Aggregates of Shape Persistent Macrocyclic Amphiphiles Detected by MALDI-TOF Spectroscopy

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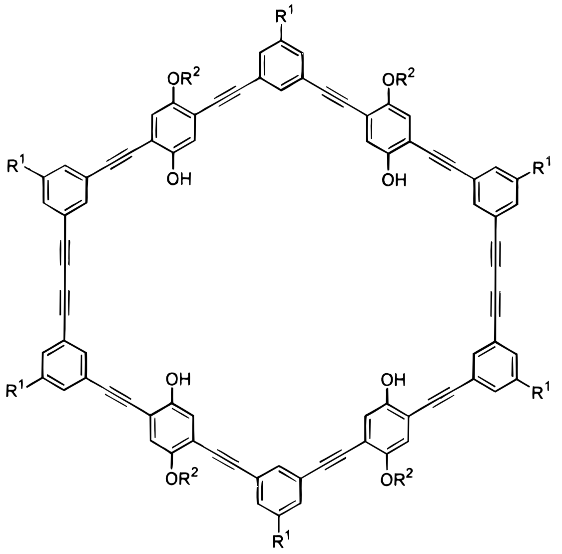
Introduction

The accurate measurement of molecular weight distributions (MWD) is critical for optimizing and for understanding the properties of polymers and the mechanism of their formation. Gel permeation chromatography (GPC) is a well-established and easy procedure for determining MWD's. However, analysis of GPC data is inevitably based on a calibration by reference polymers of defined structure and molecular weight and is thus not easily applicable to polymers with structures greatly different from those used for the calibration. To overcome this problem, the so-called "universal calibration" is suggested, which calls for a plot of $[\eta]M$ versus elution volume.[1] However, in general, it cannot be used for highly branched materials or polyelectrolytes.[2]

Accurate masses of the individual chains in disperse samples of synthetic organic polymers can now be obtained successfully by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry.[3] This relatively new method promises to become an important technique for the characterization of synthetic polymers. It also allows for the characterization of polymers which have undergone end group modification.[4] Especially in the field of dendritic molecules, it is a valuable tool for the determination of the homogeneity of the samples prepared.[5] Furthermore, the increasing interest in cyclic structures leads to applications of MALDI-TOF mass spectrometry to determine the composition of these materials since their structures prohibit end group analysis.[6] In this paper we report the aggregation behavior of macrocyclic amphiphiles of the general structure shown below and discuss the gas-phase aggregate formation of these macrocycles, as determined by MALDI-TOF.[7]



1: R^1 = Me; R^2 = n-hexyl (M = 1598.04)
2: R^1 = t-Bu; R^2 = n-hexyl (M = 1850.53)

Experimental Procedures

Materials. Macrocycles **1** and **2** were prepared via an oxidative coupling of the corresponding bis(acetylene)s according to the procedure we described recently.[8] All compounds were pure by HPLC and GPC. The GPC analysis exhibits a single monodisperse signal at the expected elution volume.[9]

Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) Mass Spectrometry. Mass spectrometry was carried out on a Bruker reflex spectrometer (Bruker, Bremen), incorporating a 337 nm nitrogen laser with a 3 ns pulse duration (10^6−10^7 W cm^{-1}, 100 μm spot diameter). The instrument was operated in a linear mode with an accelerating potential of 33.65 kV. The mass scale was calibrated using polystyrene (M_p = 6000), using a number of resolved oligomers.

MALDI-TOF Sample Preparation. Samples were prepared by dissolving the macrocycle in CH_2Cl_2 at a concentration of 10^{-4} mol L^{-1}. A 10 μL aliquot of this solution was added to 10 μL of a 0.1 mol L^{-1} matrix solution, dissolved in CH_2Cl_2. In all cases 1,8,9-trihydroxyanthracene (Aldrich, Steinheim) was used as the matrix.[10] A 1 μL amount of this mixture was applied to the multistage target and air-dried.

Results and Discussion

Figure 1 shows the MALDI-TOF mass spectrum of **1** (R^1 = Me; R^2 = *n*-hexyl; M_w = 1598.04). As expected, the peak with the highest intensity is observed at 1599 mass units. In addition to this signal, there are also peaks of high intensity at 3200, 4804, 6399, etc. mass units, which correspond to dimers, trimers, tetramers, etc. of macrocycle **1**. Each of these peaks is accompanied by several other peaks, equally spaced at 85 mass units apart, representing rings which have lost one or several of the hexyl side chains. The intensity of the peaks of the aggregated cycles strongly depends on the power of the laser beam used for the desorption/ionization of the sample. But even if the laser power is carefully adjusted to operate at the threshold energy, a considerable amount of dimer and a small amount of trimer is observed (Figure 2a).

