NEW SILOXANE COPOLYMERS WITH PENDANT AZOMETHINE MESOGENIC UNITS

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Two siloxane copolymers containing pendant mesogenic units were synthesized by reacting the chloromethyl groups of a siloxane precursor copolymer with potassium phenolates of aromatic azomethine mesogens. Their structure was confirmed by spectral methods (FT-IR and NMR) and their thermotropic behavior was studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD). Both copolymers showed liquid crystalline behavior over a large temperature range, with isotropization interfering with thermal decomposition. However, in comparison with previously reported telechelic siloxane oligomers containing similar mesogenic groups, lower melting temperatures and more ordered mesophase were observed in the case of the copolymers. Thermogravimetric analysis (TGA) and molecular modeling were used to better understand and complete the thermotropic investigations.

INTRODUCTION

Aromatic polyazomethines contain a $sp^2$-hybridized nitrogen atom in the main chain and belong to a well known class of conjugated polymers which kept the scientific interest, both in fundamental and applicative research.1-3 Their specific properties claim potential applications, such as: high thermal stability required in aerospace technology, nonlinear optical and thermotropic liquid crystalline behavior, electro and photoluminescence, semiconducting properties, ion complexing ability, anticorrosion activity, mechanical resistance, fiber-forming ability, environmental stability, etc.2-5

On the other hand, polysiloxanes have high flexibility, good resistance to extreme temperatures, oxidant agents and ultraviolet radiation, very low glass transition, good gas permeability and biocompatibility, but they exhibit rather poor mechanical properties. The increasing interest in copolymers based on polydimethylsiloxane is due to their unique combination of properties and new applications, such as nanomaterials, actuators, superhydrophobic surfaces, liquid crystals etc.6-11

Owing to the properties of the two partners and knowing that liquid crystals (LCs) are nowadays one of the most active research fields, from both theoretical and applicative approaches, the study of the thermotropic behavior of siloxane-containing polyazomethines is an interesting and actual topic. Besides the liquid crystalline properties, other aspects are of interest, like for example the ease of
processing. The wholly aromatic poly(azomethine)s have high melting or softening temperatures and low solubility. One way to reduce the transition temperatures and to improve their solubility is the introduction of siloxane segments as flexible spacers between the rigid conjugated aromatic azomethine moieties. In our group a large variety of poly(siloxane-azomethine)s, having ether or ester links have been synthesized.\textsuperscript{12-24} These compounds were obtained mainly by polycondensation reactions, either by using preformed azomethine bisphenols or by reacting organic dialdehydes with siloxane diamines. Special attention has been payed to the preservation of the siloxane chain integrity. The complexation capacity was also investigated, as well as their thermotropic properties or self assembling behavior.

In this paper we describe the preparation of new polysiloxanes with azomethine pendant groups, by chemical modification reactions, starting from a poly(dimethyl-methylchloromethyl)siloxane precursor and preformed azomethine phenolates. The optical textures were investigated by using polarizing optical microscopy (POM), while the thermal transitions have been measured by DSC and compared with those of linear polymers previously obtained with the same mesogens.\textsuperscript{12}

\section*{RESULTS AND DISCUSSION}

The chemical modification of a dimethylmethylchloromethyl siloxane copolymer with potassium salts of aromatic azomethine mesogenic phenols has been made according to Scheme 1.

The starting siloxane copolymer (CM) was obtained by hydrolysis of chloromethyl dichlorosilane, followed by a redistribution reaction with octamethylene cyclic tetrasiloxane (D4), in heterogeneous catalysis. According to the \textsuperscript{1}H-NMR results, after distillation of the formed cyclosiloxanes and volatile fraction, the resulting copolymer had a -CH$_2$Cl group content of \textasciitilde50\%, higher than the prescribed value (which was 30\%, molar) (Fig. 1a). This is probably due to different reactivity of the symmetrically and asymmetrically substituted siloxane units and to the lower boiling point of the dimethylcyclosiloxanes and small linear dimethylsiloxane oligomers, which were thus easier removed by distillation.

