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Note

Novel liquid crystalline resins based on MQ siloxanes ☆

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Abstract

MQ siloxane resins containing Si–H functions have been made from tetramethyldisiloxane and tetraethoxysilane. Hydrosilylations with mesogenic alkenes give low molecular weight liquid crystal MQ resins with potentially useful properties.

Keywords: Liquid crystalline polymers; Polysiloxanes; Resins; Phase behavior; WAXS

1. Introduction

Studies on the synthesis and applications of structurally diverse side chain liquid crystal polymers have grown exponentially over the last 20 years [1]. Their improved mechanical resistance compared to low molecular weight liquid crystal materials is of great practical importance. For many applications, such as displays, optical data storage materials, switches and shutters, etc., linear, high molecular weight materials exhibit a too long response time, when supramolecular orientation is achieved by changes in external electric or magnetic fields. [2] Therefore, much current research concentrates on so called hybrid liquid crystals of intermediate molecular weight, especially oligomers such as cyclic [3,4], linear [5,6] siloxanes, and structures of globular shape, having topologies giving decreased viscosity in melt, while preserving the robust mechanical properties of polymers (silsesquioxanes, dendritic and dendrimeric systems [7,8]).

Current research in this area proved that many structures of intermediate molecular weight (especially cyclic siloxanes) exhibit the fast electro-optical response of low molecular weight liquid crystals and can find therefore a number of applications [9]. Industrial standards for electro-optical devices are becoming ever more demanding and a search for new LC materials of such the type is still a challenge. Cost effectiveness is also an important factor.

Well-defined siloxane monomers can serve as models for studies of structure–property relations, but they are much less important as applied materials [10]. An attempt to attach mesogenic substituents to mixtures of cyclic siloxanes $(MeRSiO)_x$, where $R =$ mesogen and $x = 6–20$, led to liquid crystalline materials whose properties were not reproducible. Fractions of cyclic siloxanes were obtained by simple distillation and therefore their composition varied over a wide range [4].

2. Experimental

2.1. Materials and methods

Dichloromethane, methanol, HCl aq. 35–36%, $MgSO_4$, butanol, NaOH and Karstedt's catalyst ($Pt_2[(ViMe_2Si)_2O]_3$, 3–3.5% of Pt in xylenes) (ABCR) have been used as supplied. Toulene was dried by standard methods and stored over a molecular sieves.

4-(pent-4-enyloxy)-benzoic acid 4-methoxyphenyl ester [$CH_2{=}CH(CH_2)_3OC_6H_4C(O)OC_6H_4OCH_3$], (S)-2-chloropentanedioic acid 5-ethyl ester 1-(4′-undec-10-enyloxy-

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☆ "M" stands for Me_3SiO–, "D" for Me_2SiO_2=, "T" for $MeSiO3$= and "Q" for =O_2SiO_2=.

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biphenyl-4-yl) ester [$CH_2{=}CH(CH_2)_9OC_6H_4C_6H_4O(O)$-$CCH(Cl)CH_2CH_2C(O)OC_2H_5$] were made according to literature methods [11,12].

All organometallic syntheses were carried out under argon with exclusion of moisture. The ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions with a Bruker AC 200 or a Bruker DRX 500 spectrometers. IR spectra were obtained with an ATI Mattson spectrometer for polymer solutions in sodium dried toluene.

Molecular weights were measured by gel-permeation chromatography (GPC) using a Waters system with Wyatt/Optilab 902 Interferometric Refractometer, calibrated for monodisperse polystyrene standards. MALDI TOF spectra were recorded on a Voyager Elite spectrometer equipped with a N_2 laser working at 337 nm, operating in the linear mode. Dithranol was used as a matrix and NaI as the cationising agent.

