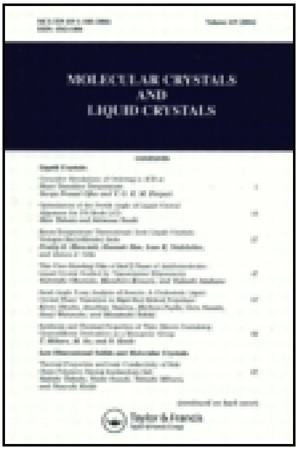

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Synthesis and Characterization of Siloxane Contained Liquid Crystalline Polymers with Two Symmetric Mesogens

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SYNTHESIS AND CHARACTERIZATION OF SILOXANE CONTAINED LIQUID CRYSTALLINE POLYMERS WITH TWO SYMMETRIC MESOGENS

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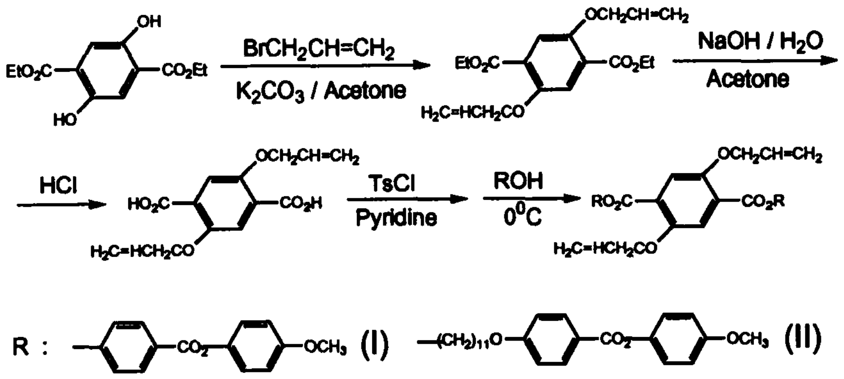
Abstract New thermotropic siloxane contained liquid crystalline polymers with two symmetric mesogens were prepared by hydrosilation with $Rh(PPh_3)_3Cl$ catalyst. It was found that $Rh(PPh_3)_3Cl$ catalyst was effective for low molecular weight polymerization. The resulting polymers exhibited good solubility in organic solvents such as tetrahydrofuran(THF), chloroform, and so on. The structures of the monomer and polymers were confirmed by IR, ^1H and ^{13}C NMR spectra. The number average molecular weight($\overline{Mn}$) values of the polymers were in the range of 2000~6000. Thermal properties of the monomers and the polymers were analyzed by differential scanning calorimetry(DSC), and polarized optical microscopy. Monomers did not show liquid crystalline phase but the polymers exhibited nematic phases.

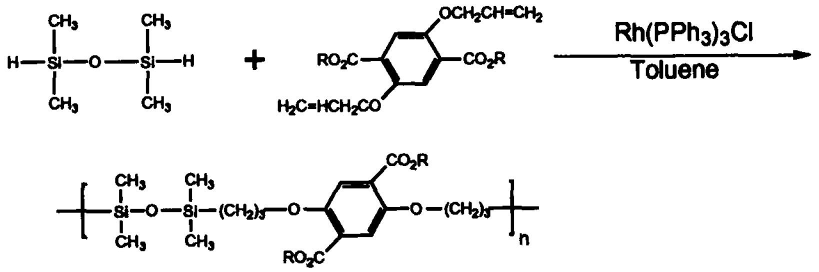
INTRODUCTION

Thermotropic liquid crystalline polymers are receiving considerable research interest for special application in piezo, pyro, and ferroelectric devices and in data storage systems[1]. Most of the studies of side chain LC polymers to date have been concerned with materials in which the mesogenic groups are attached to a flexible polymer backbone(polysiloxane[2,3], polyacrylate, and polymethacrylates[4,5], etc). The glass transition of the polyacrylate is lower than those of the corresponding polymethacrylates. This difference obviously is due to the higher flexibility of the polyacrylic backbone, thus the spacer group actually decouples the motions of the side groups and the main chain of these polymers. Consequently a futher lowering of Tg should be possible by attaching the mesogenic groups to a highly flexible backbone. In this respect, polysiloxanes can be a good backbone for fast switching and low Tg. Although the Si-O bond is strong, accounting for the high thermal stability of poly(organosiloxane), the rotational energy of the Si-O bond is low. As a result, conformational changes in backbone may easily occur [6,7,8] Hence, research attention shifted to their application as materials into which information could be written and then stored. In this paper, we describe the preparation and properties of the siloxane contained liquid crystalline polymers with two symmetric mesogens.

