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Studies of cyclic and linear poly(dimethylsiloxanes): 34 Preparation, fractionation and characterisation of the first per-deuterated macrocyclic poly(dimethylsiloxanes)

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Abstract

A range of per-deuterated cyclic poly(dimethylsiloxanes) (PDMS) have been conveniently prepared in a high dilution reaction from bis(trideuteriomethyl)diphenylsilane using a catalytic amount of trifluoromethanesulphonic (triflic) acid in the presence of water as proposed. The cyclic and linear per-deuterated polymers produced have been separated and the cyclics fractionated by preparative gel permeation chromatography (GPC). The resulting sharp fractions of per-deuterated cyclic PDMS have been obtained in up to 0.6 gram quantities ranging in size from 45 to 605 number–average number of skeletal bonds, all with dispersities less than 1.2. The purity of the samples obtained has been verified by various analytical techniques and these materials will allow the first studies of the conformations and properties of cyclic polymers in chemically identical blends using neutron scattering. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Per-deuterated poly(dimethylsiloxanes); Cyclic polymers; Neutron scattering

1. Introduction

Recently, we have reported the preparation and characterisation of small cyclic per-deuterated dimethyl siloxanes via a new convenient synthetic route [1]. The products were characterised by various analytical techniques and were shown to be mainly the per-deuterated cyclic tetramer, pentamer and hexamer. Small amounts of higher cyclic species (up to the nonamer) were also present.

Sharp fractions of larger per-deuterated cyclics are required in order that the conformational properties of cyclic polymers may be investigated in detail using neutron scattering techniques.

The preparation and characterisation of sharp fractions of hydrogenated cyclic and linear poly(dimethylsiloxanes) (PDMS) have been described in previous papers [2, 3]. Many sharp fractions have been obtained, each on a scale of several grams, using preparative gel permeation chromatography (GPC) [2]. The fractions consist of ring molecules ($((CH_3)_2\ SiO)_x$), with number–average numbers of skeletal bonds, n_n, up to ~ 700. A number of studies of cyclic PDMS have been made, comparing their properties with those of the corresponding linear polymers [4, 5]. For example, GPC retention volumes [2, 6], dilute solution viscosities [3], neutron scattering behaviour and radii of gyration in dilute solution [7] have all been investigated experimentally.

Here we report the preparation, fractionation and characterisation of per-deuterated cyclic PDMS for future use in studying the conformations of cyclic and linear PDMS in chemically identical blends.

2. Experimental

Both per-deuterated macrocyclic and linear PDMS have been prepared in one reaction from bis(trideuteriomethyl)-diphenylsilane ($(CD_3)_2SiPh_2$) by treating with a catalytic amount of trifluoromethanesulphonic (triflic) acid (CF_3SO_3H) at high dilution in dichloromethane in the presence of water.

The $(CD_3)_2SiPh_2$ was prepared from trideuteriomethyliodide (CD_3I) as detailed previously [1]. 145.0 g (0.665 mol) of the silane was dissolved in 220 ml of CH_2Cl_2 under a nitrogen atmosphere. 20.0 g (0.133 mol) of triflic acid was slowly added over 30 min and the solution gently stirred at room temperature. The concentrations were chosen such that complete conversion of the silane to siloxanes would result in an overall siloxane concentration of ~ 230 g l^{-1} shown by Brown and Slusarczuk [8] (in the case of PDMS in

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Table 1
Analytical GPC data for the sharp fractions of per-deuterated cyclic PDMS

Fraction	Weight Average Molar Mass M_w (g mol^{-1})	Number Average Molar Mass M_n (g mol^{-1})	Dispersity (M_w/M_n)	Number Average Number of Bonds (n_n)	Yield (g)
1	25 500	24 200	1.05	605	0.033
2	21 200	20 100	1.05	503	0.189
3	18 400	17 400	1.06	435	0.420
4	15 100	14 000	1.08	350	0.529
5	12 400	11 400	1.09	285	0.634
6	10 300	9300	1.11	233	0.638
7	8000	6900	1.16	173	0.597
8	6200	5400	1.15	135	0.551
9	4400	3900	1.13	98	0.518
10	3300	2900	1.14	73	0.482
11	2600	2200	1.18	55	0.388
12	2000	1800	1.11	45	0.216

toluene) and by Lebrun and coworkers [9] (in the case of PDMS in dichloromethane) to yield good amounts of cyclic PDMS in dilute solution conditions. The amount of triflic acid added was one tenth of the stoichiometric amount required to replace the phenyl groups with triflate groups as carried out in our earlier investigations of this reaction [1]. Once the triflic acid was completely added, one drop of de-ionised water was added and the reaction continued to be gently stirred at room temperature under nitrogen.

