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# Supramolecular association of acid terminated polydimethylsiloxanes

## 1. Synthesis and characterization

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## Summary

Benzoic acid terminated polydimethylsiloxanes (PDMS) have been synthesized by hydrosilylation of allyloxybenzylbenzoate with SiH terminated precursors followed by deprotection. These oligomers have been characterized by $^{1}$H, $^{13}$C and $^{29}$Si NMR, by FTIR and by SEC in tetrahydrofurane. Because of the flexibility and low polarity of the siloxane backbone, they are ideally suited to study the effect of hydrogen bonding on macromolecular properties.

## Introduction

Interest in supramolecular association is growing rapidly, especially in the field of polymer science. The components, which can be low molecular weight compounds or macromolecules, are assembled by non-covalent interactions to yield higher molecular weight assemblies. Among non-covalent interactions, hydrogen bonding is the most popular because it is reasonably strong, it is directional and it can lead to complexes with a controlled stoichiometry.

For instance, side-chain liquid crystalline polymers have been built through self-assembly of a hydrogen bond donor (or acceptor) polymer and a hydrogen bond acceptor (or donor) low molecular weight compound (1,2). The resulting complex can be liquid crystalline even if both precursors are nonmesogenic (3). Main-chain liquid crystalline polymers have also been obtained by associating flexible diacids and rigid bispyridines in a way analogous to step-growth polymerization (4). To stabilize the intrinsically reversible structures obtained, tetrafunctional (5) or triply hydrogen bonded components (6) have been used. This topic of thermotropic liquid crystals formed by intermolecular hydrogen bonding interactions has been recently reviewed (7).

Introducing hydrogen bonds at the chain ends of telechelic polymers can also strongly affect their properties. Indeed, hydrogen bonding groups attached at the chain ends of poly(tetramethylene oxide) (8) and polyisobutylene (9) have been shown to be responsible for large modifications of rheological properties of the starting polymers. Hydrogen bonding groups have also been shown to induce liquid crystallinity in the case of several polymer backbones (10). These hydrogen bonded telechelic polymers have been studied to a lower extent than telechelic ionomers (11-14). This is probably due to the comparatively larger influence the formation of ionic clusters has on solution and bulk properties of polymers. Nevertheless, hydrogen bonded telechelic polymers are of interest because it is possible to induce only a dimerization of chain-ends instead of a multifunctional cluster. In this case, a reversibly chain-extended polymer is obtained which can be characterized by usual solution techniques.

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In order to thoroughly study bulk as well as solution properties of hydrogen bonded telechelic polymers, the polydimethylsiloxane backbone was chosen because of its very low glass transition temperature and of its low polarity which should enhance hydrogen bonding in the bulk polymer and which should also ensure solubility in low polarity solvents. For the hydrogen bonding part, the benzoic acid moiety was selected because it is well known to form stable dimers.