Scheme 1



Scheme 2



EXPERIMENTAL

Esterification of acid

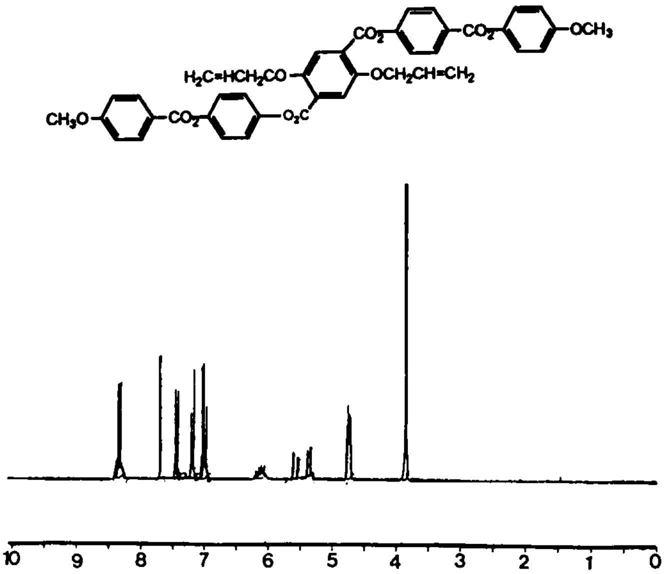
The following is esterification procedure for monomer synthesis. The acid(1.0g, 0.0036mol) is dissolved in anhydrous pyridine(15ml) and p-toluenesulfonyl chloride(2.7g, 0.0144mol) is added. The solution is kept cold for 3h and then poured into water. Solid esters are collected by filtration. A crude product was purified by column chromatography on silicagel using a mixture of ethyl acetate and hexane as an eluent; yield 40~60%.

Polymerization

The monomer(1.0g) was dissolved in 5ml of freshly distilled toluene together with one equivalent of 1,1,3,3-tetramethyldisiloxane. The reaction mixture was heated to 90^{0}C under nitrogen and then 0.001g of Rh(PPh_3)$_3$Cl was added. The reaction mixture was stirred for 2 days. The polymers were separated and purified by several precipitations from tetrahydrofuran solution into methanol and further purified by acetone and then dried under vacuum.

Analysis

^{1}H-NMR spectra were recorded on a Brucker AM 300 spectrometer and IR spectra were obtained on a Bomem Michelson series FT-IR spectrometer. The differential scanning calorimetry (DSC) was recorded on a Dupont 9900 analyzer. A heating rate of 10^{0}C was utilized.



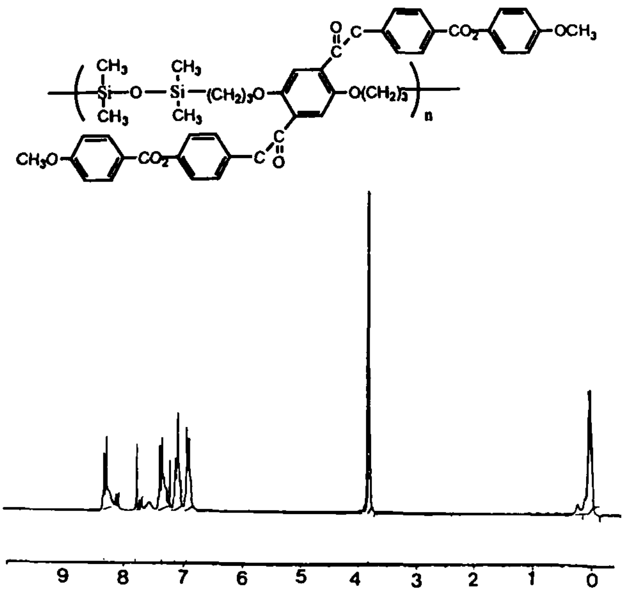


FIGURE 1. ^{1}H-NMR spectra of Monomer(I) and Polymer(I)