The reaction was monitored using gas liquid chromatography (GLC), and as observed previously [1], was seen to produce a series of phenyl terminated linear siloxane oligomers over time. Once the distribution of these oligomers was seen not to change with time a further drop of de-ionised water was added to the reaction. Eventually, the smaller siloxanes were produced via the reaction mechanism detailed in our previous paper [1] and the distribution of phenyl terminated linear oligomers was seen to reduce. Further evidence confirming our proposed mechanism came from the observation of turbidity in the reaction mixture after the addition of the water which was seen to clear after some time. This turbidity has been reported previously by Lebrun and co-workers [9] as a result of the water released on condensation of silanol groups produced in a ring/chain equilibration of hexamethylcyclotrisiloxane (D_3) with triflic acid in dichloromethane (such silanol groups would result here from the rapid hydrolysis of the highly reactive silyl triflates produced).

The cycle of dropwise addition of water and monitoring of the reaction by GLC until no further change in the distribution of products occurred, was continued for 10 days. (Once all of the phenyl groups have been removed from the reaction this becomes essentially a ring-chain equilibration as identified by Chojnowski and co-workers [10].)

Once equilibrated, a copious amount of sodium hydrogen carbonate ($NaHCO_3$) was added to neutralise the triflic acid. The dichloromethane solution was then washed several times with de-ionised water before being evaporated down under reduced pressure.

This resulted in 45.9 g of a clear colourless viscous oil containing a mixture of cyclic and linear polymers. The small cyclic per-deuterated dimethylsiloxanes were carefully distilled off this residue. The cyclics and high molar mass linear polymer in the residue were separated by precipitating the linear polymer from a hot solution of the equilibrate in acetone (10% w/v), allowing the solution to cool to room temperature and stand for 24 h. The supernatant solution containing the cyclics was decanted from the viscous linear polymer and the acetone removed by evaporation under reduced pressure yielding 6.5 g of polydisperse cyclic polymer.

3. Fractionation

The polydisperse per-deuterated cyclic PDMS recovered from the catalytic reaction was fractionated in to twelve sharp fractions using our preparative GPC instrument [2] with toluene as the chromatographic solvent. The fractions were analysed by analytical GPC calibrated with cyclic PDMS standards and the results of the analysis are shown in Table 1.

The toluene solvent used for the fractionation was removed from the samples by rotary evaporation and each of the sharp fractions was washed with small amounts (1–2 ml) of methanol to remove any traces of benzaldehyde or benzoic acid formed by the preparative instrument through the distillation of the solvent.

The molar masses of the cyclic fractions show a typical spread for a ring/chain equilibration reaction with ring sizes ranging from $n_n = 45$ (number–average number of bonds in a ring) up to $n_n = 605$ for the highest fraction obtained. The dispersities (M_w/M_n) of the samples were also typically low, all being less than 1.2.

The purity of the fractions were verified as previously using infrared absorption, mass spectrometry and ^{1}H, ^{13}C and ^{29}Si nuclear magnetic resonance spectroscopies [1].

4. Conclusions

Despite the extensive literature which is available on the behaviour of linear and cyclic polymers in dilute solution [4, 5], the static and indeed the dynamic properties of ring polymers in the melt remain largely unexplored. Only two limited SANS conformational studies of linear PDMS have been reported [11, 12].

Our aim is to investigate the conformations of cyclic polymers in the melt and compare these measurements with theoretical predictions [13–15], Monte Carlo calculations [16], computer simulations [17, 18] as well as to experimental SANS measurements in dilute solution [7, 19, 20]. We also intend to investigate the effect of topology on the motion of polymer molecules using incoherent and coherent quasielastic neutron scattering techniques.

The identification of a viable route which yields sufficient quantities of per-deuterated cyclic polymers to allow fractionation into very sharp fractions, now enables us for the first time to carry out such neutron scattering experiments investigating the conformations and properties of cyclic and linear polymers in chemically identical blends.

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