Additionally, at 1825 mass units a signal for a cluster composed of a matrix (M_w = 226.23 Da) and an analyte molecule is observed in the spectrum.[11] When a mixture of two different macrocycles (macrocycle **1** and macrocycle **2**, R^1 = *t*-Bu; R^2 = *n*-hexyl; M_w = 1850.53 Da) was analyzed, we also could observe mixed dimers and trimers. Figure 2b shows the signals for the corresponding macrocycles, for their clusters with the matrix, and for the dimer of **1** (M_w = 3197 Da) and the dimer of **2** (M_w = 3701 Da), the mixed dimer of **1** and **2** (M_w = 3450 Da), the trimers of **1** (M_w = 4795 Da) and **2** (5551 Da), and the two mixed trimers (M_w = 5047 and 5299 Da).

There are in principle two pathways for the formation of these aggregates. They can be formed either during the preparation of the sample (condensed phase pathway) or during the vaporization of the matrix/analyte molecules (gas phase pathway). The fact that the amount of cluster formation increases with increasing laser power contradicts the asssumption that the clusters are formed during the sample preparation. Increasing laser power should, in this case, decrease the

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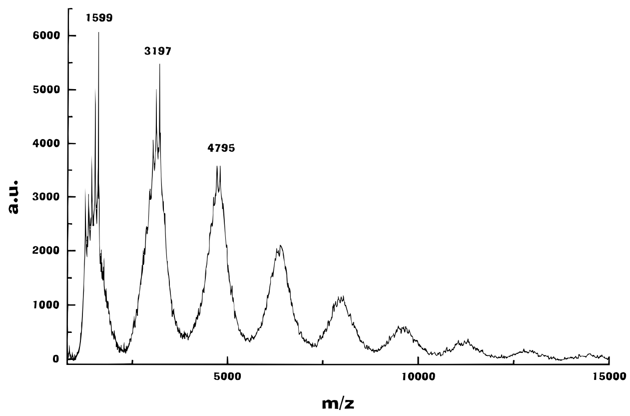

Figure 1. Mass spectrum of **1**, showing clusters of the ring up to the octamer. The splitting results from a different loss of hexyl side chains. Intensities are given in arbitrary units (a.u.).

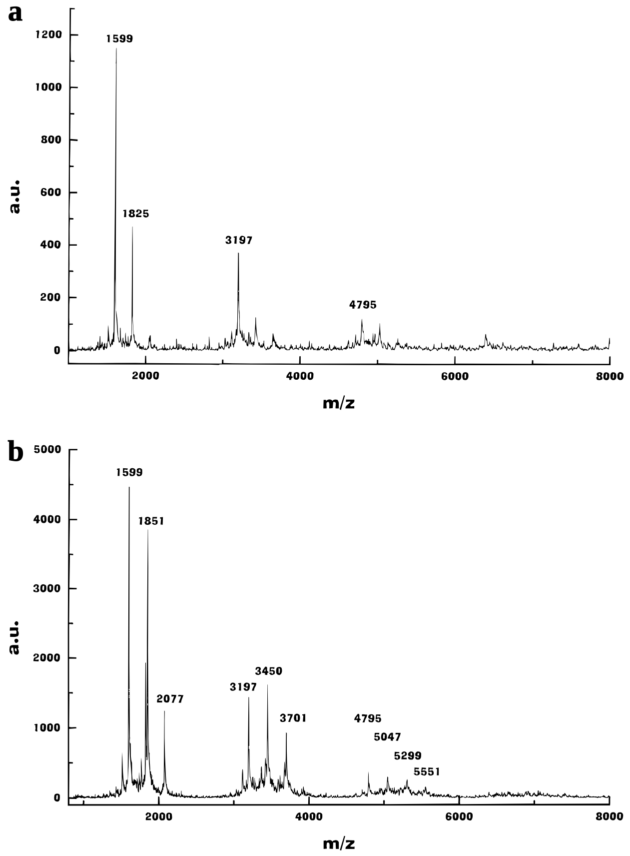

Figure 2. (a) Mass spectrum of **1** using a minimum of laser power. Dimers and trimers are easily observed together with clusters composed of matrix and analyte molecules. (b) Mass spectrum of a mixture of **1** and **2** showing the rings, their clusters with matrix molecules, the dimers of **1** and **2**, and the mixed dimer. A small amount of trimers and mixed trimers is also detectable.

amount of higher clusters due to a higher probability of splitting (as it is observed for the increasing loss of side chains with increasing laser power). Therefore, it is more probable that with increasing laser power the concentration of the analyte molecules in the gas phase increases and favors the formation of the clusters.

It is interesting to note that in all investigations thus far, only integer multiples of the molecular masses of the macrocycles are observed. This suggests that no other clusters, except for single charged ones are stable under the conditions employed.[12] The observation of sharp signals indicates that the clusters are formed immediately after the vaporization within a short period of time compared to the time of acceleration.

Although the origin of these cluster formations is not fully understood, one might speculate that the origin is π-stacking of the aromatic units of the more or less flat macrocycle or aggregation via hydrogen bonding between the polar phenoxy groups of the ring.[13]

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