Phase transitions were verified by optical microscopy, DSC and X-ray diffraction studies. Thermal phase behaviour was studied with differential scanning calorimetry (DSC) using a DuPont DSC-910, calibrated with an indium standard. Wide angle X-ray scattering (WAXS) techniques have been used to characterize the structure. Measurements have been performed at room temperature using a θ–θ diffractometer (Siemens), as well as a 2D position sensitive detector with a pin–hole collimation of the incident beam. Cu Kα radiation ($\lambda = 0.154$ nm) was used. The 2D scattering patterns have been recorded for filaments macroscopically oriented by extrusion in the temperature range ~10–20 K below the isotropization temperature, using a mini-extruder described elsewhere [13].

2.2. Preparation of the Si–H functionalised resin (M^HQ)

Tetraethoxysilane (100 g, 0.48 mol) and 1,1,3,3-tetramethyldisiloxane (85.5 g, 0.48 mol) were dissolved in toluene (200 cm^3) and stirred at 50 °C. Aqueous HCl (114 cm^3 of 37% solution) was added drop-wise over a period of 3 h and the reaction mixture was stirred for additional 30 min. The organic layer was separated, washed three times with water and dried over $MgSO_4$. Solvent was stripped off, yielding the resin of $M_n = 540$ and $M_w = 650$ (GPC calibrated for polystyrene standard). The proportion of linear (branched) to cyclic siloxanes was 1:2 (as determined by MALDI-TOF analysis). It shows that individual components of the resin have real molecular weight between 950 and 1580 Da. The content of Si–H bonds, based on gasometric titration with BuONa was 9.9 mmol/g. ^{1}H NMR ($CDCl_3$) $\delta = 4.25$ (m, SiH,), 3.85–3.75 (m, OCH_2CH_3), 1.25–1.15 (m, OCH_2CH_3,), 0.15–0.10 (m, $SiCH_3$,).

2.3. Hydrosilylation of mesogenic alkenes with M^HQ resin (an example)

$CH_2{=}CH(CH_2)_9OC_6H_4C_6H_4OC(O)CH(Cl)(CH_2)_2C(O)$-$OCH_2CH_3$ (1 g, 1.94 mmol) and M^HQ resin were dissolved in dry toluene and stirred under argon. Platinum tetramethyldivinyldisiloxane (PTDD) complex in xylenes (10^{-4}

