ± 2.4	25.0 ± 2.3
6	34.5 ± 3.3	33.4 ± 3.1	32.3 ± 3.0	31.2 ± 2.8
8	40.8 ± 4.1	39.1 ± 3.8	37.8 ± 3.6	36.7 ± 3.4
(BEPD–TPA)$_n$				
4	27.0 ± 2.5	26.8 ± 2.4	26.6 ± 2.3	26.2 ± 2.3
6	34.3 ± 3.2	34.2 ± 3.1	33.5 ± 3.0	33.2 ± 2.9
8	40.4 ± 4.0	40.2 ± 3.9	39.5 ± 3.7	39.1 ± 3.7

3.2. Modeling results

The RMMC [4] results for the end-to-end distances are given in Table 3. The probability distributions of the end-to-end distances at 400 K are shown in Fig. 2A–D. The oxygen atoms in the hydroxyl groups of the chain end units are defined as end atoms. The probability of close contacts of the end groups is in each case found to be small. For BEPD–AA (Fig. 2A and Table 3) it can be seen from the probability distributions that the maxima for the end-to-end distance distributions are above 20 Å. As the chain becomes longer, the maximum broadens and the tail corresponding to longer distances between the chain ends increases. The same trend holds for all the polyesters studied in this work.

Table 2
Relative area of cyclic dimer peaks in gel permeation chromatograms. M_w is the weight average molecular weight and D is the polydispersity. Cyclic dimers of BEPD–IPA were not observed. Polyesterification was performed under hydroxyl group excess, unless otherwise mentioned

Composition	Cyclic area (%)	Apparent mol. wt. GPC	Theoretical mol. wt. of dimer	M_w	D
BEPD–AA	2	560	540	6500	2.3
BEPD–PA	11	500	580	2400	1.6
BEPD–PA COOH excess	9	500	580	3600	2.2
NPG–PA	6	410	470	3200	1.9
BEPD–TPA	4	500	580	5800	2.3
NPG–TPA	2.5	400	470	5700	2.2