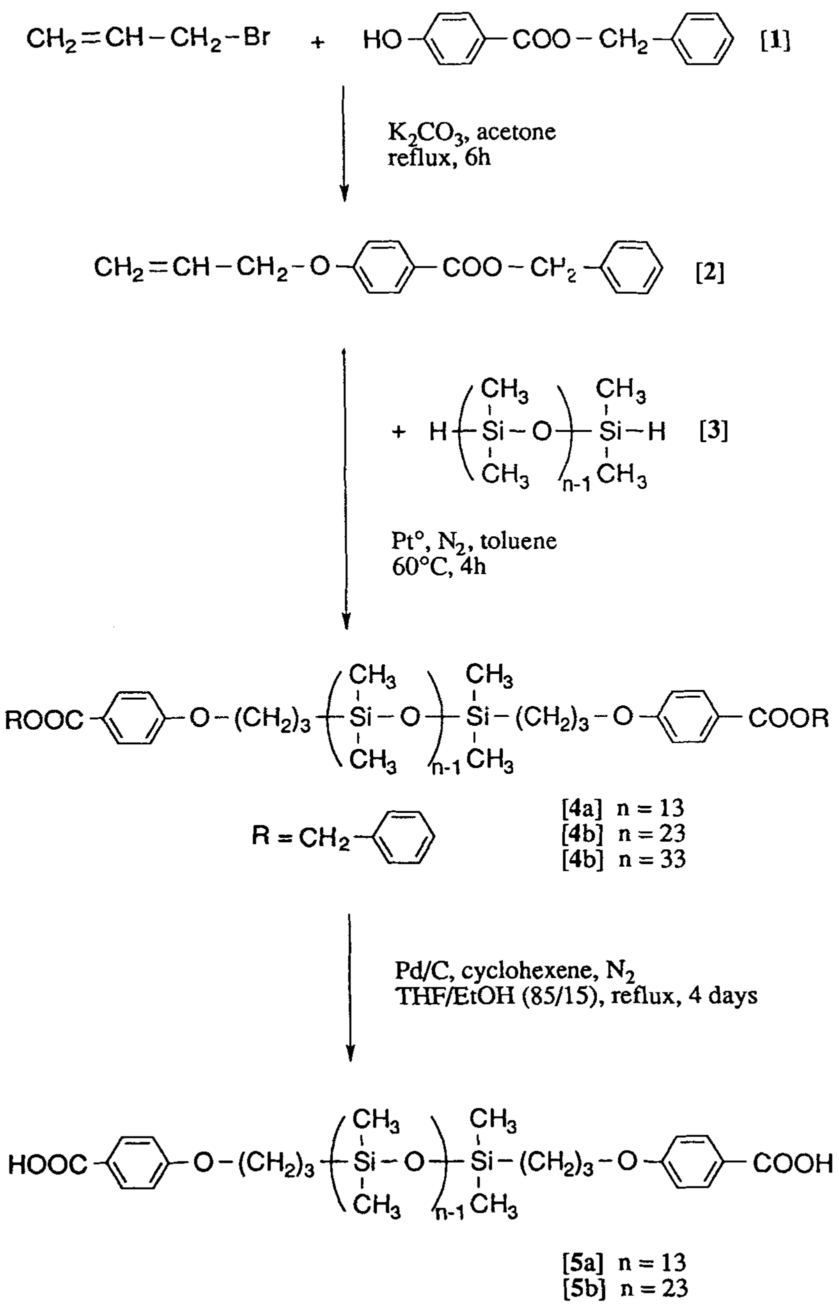
Synthesis and characterization of benzoic acid terminated PDMS are described in this paper. Their solution and bulk properties, as well as their supramolecular association with various hydrogen bonding building blocks will be published in forthcoming papers.

## Experimental

$^1H$, $^{13}C$ and $^{29}Si$ NMR spectra were recorded in $CDCl_3$ with a AM 200 SY Bruker apparatus, and FTIR spectra were recorded with a Vector 22 Bruker apparatus. SEC measurements were performed in tetrahydrofurane with UV and refractive index detections using a polystyrene calibration curve. The columns used were two PLGel mixed C 300. Refractive indices were measured with an Abbe refractometer and densities with a pycnometer at room temperature ($d_{PDMS} = 0.934$ and $d_{[2]} = 1.129$).

*Synthesis of para-allyloxybenzylbenzoate [2] :* in a round bottom flask, 2.00g ($8.76\ 10^{-3}$mol) of para-hydroxybenzylbenzoate [1] (Aldrich) and 0.83ml ($9.63\ 10^{-3}$mol) of allyl bromide (Aldrich) were dissolved in 10ml of acetone (Carlo Erba). Then, 1.21g ($8.76\ 10^{-3}$mol) of potassium carbonate (Prolabo) were added and the reaction mixture was refluxed for 6 hours. After solvent evaporation, 100ml of methylene chloride were added and the mixture was washed twice with 50ml of aqueous sodium hydroxide (2mol/l) and then with water. The organic phase was dried over magnesium sulfate, evaporated and purified by silica gel column chromatography with methylene chloride/hexane (3/1) as eluent. After evaporation of solvents, the desired liquid was obtained in 89% yield. $^1H$ NMR (ppm) : 8.0 and 6.9 ($C_6H_4$), 7.4 ($C_6H_5$), 6.1 ($CH=$), 5.4 ($CH_2=$), 5.3 ($COOCH_2$), 4.6 ($=CH-CH_2-O$).