The CM precursor had a number average molecular weight $M_n = 24240$, with a polydispersity index of 1.8 determined by GPC in chloroform.

\begin{center}
\includegraphics[width=\textwidth]{Scheme1.pdf}
\end{center}

\textbf{Scheme 1 – Synthesis of siloxane precursor copolymer CM and copolymers CLP1 and CLP2.}
New siloxane copolymers

The copolymers CLP1 and CLP2 have been prepared by the reaction of pendant chloromethylene functional groups with potassium phenolate groups of the mesogenic compounds, having preformed azomethine moieties. We chose this reaction in order to preserve the siloxane chain. The same compounds could have been obtained by direct reaction of the -CH₂Cl groups in the siloxane copolymer precursor with the mesogenic phenols, in presence of K₂CO₃, but in such conditions, the siloxane chain could have been broken in some degree. By transforming the phenols into phenolates, which are isolated and purified, the probability of this unwanted side reaction is significantly reduced.

The ¹H-NMR confirmed the reaction and the integrity of the siloxane chain. As can be observed in Fig. 1b, in the reaction product all the expected protons are present, in the correct ratio. In the modified copolymer, significant shifts of the protons in CH₂ groups (from 2.75 to 3.51 ppm) and CH₃ from the same Si atom (from 0.3 to 1.23 ppm) were observed, compared with CM. This could be explained by the pronounced polarity of the aromatic azomethine moieties, and could also be an effect of the polar solvent (DMSO) used for NMR analysis of the modified polysiloxane.
The precursors and the reaction products were analyzed by FTIR spectroscopy. First we verified the integrity of the azomethine bond after treatment with excess KOH solution. Based on FTIR data registered after 2 days, it seems that in our reaction conditions, no significant changes occurred, so that the pre-existing azomethine groups were not affected.

In the reaction products we monitored the disappearance of C-Cl absorption band at 654 cm$^{-1}$, and the presence in the IR spectrum of absorption bands specific for polysiloxanes at: 800 cm$^{-1}$, 1026 cm$^{-1}$, 1100 cm$^{-1}$ and 1260 cm$^{-1}$, besides those in aromatic azomethines at: 1606 cm$^{-1}$, 1588 cm$^{-1}$ (aromatic) and 1623 cm$^{-1}$ (CH=N). As can be observed in Fig. 2, the C-Cl band disappeared completely in the spectra of CLP1 and CLP2. Also, the large and shifted siloxane band at 1026-1100 cm$^{-1}$ has the same aspect (large, shifted and asymmetrical) corresponding to substituted copolymers, as in the precursor.

The differential scanning calorimetry (DSC) analysis in the low temperature range revealed single glass transition temperatures, at -52°C for CLP2 and at 21°C for CLP1 (measured in the second heating scan). The absence of phase separation according to DSC results indicates unitary behavior of substituted and unsubstituted siloxane segments, probably due to the balanced chemical composition (about 50% substitution). These temperatures are higher than that of CM (-114 °C), which shows increased chain rigidity due to the pendant aromatic branches. The higher $T_g$ value for CLP1 is due to the longer aromatic moiety. The much higher values of glass transition temperature also indicate the successful chemical modification reactions.

The thermotropic behavior of the siloxane copolymers with pendant azomethine groups was investigated by polarizing optical microscopy (POM) and DSC. The thermal transitions and the main optical observations are summarized in Table 1 and
Figs. 3 and 4. For comparison, the LC behavior of the starting mesogens and a telechelic siloxane oligomer having AM1 chain ends and 10 dimethylsiloxane units\textsuperscript{12,25} are also included in Table 1.

Both CLP1 and CLP2 showed thermotropic liquid crystalline (LC) properties over a large temperature range. Compared to the starting aromatic mesogenic phenols and to telechelic polysiloxanes\textsuperscript{12} important decrease of both melting and isotropization temperatures were obtained when the mesogen was attached in the lateral position to a polysiloxane chain. On the other hand, the isotropization temperature remained very high, interfering with the thermal decomposition. Thus, the mesophase range was extended. By mesophase range we mean the difference: $T_{\text{LC-I}} - T_{\text{Cr-LC}}$, where: $\text{Cr} = \text{crystalline phase}$; $\text{LC} = \text{liquid crystalline phase}$; $\text{I} = \text{isotropic phase}$.

A better defined texture, evidencing a more ordered mesophase, was obtained for the copolymers than for the telechelic oligomers, which exhibited only nematic textures.\textsuperscript{12} By POM, CLP1 first developed a grainy texture, followed by a focal conic texture, which is typical for a smectic A mesophase (Fig. 3 a, b). In the DSC thermogram (Fig. 4), three endothermic transitions were detected, before the onset of the decomposition process.