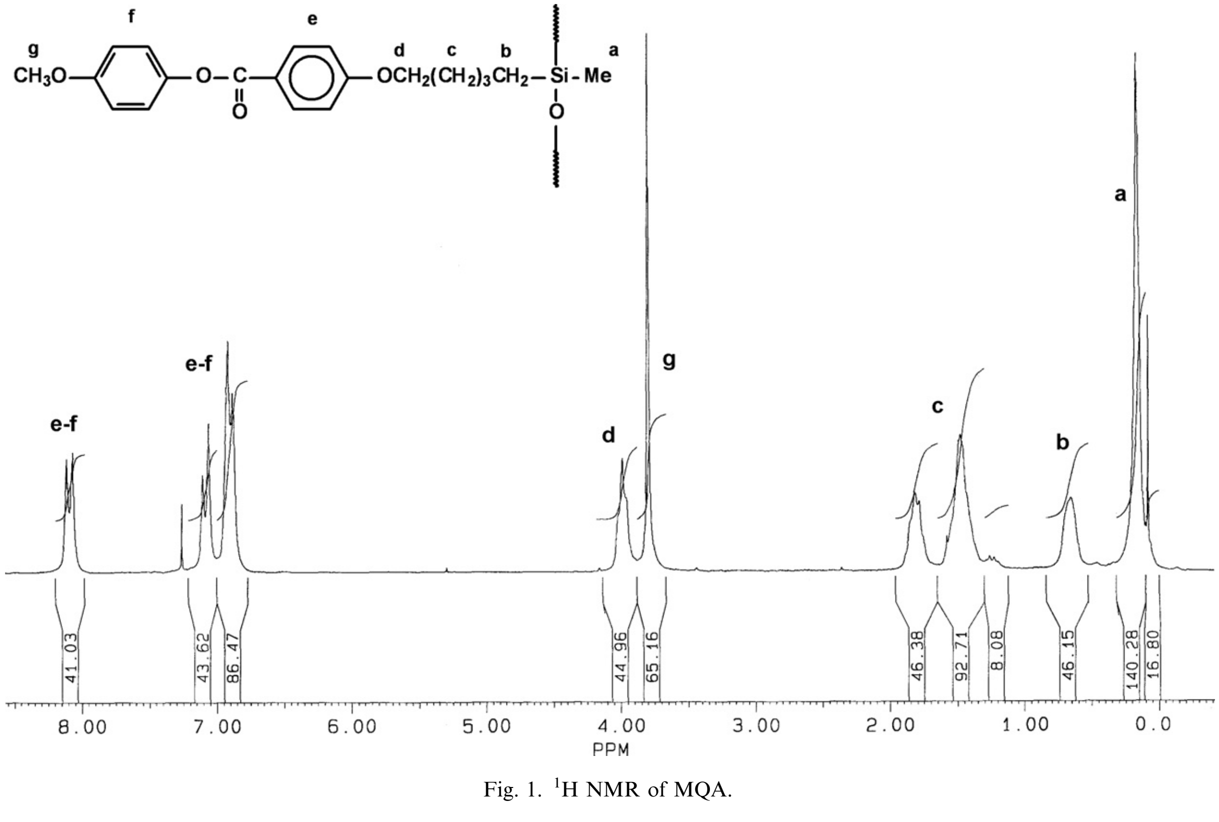


Fig. 1. ^{1}H NMR of MQA.

mol Pt/mol SiH) was added and the reaction mixture was stirred at 60 °C. Reaction progress was followed by FTIR (disappearance of Si–H absorption band at $2150\,\mathrm{cm}^{-1}$). The reaction was stopped after 24 h and solvent was removed on vacuum, leaving yellowish solid. The liquid crystalline MQ resin was purified by multiple precipitation from dichloromethane/methanol and dried (75 °C, 1 mmHg). Yield: 81%. The structure was proved by ^1H NMR (Fig. 1).

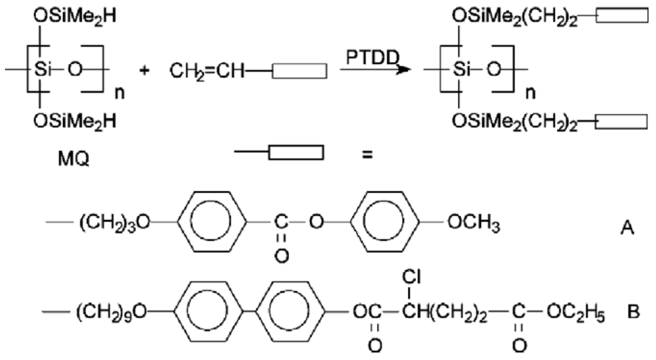
3. Results and discussion

The use of M^HQ resins ($R_nSiX_mO_y$, where $R = CH_3$, $X = H$, $n + m + y = 4$) as a novel anchoring backbone for mesogens opens up a way to a new group of readily available hybrid liquid crystalline materials. MQ resins themselves, including those bearing reactive groups, have been widely used for pressure release adhesives, silicone rubbers, coatings and additives [14]. Currently vinyl functionalised $M^{Vi}Q$ resin platinum complexes are used as silicone-soluble hydrosilylation catalysts [15].

Some of them are available commercially. Contrary to the use of fractions containing cyclic siloxanes [3,4] their simple synthesis offers highly reproducible M^HQ resin compositions, obtained in an equilibration process. Such resins were further used for hydrosilylation of mesogenic alkenes in a single step process, catalysed by platinum tetramethyldivinyldisiloxane (PTDD), leading to liquid crystalline materials with over 80% yield of purified samples (Scheme 1).