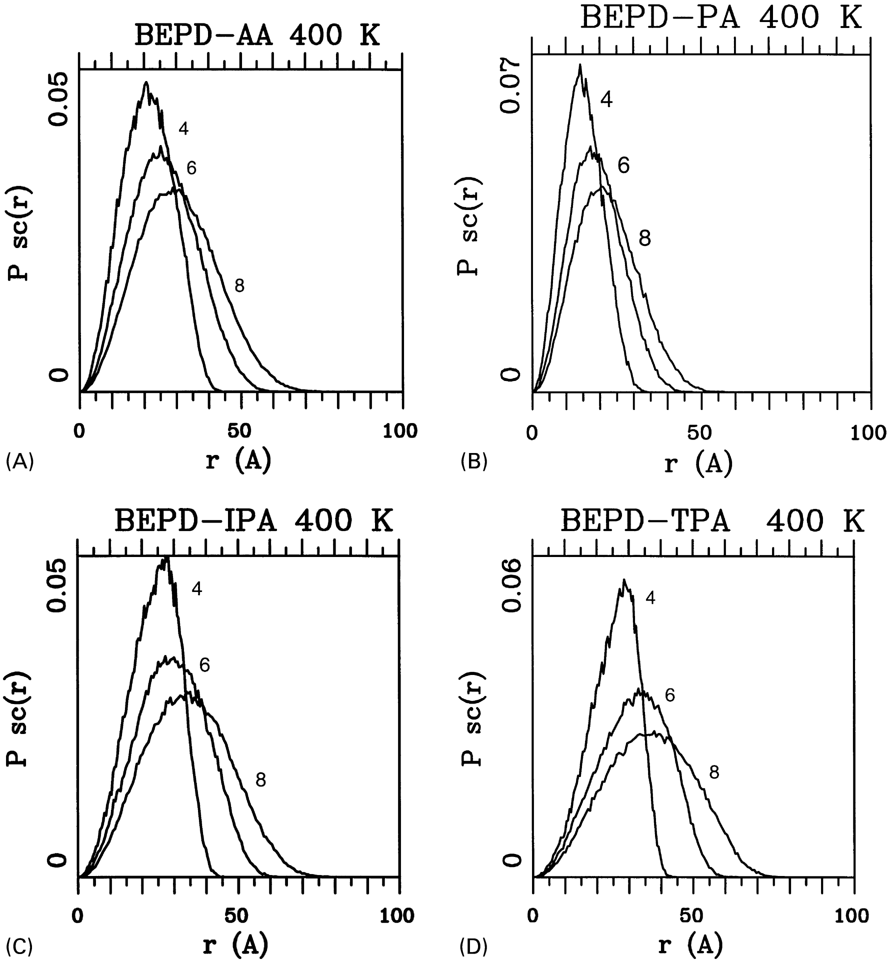


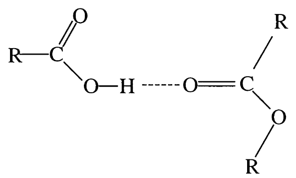
Fig. 2. (A–D) The probability distributions of the end-to-end distances with different chain lengths at 400 K.

The relationship between the energy and end-to-end distance for each case is shown in Fig. 3A–D. The data obtained explain the low probability of those conformations where the end groups are close to each other, since the number of such conformations is small and in most cases their relative energy is high.

The RMMC calculated persistence lengths of the longest chains studied in this work ($n = 8$) are given in Table 4. These values are much smaller than the contour lengths of the chains with $n = 8$ (70–80 Å, see the tails of the probability distributions in Fig. 2A–D), and the results can be used to analyze local properties of long chains. Thus, the reactions corresponding to Scheme 2 can also be analyzed.

Pair correlation functions give information on the distribution of certain types of atom–atom distances in the molecule. The pcfs between the hydrogen atom of the carboxylic acid end group (= a) and the double bonded oxygen atom in the ester or carboxylic acid groups (= b), $g_{ab}(r)$ were calculated, as well as the pcfs between two double bonded oxygen atoms in the ester groups, $g_{bb}(r)$, from the MD/MM structures generated above for the chains with $n = 8$. The results are given in Fig. 4A–C.

The pcfs for BEPD–AA are given in Fig. 4A. In $g_{ab}(r)$, there are two sharp peaks at about 1.8 and at 2.2 Å, respectively. The second peak at 2.2 Å represents the distance between the hydrogen and carbonyl oxygen atoms in the same carboxylic acid group, while the first peak at 1.8 Å represents the hydrogen bonded structure



In conformations where this structure is present, the cyclic structure can form via the back biting mechanism (Scheme 2). In BEPD–AA, there are a large number of conformations available, enabling back biting to take place, as can be seen from the height of the first peak (Fig. 4A). Thus, for the formation of cyclic structures Scheme 2 is more probable than Scheme 1. Similar conclusions can be made from the $g_{ab}(r)$ graphs of BEPD–PA and BEPD–IPA.