Fig. 3 – POM microphotographs of: CLP1 a) 120 °C, magnification 200x; b) 195 °C, magnification 400x; c) 244 °C, magnification 400x; CLP2 d) 230 °C, magnification 200x.

Fig. 4 – DSC curves of copolymers CLP1 and CLP2 during the first heating scan.
Table 1
Thermotropic properties of the copolymers CLP1 and CLP2, determined by POM

| Copolymer | Transition temperatures (°C) | ΔT
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<tr>
<td>AM1(^1)</td>
<td>Cr 285 LC &gt;330</td>
<td>&gt;45</td>
</tr>
<tr>
<td>AM2(^2)</td>
<td>Cr 242 N &gt;330</td>
<td>&gt;88</td>
</tr>
<tr>
<td>CLP1</td>
<td>Cr 100 LC 170 SmA 195 N &gt;240 I</td>
<td>&gt;140</td>
</tr>
<tr>
<td>CLP2</td>
<td>Cr 95 LC1 150 LC2 200 N &gt;235 I</td>
<td>&gt;140</td>
</tr>
<tr>
<td>Oligomer(^2)</td>
<td>Cr 170 LC &gt;300</td>
<td>&gt;130</td>
</tr>
</tbody>
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\(^1\)Cr crystalline; LC liquid crystalline; SmA smectic A; N nematic; I isotropic;
\(^2\)Mesophase temperature range, ΔT = T\(_{LC\rightarrow I}\) – T\(_{Cr\rightarrow LC}\)

The copolymer CLP2 showed slightly lower transition temperatures and similar mesophase range in comparison with copolymer CLP1. When investigated by POM, the copolymer CLP2 exhibited only a granular texture, prior to the nematic phase (Fig. 3 d). The granular texture could be an indication of a smectic mesophase.\(^2\) Additionally, in the DSC thermogram, three endothermal peaks (the last one very faint) were detected within the scanning range (Fig. 4 b). In order to verify the hypothesis of a smectic ordering for copolymer CLP2, powder WAXD measurements were performed at room temperature, since LC compounds presented often small or medium angle diffraction peaks, below the melting temperature, due to preservation of the high distance order. As can be seen from Fig. 5, some peaks in the medium angle region, fit well the mesogenic length, as was verified by molecular modeling.\(^2\)

The differences observed in the thermotropic behavior between the azomethine-side-group siloxane copolymers (CLP1, CLP2) and the telechelic polysiloxanes\(^1\) might have an explanation in the chain microstructure, i.e. single phase, balanced composition random copolymers versus phase separated organo-inorganic oligomers. The lower melting temperatures registered for CLP1 and CLP2, compared with the starting mesogens and with the telechelic oligomers can probably be explained on the one hand by the highly flexible structures, as indicated by the low Tg values, and, on the other hand, by the chain conformation (suggested by molecular modeling) – which is bulky and forms a loose helix (Fig. 5).

As mentioned above, in both copolymers, the isotropization was observed only by POM. The degradation process occurred almost simultaneously. That was the reason why in Table 1 only the onset of isotropization-degradation process, based on POM data, was given. The samples became completely isotropic at 300°C. The TGA-DTG analysis confirmed the microscopic observations concerning the beginning of thermal degradation. The results for sample CLP2 are presented in Fig. 6. The onset of the thermal degradation was found at around 230 °C and two degradation processes were registered under 700°C. The first DTA peak, centered at 300 °C, corresponds to 10% weight loss. This process could be assigned to the break of the ether bonds. The second degradation process, occurring between 400 and 600 °C, was assigned to the breakage of the other bonds in the copolymer (azomethine bonds, aromatic rings, Si-C). A large amount of residue (48%) was registered, which is mostly due to silica formed and possibly ceramic materials.
EXPERIMENTAL

Materials

All reagents and solvents were high purity commercial products (Fluka) and were used as received. The catalyst for equilibration reaction, Purolite CT175, a macroporous styrene – divinylbenzene copolymer with sulfonic groups (exchange capacity 1.87 meq/ml) was supplied by Viromet. It was conditioned by successive washings with water, 4% NaOH solution, 4% HCl solution, water, dehydration by azeotrope distillation with toluene and vacuum drying.