*Ester terminated polysiloxanes [4a,b,c] :* 25.38g ($40.6\ 10^{-3}$mol of SiH) of $\alpha,\omega$ hydride terminated PDMS [3] (Rhône-Poulenc, $\overline{DP}_n = 17$, $I_p = 1.4$) and 10.95g ($40.9\ 10^{-3}$mol) of [2] were introduced in a round bottom flask. After purging with nitrogen, 26ml of toluene (distilled over sodium) and 24µl of platinum catalyst PC085 (platinum-cyclovinylmethylsiloxane complex from ABCR) ($[Pt]/[SiH] = 10^{-4}$) were added and the reaction mixture was heated at 65°C for 4 hours. Disappearance of the SiH band at $2125cm^{-1}$ was checked by FTIR. After solvent evaporation, the crude polymer was purified by silica gel column chromatography with hexane/methylene chloride mixtures as eluents (starting from pure hexane and finishing with pure methylene chloride). The collected fractions yielded 16.60g of a colourless liquid. By selecting the fractions, it is possible to collect several samples of different molecular weights and narrow molecular weight distributions. $^1H$ NMR (ppm) : 8.0 and 6.9 ($C_6H_4$), 7.4 ($C_6H_5$), 5.3 ($COOCH_2$), 4.0 ($CH_2-CH_2-O$), 1.9 ($CH_2-CH_2-O$), 0.7 ($Si-CH_2$), 0.1 ($Si-CH_3$), see figure 1a. $^{13}C$ NMR (ppm) : 166 ($COOCH_2$), 162/136/132/128/122/114 ($C_6H_4$ and $C_6H_5$), 70.6 ($O-CH_2$), 66.2 ($COOCH_2$), 23.1 ($CH_2-CH_2-CH_2$), 14.1 ($CH_2-Si$), 1.0 ($O-Si(CH_3)_2-O$), 0.1 ($CH_2-Si(CH_3)_2-O$). $^{29}Si$ NMR (ppm): 7.8 ($CH_2-Si$), -20.9 ($CH_2-Si-O-Si$), -21.6 ($-(Si-O)_n-$), see figure 2a.


CH2=CH–CH2–Br + HO–C6H4–COO–CH2–C6H5 [1]
K2CO3, acetone
reflux, 6h
CH2=CH–CH2–O–C6H4–COO–CH2–C6H5 [2]
+ H–(Si(CH3)2–O)n-1–Si(CH3)2–H [3]
Pt°, N2, toluene
60°C, 4h
ROOC–C6H4–O–(CH2)3–(Si(CH3)2–O)n-1–Si(CH3)2–(CH2)3–O–C6H4–COOR
R = CH2–C6H5
[4a] n = 13
[4b] n = 23
[4b] n = 33
Pd/C, cyclohexene, N2
THF/EtOH (85/15), reflux, 4 days
HOOC–C6H4–O–(CH2)3–(Si(CH3)2–O)n-1–Si(CH3)2–(CH2)3–O–C6H4–COOH
[5a] n = 13
[5b] n = 23

Scheme 1

*Acid terminated polysiloxanes [5a,b]* : deprotection was performed according to literature procedure (1a). In a round bottom flask, 3.42g (5.02 $10^{-3}$mol of benzyl ester functions) of $\alpha,\omega$ ester terminated PDMS [4a], 0.551g of Pd/C catalyst (10% Aldrich), 86ml of tetrahydrofurane and 16ml of absolute ethanol were introduced. After purging with nitrogen, 7.6ml (7.5 $10^{-2}$mol) of cyclohexene (Aldrich) were added and the reaction mixture was refluxed for 4 days. Disappearance of the ester carbonyl vibration at 1720cm$^{-1}$, and appearance of the acid carbonyl vibration at 1690cm$^{-1}$ were checked by FTIR. After filtration and solvent evaporation, the crude polymer was purified by silica gel column chromatography with methylene chloride/tetrahydrofurane mixtures as eluents (starting from pure methylene chloride and finishing with pure tetrahydrofurane). The collected fractions yielded 1.78g of a white solid. $^1$H NMR (ppm) : 8.1 and 6.9 ($C_6\mathit{H}_4$), 4.0 ($CH_2$-$C\mathit{H}_2$-O), 1.9 ($C\mathit{H}_2$-$CH_2$-O), 0.7 (Si-$C\mathit{H}_2$), 0.1 (Si-$C\mathit{H}_3$), see figure 1b. $^{13}$C NMR (ppm) : 172 ($\mathit{C}$OOH), 164/132/121/114 ($\mathit{C}_6H_4$), 70.6 (O-$\mathit{C}H_2$), 23.1 ($CH_2$-$\mathit{C}H_2$-$CH_2$), 14.1 ($\mathit{C}H_2$-Si), 1.0 (O-Si($\mathit{C}H_3$)$_2$-O), 0.1 ($CH_2$-Si($\mathit{C}H_3$)$_2$-O). $^{29}$Si NMR (ppm) : 7.8 ($CH_2$-*Si*), -20.9 ($CH_2$-Si-O-*Si*), -21.6 (-(*Si*-O)$_n$-).