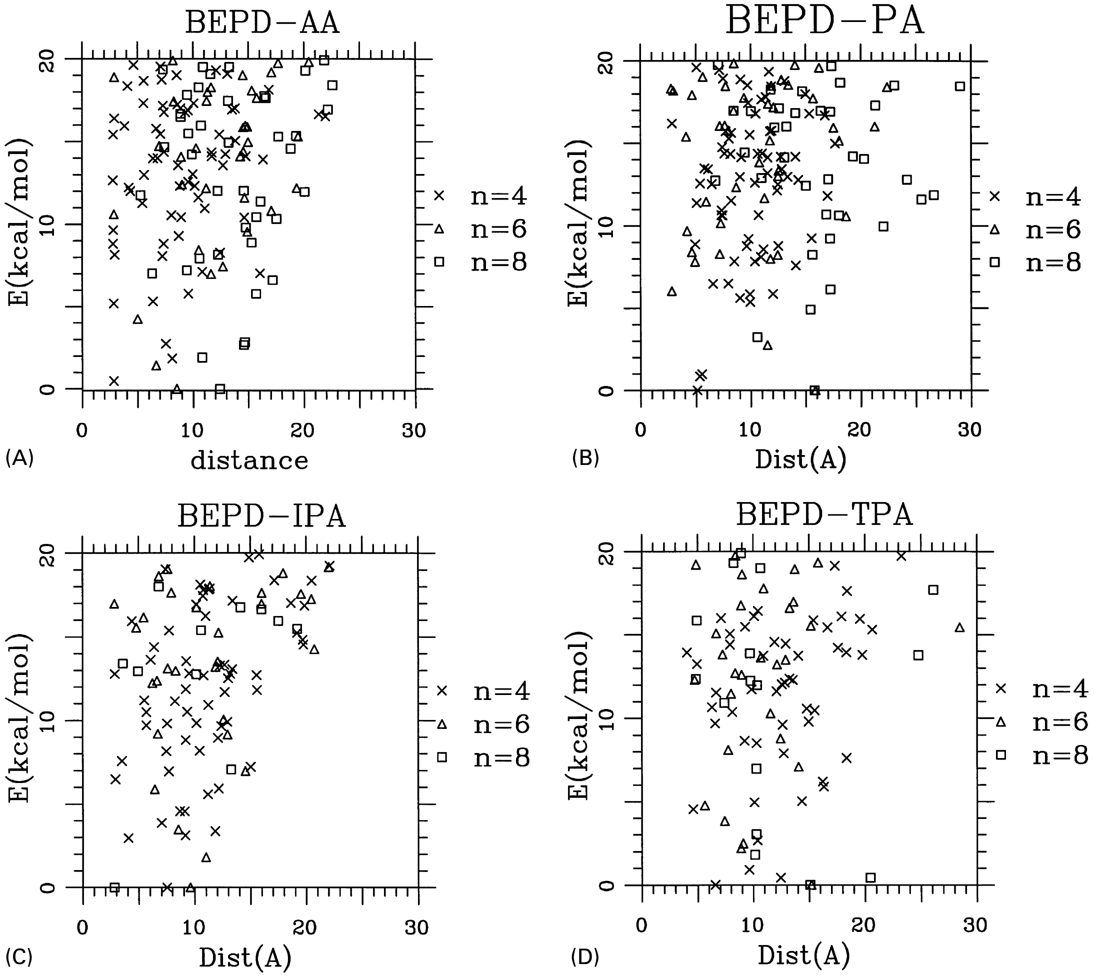


Fig. 3. (A–D) Comparison of the end-to-end distance (Å) and the conformational energy.

However, the back biting mechanism for the formation of macrocyclic structures in BEPD–TPA is improbable, as can be seen from the smallness of the peak at 1.8 Å in the $g_{ab}(r)$ graph (Fig. 5) obtained by optimizing the 200 structures saved in the RMMC calculation for $(\mathrm{BEPD{-}TPA})_8$ at 400 K. The results of the pcf analysis of these structures are similar to those obtained from the MD/MM calculations (see Fig. 3D). Visual inspection of the optimized structures of $(\mathrm{BEPD{-}TPA})_8$ reveals the reason for the different behavior. In BEPD–TPA ring stacking is more common than in other chains and the interaction energies for the ring stacking is of the same order as that of hydrogen bonding. Further, TPA does not introduce a rigid kink into the chain like PA and IPA do.

Table 4
The RMMC calculated persistence vectors (Å)

	Temperature (K)			
	250	300	350	400
$(\mathrm{BEPD{-}AA})_8$	5.34 ± 0.03	5.22 ± 0.03	5.15 ± 0.03	5.11 ± 0.03
$(\mathrm{BEPD{-}PA})_8$	3.63 ± 0.02	3.57 ± 0.02	3.58 ± 0.02	3.54 ± 0.02
$(\mathrm{BEPD{-}IPA})_8$	8.63 ± 0.05	7.89 ± 0.05	7.38 ± 0.05	6.91 ± 0.04
$(\mathrm{BEPD{-}TPA})_8$	7.80 ± 0.04	7.74 ± 0.04	7.37 ± 0.04	7.18 ± 0.04

The $g_{bb}(r)$ graphs ($C{=}O\cdots O{=}C$ distances of the ester groups) in Fig. 4 do not give as detailed information as the $g_{ab}(r)$ graphs, since in $g_{bb}(r)$ there are many overlapping features making the evaluation more difficult. In BEPD–AA, BEPD–IPA and BEPD–TPA there are peaks at separation distances shorter than 5 Å indicating the proximity of the ester groups, i.e. macrocyclic structures can form through a series of transesterification reactions. Some of the peaks are related to the separation between the ester groups bonded onto the same BEPD group. In BEPD–PA these peaks overlap with those originating from the distances between carbonyl oxygen atoms of the ester groups bonded onto the same aromatic ring. However, since $\langle r^2 \rangle$ for BEPD–PA is smaller (see Table 3) than for the other chains studied here, the chain is strongly coiled and, therefore, a series of transesterification reactions can take place.