Measurements

The infrared spectra were registered on a Bruker Vertex 70 FT-IR instrument, in transmission mode, in the 300-4000 cm⁻¹ range (resolution 2 cm⁻¹, 32 scans), at ambient temperature. ¹H-NMR spectra were registered on 400 MHz Brüker spectrometer in CDCl₃ or DMSO-d₆, without internal standard. GPC measurements were made in THF on a PL-EMD 950 evaporative mass detector instrument. The calibration was made with polystyrene standards. The thermotropic behavior was investigated by differential scanning calorimetry (DSC), using a Perkin Elmer scanning calorimeter, with heating and cooling rates of 10°C/min, and by polarizing optical microscopy (POM) using an Olympus BH-2 microscope fitted with a THMS 600/HSF91 hot stage and a digital camera attached to the ocular. PowderXRD spectra were registered on an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation. The as acquired spectra were then converted to Cu-Kα wavelength. Thermo-gravi metric analysis (TGA) was made on a Mettler 681e Instrument, in N₂, with 10oC/min, between 20 and 700 °C.

New siloxane copolymers

The compound has been synthesized according to the previously reported procedure.¹² Equimolar amounts of the phenolic azomethine derivative of benzidine and p-nitrobenzaldehyde were reacted in DMSO. Yield 80 %. Mp. 213 °C. Elemental analysis:  C₃₆ H₂₇ N₃ O₃; calcd.: N % 9.97; found: N % 9.52. IR (KBr, cm⁻¹): 3460 (O-H), 1624 (CH=N), 1600, 1576 (C=C aromatic), 1514 (NO₂ asym.), 1341 (NO₂ sym.), 852, 832 (1,4-phenylene ring).

Synthesis of dimethyl-methylchloromethyl siloxane copolymer (CM)

Poly(methylchloromethyl)siloxane has been obtained by acid hydrolysis of methylchloromethylchlorosilane with distilled water, in ethyl ether, followed by neutralization, separation and drying. Poly(methylchloromethyl)siloxane (1g, 9.2 mmole siloxane units) and octamethylcyclotetrasiloxane (D₄, 1.6g, 21.6 mmole siloxane units) were mixed and then 0.065g Purolite CT175 cation exchanger was added (2.5 % wt.). The equilibration reaction proceeded at 80 °C for 8 h. The reaction mixture was filtered with chloroform and the catalyst was filtered off. The solvent was removed, then the siloxane volatile fractions were distilled at 120 °C and 2 mm Hg. ¹H-NMR (δ, ppm, CDCl₃): 2.75 (m, 2H, CH₂), 0.30 (m, 3H, CH₃-Si- CH₂), 0.07 (m, 6H, (CH₃)₂Si<).

Synthesis of the copolymer CLP2

The phenolate of the azomethine AM1 was obtained by titrating the phenol AM1 with KOH in methanol, followed by solvent evaporation. The siloxane copolymer (0.042 g) dissolved in THF, was mixed with the mesogenic phenolate (0.127 g) dissolved in DMF and the reaction mixture was stirred at 110 °C for 33 h. After removal of the solvents by distillation, the reaction product was washed with water, then extracted with chloroform. The soluble fraction was concentrated at rotatory evaporator, then dried under vacuum over night. ¹H-NMR (δ, ppm, DMSO-d₆): 8.91, 8.54 (m, 2H, CH=N), 8.38-6.64 (m, 16 H, aromatic), 3.51 (s, 2H, CH₂),
1.23 (s, 3H, CH$_3$-Si), 0.08 (m, 6H, (CH$_3$)$_2$Si<). The copolymer CLP1 was obtained in a similar manner.

**CONCLUSIONS**

Two siloxane copolymers containing pendant azomethine mesogenic units were synthesized by chemical modification reaction of a siloxane precursor copolymer, having a 1/1 chloromethyl/dimethylsiloxane units ratio, with potassium phenolates of two aromatic azomethine mesogens. Their structure was confirmed by spectral methods and their thermotropic behavior was studied by POM, DSC and WAXD. Both copolymers showed LC behavior, presenting a wide temperature range mesophase, with isotropization interfering with thermal decomposition. A comparison between the side chain azomethine copolymers and the telechelic oligomers, previously reported by us, revealed that lower melting temperatures and more ordered mesophases were observed in the case of side-chain copolymers.

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