## Results and discussion

### *Synthesis*

Different methods have been reported for the synthesis of carboxylic acid terminated polydimethylsiloxanes. Carboxypropyl terminated PDMS have been synthesized by equilibration polymerization of cyclic siloxanes and functional disiloxanes in the presence of acid catalysts (15,16) or by reacting lithium silanolate end groups of living PDMS with a suitable terminating agent (17). Chemical modification of chlorosilane terminated oligosiloxanes (18) or hydrosilylation of unsaturated and protected acids by Si-H terminated polysiloxanes (19,20) have also been reported.

The route we have selected is also based on hydrosilylation : the three step synthesis is detailed on scheme 1. The first step affords para-allyloxybenzylbenzoate [2] in high yield (89%) from benzyl bromide and para-hydroxybenzylbenzoate [1]. The unsaturated ester is then hydrosilylated with Si-H terminated polysiloxane [3] ( $\overline{DP}_n = 17$, $I_p = 1.4$) to give benzyl ester terminated polysiloxane [4]. This polymer is purified and fractionated by silica gel column chromatography, so that three fractions are isolated : [4a], [4b] and [4c]. Each fraction can then be deprotected and again purified by chromatography to yield pure benzoic acid terminated polydimethylsiloxanes [5a] and [5b]. Hydrosilylation was performed on protected benzoic acid [2] both to avoid side reactions which would occur with the acid moiety and because benzyl ester terminated PDMS [4] will be used as a reference to monitor the influence of hydrogen bonding on properties of benzoic acid terminated PDMS [5].

### *Characterization*

All five polymers [4a], [4b], [4c], [5a] and [5b] have been characterized by $^1$H, $^{13}$C and $^{29}$Si NMR and FTIR. Figure 1 shows the $^1$H NMR spectra of [4a] and [5a]. It can be seen that the chain ends are well characterized and that only $\beta$-addition has occured. Table 1 shows the degrees of polymerization determined from integrations. $^{29}$Si NMR is a very convenient tool to check the nature of chain ends of siloxane polymers. The spectrum for [4a] is displayed on figure 2 : no trace of SiH or SiOH can be detected (they would appear at around -7 or -10 ppm, respectively).