Within the limits of detection it appears that the hydrosilylation occurs according to the anti-Markovnikov principle. The integration ratio of ^1H resonances (Fig. 1), centered, respectively, at 0.50 ppm (CH_2Si) and 4.05 ppm (CH_2O) is 1.03, whereas in the case of α-addition product and formation of the Si–CH(CH_3) bond the integration ratio should be much less than unity. Thus, at each $\sim$Si(OSiMeH)$_2$–O$\sim$ moiety two mesogenic side chains are attached with a uniform structural arrangement.

Differential scanning calorimetry (DSC) has shown, that the MQ resin provides the same useful features as typical linear and cyclic siloxanes in promoting liquid crystalline properties for originally non-mesogenic low molecular weight alkenes [6,11]: Mesogen A – C 90 °C I [6]; resin MQA – C 53 °C SmA1 75 °C N 98 °C I; mesogen B – C 93.9 °C I [11]; resin MQB – C 44.8 °C SmC * 86.1 °C N* 107.4 °C I (C – crystal, Sm – smectic, N – nematic, I – isotropic liquid).



Scheme 1. Hydrosilylation of M^HQ resin with M/Q = 2.

The relevant textures from polarised optical microscopy (POM) are presented in Fig. 2, corresponding to a lamellar smectic phase (MQA) (2a) and a smectic C* (MQB) (2b). In the latter case ferroelectric properties were generated using mesogen (B) having a chiral carbon centre.

The types of liquid crystal phases were confirmed using wide angle X-ray scattering (WAXS), as shown for MQB in mechanically (Fig. 3a) and magnetically (Fig. 3b) oriented samples, quenched to room temperature. The temperature range of generated mesophases, using MQ resin (being an equilibrium mixture) of linear, branched, cyclic and cage siloxanes turns out to be even slightly broader than for well defined organosilicon liquid crystal polymers studied in the past. For a side chain polycarbosilane (Mn = 4500) with mesogen B it is 58 °C [12], compared to 62 °C for MQB. In the case of systems bearing mesogen A, it is 44 °C for cyclic hexasiloxane10, 58 °C for side chain polycarbosilane

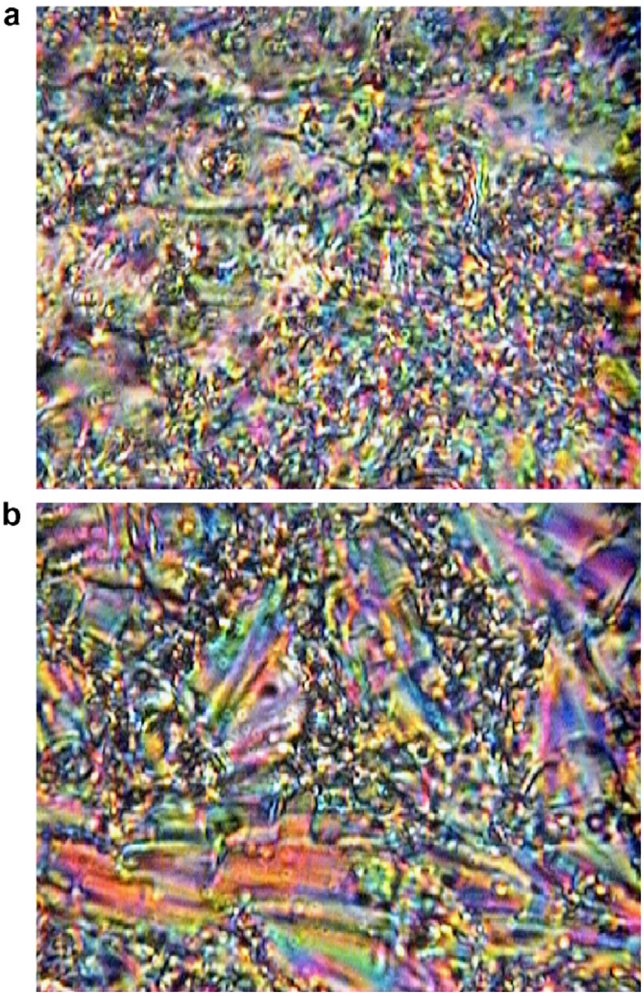


Fig. 2. Microphotographs (400×) of (a) MQA at 60 °C (b) MQB at 75 °C.