The Jacobson–Stockmayer theory [6–9] does not take the steric strain in the small macrocyclic rings properly into

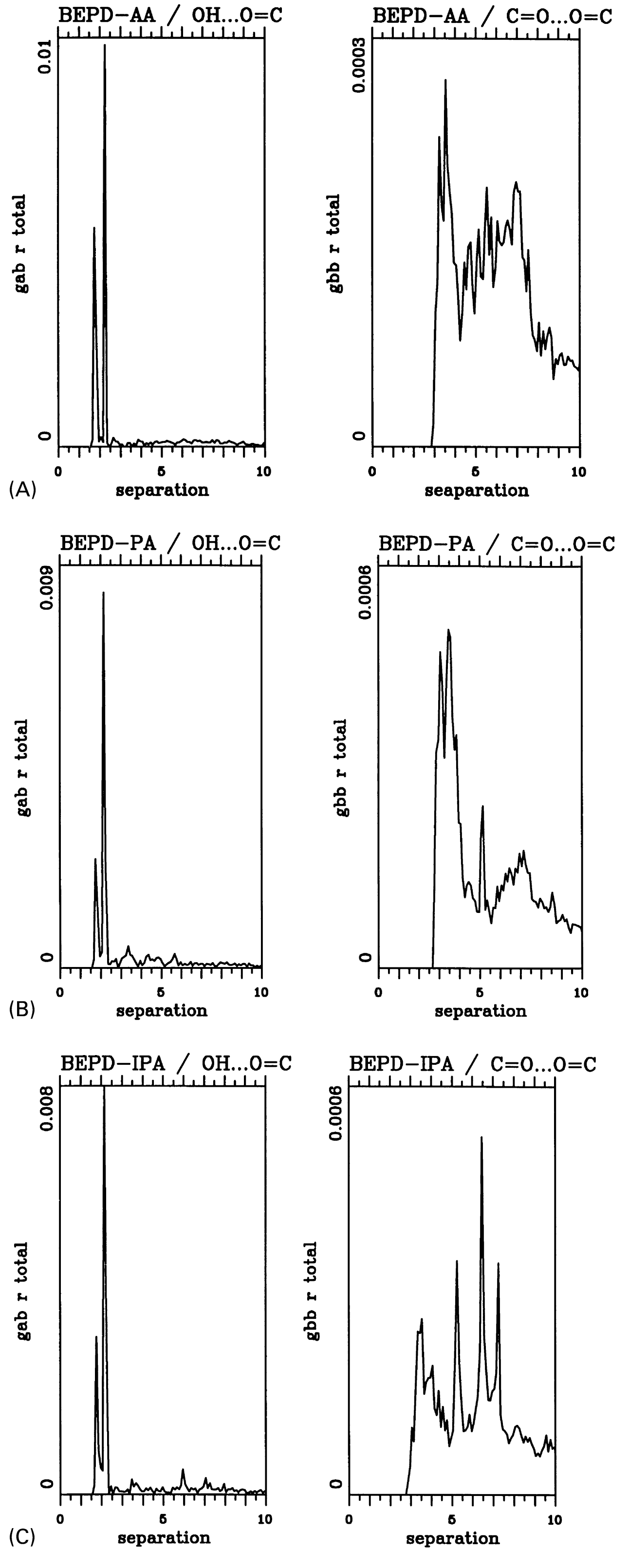


Fig. 4. Pair correlation functions. The graph on the left is for distances OH···O=C. The graph on the right is for distances C=O···O=C: (A) $(\text{BEPD–AA})_8$; (B) $(\text{BEPD–PA})_8$; (C) $(\text{BEPD–IPA})_8$.

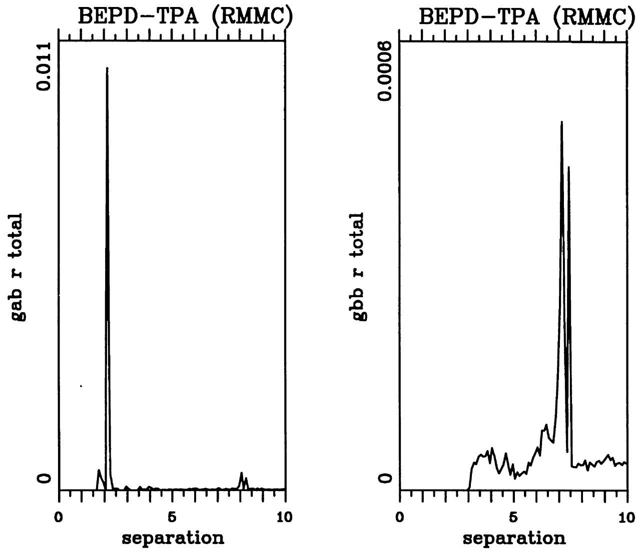


Fig. 5. Pair correlation functions for $(\text{BEPD–TPA})_8$ calculated from RMMC generated conformers. The graph on the left is for distances OH···O=C. The graph on the right is for distances C=O···O=C.

account. We tested whether the smallest rings with $n = 2$ can be formed without significant strain. In each case the comparison of the energy terms of cyclic and non-cyclic structures revealed no significant increase in strain in the cyclization process. An example is given in Fig. 6. Due to the stacking of the planar aromatic rings, the molecules have small volumes and due to their shape (see Fig. 6), they migrate easily, and cause the blooming effect.