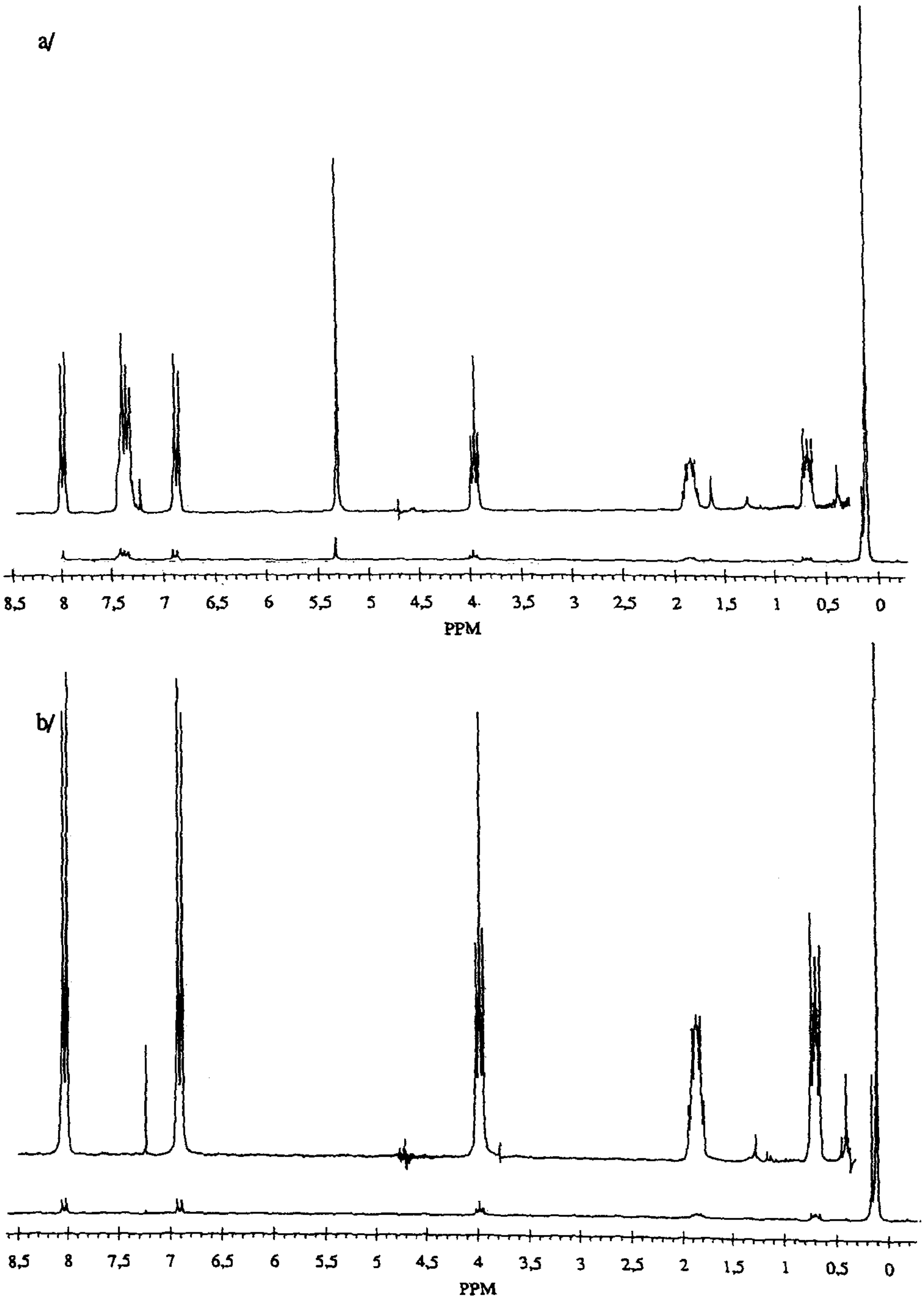


Figure 1 : $^1$H NMR of a/ ester terminated polysiloxane [4a] and b/ acid terminated polysiloxane [5a]

### *Size exclusion chromatography*

In order to measure the polydispersity of the polymers, size exclusion chromatography (SEC) has been performed in THF. Unfortunately, the usual refractive index detection cannot be used because of the large dependence of refractive index on the degree of polymerization. Indeed, PDMS is a low refractive index polymer ($n_{PDMS} = 1.404$) and the chain ends have a high refractive index : the refractive index of [2] is $n_{[2]} = 1.576$. It is possible to estimate the refractive index of polymer [4] as a function of the degree of polymerization by calculating the molar refractivities (21) : the results are displayed on figure 3. Refractive index of oligomers shorter than 50 repeating units decreases by more than 0.1. This variation is much larger than that already reported for other oligomers (22-24) and it is clear that if the refractive index detection is used to measure average molecular weights, the longest oligomers will be underestimated (refractive index of THF is $n_{THF} = 1.407$).

As a consequence, a UV detector ($\lambda = 260$ nm) has been used, bearing in mind that the signal delivered by the UV detector is not proportionnal to the weight concentration of the polymer in solution but to its molar concentration, because only the chain ends absorb at 260 nm. If we define $h_i$ as the height of the signal corresponding to the polymer fraction of molecular weight $M_i$, then : $\overline{M}_n = \frac{\sum h_i M_i}{\sum h_i}$ and $\overline{M}_w = \frac{\sum h_i M_i^2}{\sum h_i M_i}$. Using this modified treatment, degree of polymerization and polydispersity index have been calculated (see table 1). Degrees of polymerization determined by SEC (polystyrene equivalent) are in good agreement with NMR results. Moreover, polydispersity is narrower than for the starting polymer [3] because of fractionation during silica gel column chromatography.