RESULTS and DISCUSSION

Monomer and polymer structures were characterized by IR, NMR, and DSC. The molecular weights of polymers were detected with $\overline{Mw}$=2000~6000 from GPC. The ^{1}H-NMR spectra of monomer and polymer are shown in Figure 1. As the hydrosilation proceeded, allyl proton peak at about 4.7-6.3 ppm disappeared. Figure 2 shows the stretching vibration for Si-O-Si of polymer nearly in 1070 cm^{-1}.

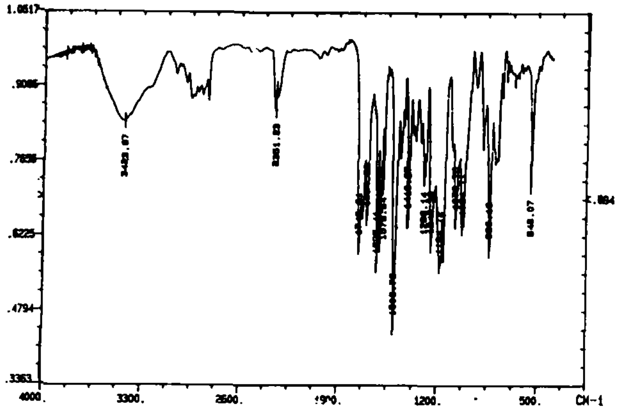


Figure 2. FT-IR spectrum of Polymer(I)

Polymer II with its long spacer was highly soluble in various organic solvents such as chloroform, THF, and 1,4-dioxane. On the other hand, polymer I was partially soluble in organic solvents because of its short spacer length. Figure 3 shows DSC thermograms of first heating for the siloxane contained liquid crystalline polymers with two symmetric mesogens. The transition from the liquid crystalline state to isotropic state was relatively broad which is probably due to low molecular weight of the polymeric product. In polymer II, two endothermic peaks are observed at T_{NI}=135^{0}C and Tm=80^{0}C. Polymer I shows the higher endothermic peaks at T_{NI}=255^{0}C and Tm=155^{0}C compared with those of polymer II. The high temperature endothermic peak is due to the transition from the isotropic to the nematic phase which was confirmed by microphotographs.

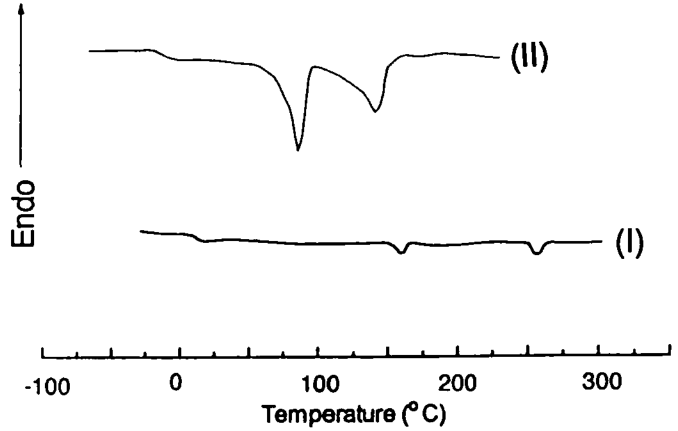


FIGURE 3. DSC Thermogram of Liquid Crystalline Polymers (10^{0}C/min)

From the observed data, we can discuss about the role of a flexible spacer. Since polymer II has 11 methylene units spacer, its Tg and Tm rapidly decrease. The region of liquid crystallinity, the stability of the mesophase, Tm, and Ti are strongly depending on the spacer length. When polymer I and II were heated, shileren textures corresponding to a typical nematic mesophase were formed. It is interesting to observe that monomers did not show liquid crystalline phases on heating, but polymers exhibited nematic phases. We are still studying siloxane contained liquid crystalline polymers with various mesogens and the role of flexible spacer length.

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