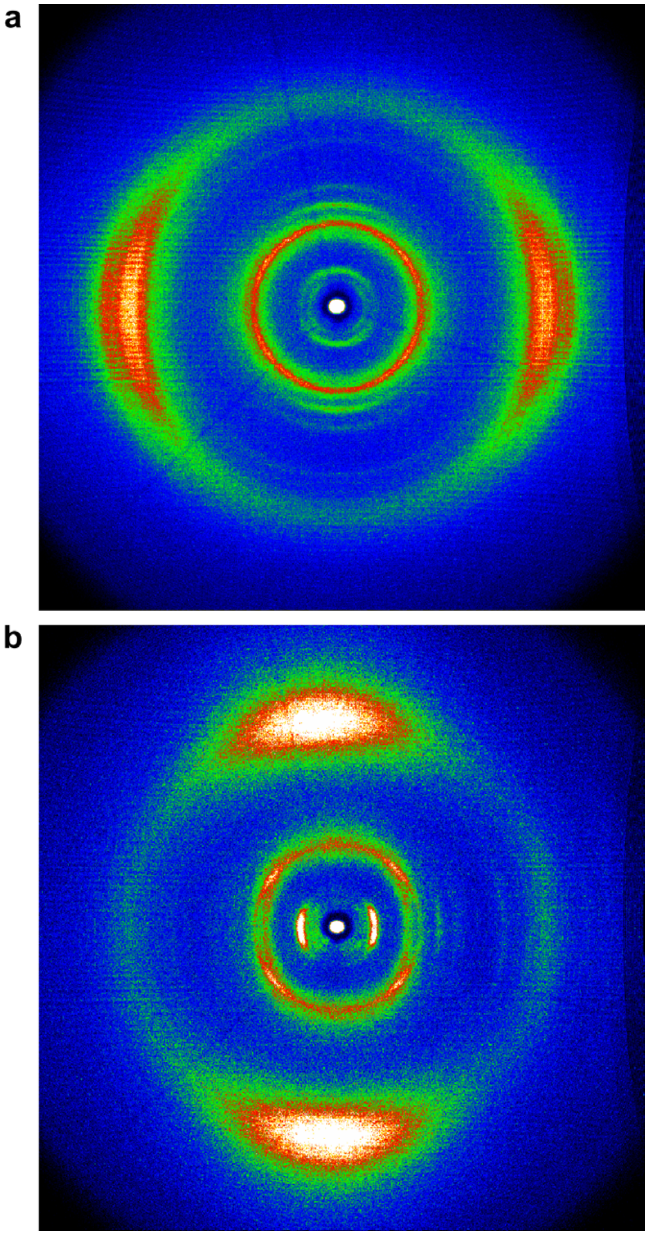


Fig. 3. WAXS of MQB (a) oriented mechanically at 55 °C and (b) oriented magnetically at 85 °C.

(Mn = 4300) and 48 °C for analogous polysiloxane[13] compared to 62 °C for MQA. These novel group of MQ resin-anchored liquid crystals seem, thus, to promise a wide field of potential application.

In summary, this report describes for the first time the successful use of $M^{H}Q$ resins as a polymeric backbone for hybrid liquid crystalline materials. The simple and effective hydrosilylation pathway of mesogenic alkenes with inexpensive type of resins, containing Si–H bonds, leads to a new group of versatile materials. We are currently carrying out more detailed studies devoted to this novel generation of siloxane-based liquid crystals, having a useful temperature range of mesophase formation (the transition to the liquid crystal phase occurs slightly above room temperature, which is important for a variety of electro-optical applications). The effect of structure of mesogenic alkenes and the composition of $M^{H}Q$ resin, made at variable M/Q ratio, is being studied.

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