### *Influence of hydrogen bonding on properties*

Eventhough their molecular weights are identical, polymers [4a] and [5a] have very different properties. For example, ester terminated PDMS [4a] is a liquid at room temperature whereas acid terminated PDMS [5a] is a white solid which melts at 46°C. A more thorough characterization is under way, but it is already clear that hydrogen bonding is at least partly responsible for these differences : FTIR spectrum of [5a] shows only one carbonyl absorption at 1690cm$^{-1}$ which is characteristic of benzoic acid dimer.

## Conclusion

We report on the synthesis and characterization of benzoic acid terminated polydimethylsiloxanes. Because of the flexibility and low polarity of the siloxane backbone, these oligomers are ideally suited to study the effect of hydrogen bonding on macromolecular properties. Furthermore, they will be used to prepare supramolecular architectures with other hydrogen bonding building blocks.

| polymer | $\overline{DP}_n$ ($^1$H NMR) | $\overline{DP}_n$ (SEC in THF) | $I_p$ (SEC in THF) |
|---|---|---|---|
| [4a] | 13 | 14 | 1.2 |
| [4b] | 23 | 28 | 1.2 |
| [4c] | 33 | 44 | 1.1 |
| [5a] | 13 | 14 | 1.1 |
| [5b] | 23 | 30 | 1.2 |

Table 1 : Degree of polymerization and polydispersity index of ester terminated polysiloxanes [4a], [4b] and [4c] and acid terminated polysiloxanes [5a] and [5b], determined by $^1$H NMR and by size exclusion chromatography in THF.

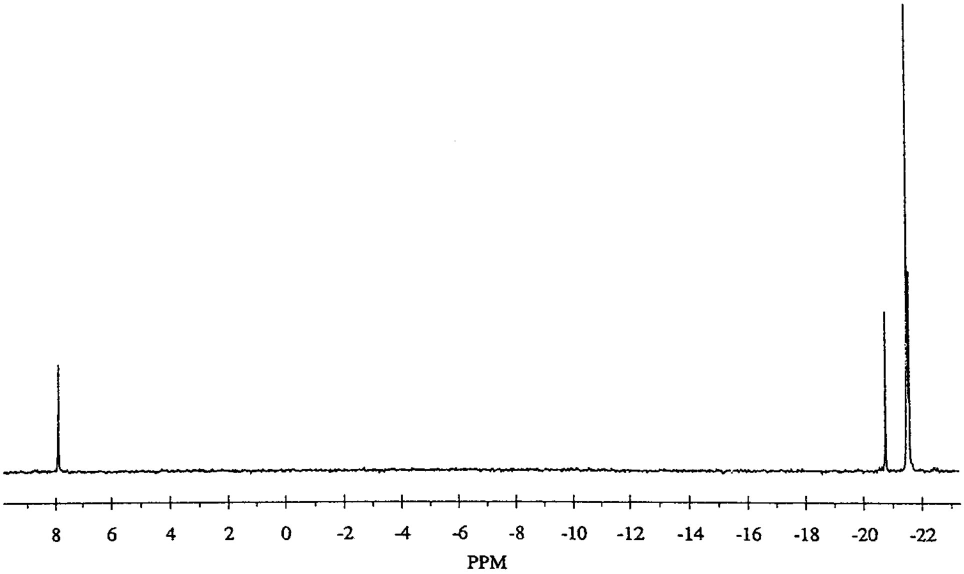


Figure 2 : $^{29}$Si NMR of ester terminated polysiloxane [4a]

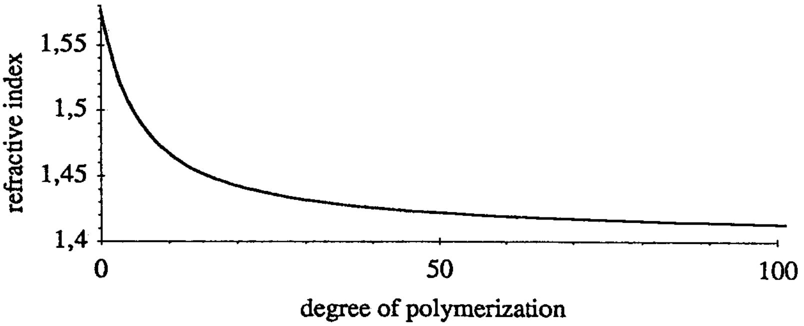


Figure 3 : Calculated refractive index of ester terminated polysiloxane [4] versus degree of polymerization

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