From Table 3 ($n = 8$) and Eq. (1) it is seen that the probability of the formation of macrocyclic structures decreases in the order:

$$\text{BEPD–PA} > \text{BEPD–AA} \geq \text{BEPD–IPA} > \text{BEPD–TPA}$$

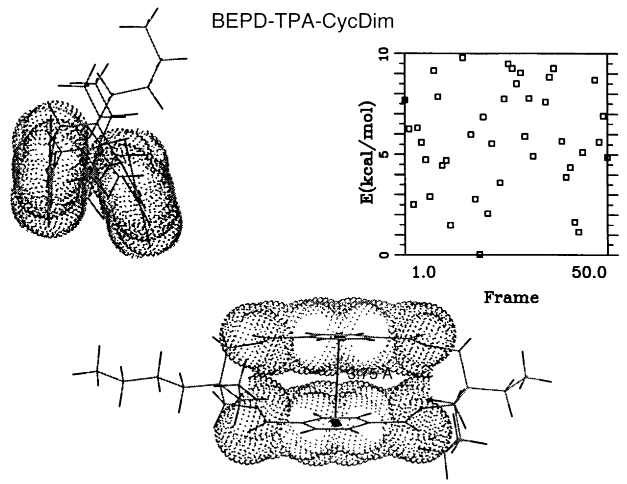


Fig. 6. Distribution of energy (kcal/mol) in the low energy conformations found for the cyclic dimer $(\text{BEPD–TPA})_2$. The minimum energy conformation is viewed from two angles.

The temperature dependence is, in general, small (see Table 3). For BEPD–IPA the probability of macrocyclic structures increases with increasing temperature somewhat more than in the other cases.

4. Conclusions

The possibility of macrocyclic ring formation in some saturated polyesters has been modeled using RMMC and high temperature MD/MM methods. Two main routes, ring closure reaction and back biting, have been investigated. The probability of ring closure reaction was in each case found to be very low. Further, ring closure reactions take place mainly at low concentrations. The Jacobson–Stockmayer theory [6–9] gives the following order for the probability for thermodynamically controlled back biting cyclization:

$$(\text{BEPD–PA})_n > (\text{BEPD–AA})_n \geq (\text{BEPD–IPA})_n > (\text{BEPD–TPA})_n$$

The analysis of various pair correlation functions revealed that the backbiting mechanism for macrocyclization of BEPD–PA, BEPD–AA and BEPD–IPA can take place readily. Even the smallest macrocyclic structures, i.e. those with $n = 2$, can form without significant increase in strain. Particularly in BEPD–TPA, ring stacking takes place, which decreases the probability of the formation of cyclics. The calculations also showed that macrocyclic compounds form mainly due to transesterification reactions in the back biting mechanism. The temperature dependence is generally small as can be seen from Table 3 and Eq. (1).

PA has a high tendency to form cyclic dimers, according to analytical data. Modeling data indicate that PA containing polymers also have a high probability for transesterification and thus larger cyclic compounds could be present. This is in excellent agreement with MALDI observations, where significant amounts of larger cyclic oligomers were observed, when polyesterification was continued to completion.

TPA and PA form stable cyclic dimers with BEPD and NPG. These dimers are small in size and the aliphatic groups of the diols give the egg-shaped molecules a non-polar surface. These dimers are non-reactive and have low affinity to the polyester matrix. They are free to migrate to the surface and cause blooming.

The combination of analytical characterization and molecular modeling has proved to be successful in studying the structure–property relationship in polymeric materials.

Acknowledgements

The authors are grateful to the Technical Development Centre of Finland (Marketing Molecules Technology Programme) for financial support. We thank Maaria Seläntaus of Fortum Oil and Gas for GPC analyses and Olli Laine of the University of Joensuu for MALDI analyses. We also thank Per Nyholm, Neste Chemicals, for his support.

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