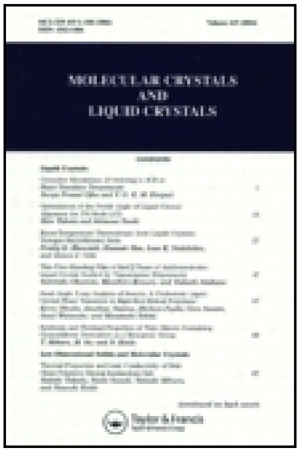

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gmcl19

The Synthesis of Side-Chain Liquid Crystalline Polymethylsiloxane Containing Benzo-15-Crown-5 Unit

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To cite this article: Chun Wu, Qing Jiang, Yong-Chang Zhen & Ming-Gui Xie (1997): The Synthesis of Side-Chain Liquid Crystalline Polymethylsiloxane Containing Benzo-15-Crown-5 Unit, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 304:1, 31-39

To link to this article: http://dx.doi.org/10.1080/10587259708046940

Mol. Cryst. Liq. Cryst., 1997, Vol. 304, pp. 31–39
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THE SYNTHESIS OF SIDE-CHAIN LIQUID CRYSTALLINE POLYMETHYLSILOXANE CONTAINING BENZO-15-CROWN-5 UNIT

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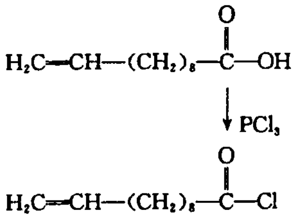
Abstract Side-Chain liquid crystalline polymethylsiloxane containing 4-(4′-undecylenoyloxy) benzoyl amino benzo-15-crown-5 used as stactionary phase for capillary gas chromatogrophy was synthesized. The polymer showed nematic phase. The main chromatographic characteristics, including polarity and selectivity, were examined. The results showed the side-chain liquid crystalline polymethylsiloxane containing benzo-15-crown-5 stationary phase possessed the behaviours of liquid crystal staionary phase.

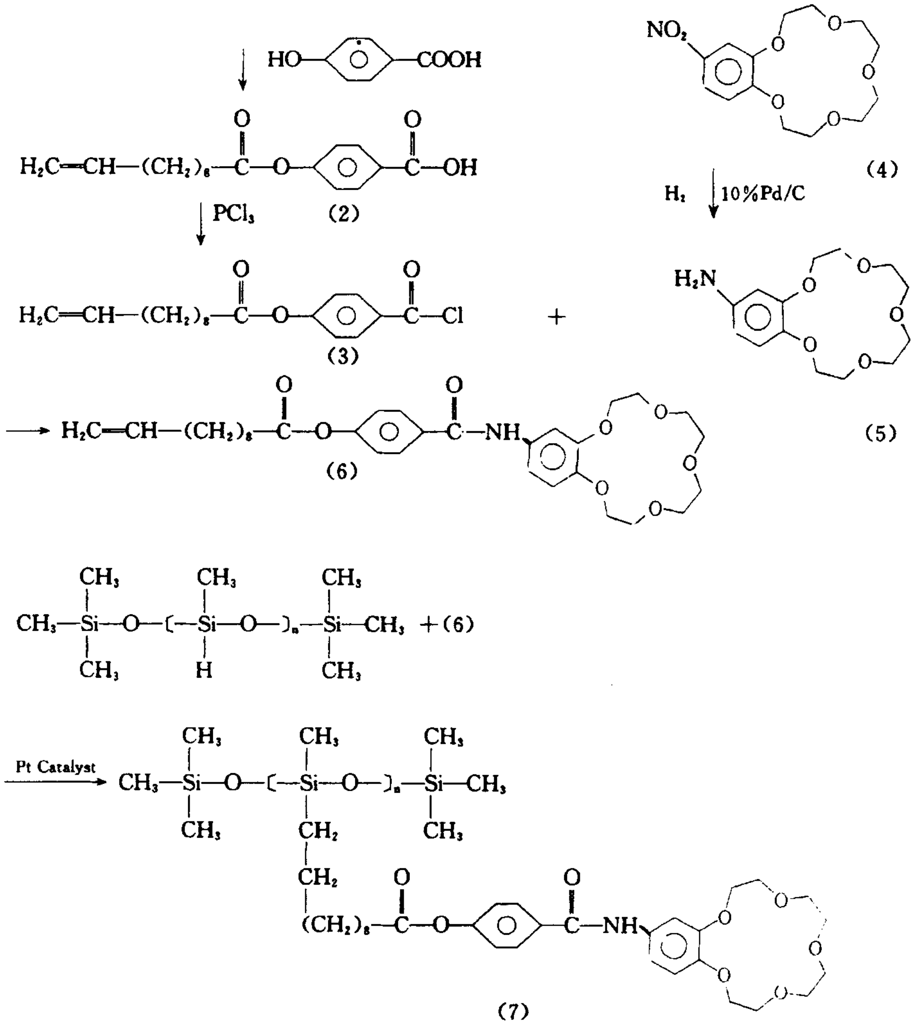
INTRODUCTION

The research of liquid crystalline polymers containing crown ether as stationary phase for CGC is an active field in chromatographic analyses at the precent time. Although the high selctivity of liquid crystal stationary phase combining with high efficiency by using capillary columns was obtained[1,2], several factors, such as its low bleed temperature[3] and insolubility in common organic solvents[4], have hindered its applications. Since the heat resistance of amide is better, we designed and synthesized an amido side-chain liquid crystalline polymethylsiloxane containing crown ether, with which used as stationary phase for capillary gas chromatography.

SCHEME OF SYNTHESIS



$$\begin{array}{c} H_2C{=}CH{-}(CH_2)_8{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH \\ \Big\downarrow PCl_3 \\ H_2C{=}CH{-}(CH_2)_8{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl \end{array}$$



EXPERMENTAL SECTION

Instrument.

Infrared spectra were recorded on Perkin Elener PC FI-IR Spectrometer as neat films on KBr Plates. ^{1}HNMR spectra were recorded on a JNM FX-90Q spectrometer. MS were carried out on Finnigan-Mat 4501 GC-MS spectrometer. Elemental analyses were obtained on Carlo Erba 1106. Differential scanning calorimetry (DSC) were obtained from a Perkin-Elangr Model DSC-7. Textures were taken on XPT-7 Microscope with Polariscope made in Jiangnan Opteal Instrument Factory with the attachment of a heat plate.

Reagant.

Polymethylsiloxane ($\overline{M}$ 3164, H% 1.58, DP50) was obtained from the Center of Organic Silicon Sichuan, China. 10% Pd/C was prepared according to the procedure of R. Mojing[5]. Other reagent were dehydrated and then redistilled.

The Synthesis of Intermediates and Title Compound.

10-undecenoylchloride (1). 50mL (0.246mol) 10-undencenoyl acid and 7mL (0.081mol) PCl_3 were mixed in 250mL three-neck round-bottom flask equipped with a reflux condenser and a dry tube. The mixture was stirred for 24h at 30℃, After it was placed motionlessly, the mixture was seperated into two layers: the upper layer was red-brown liquid, the lower layer was dark-brown solid (H_3PO_3). The upper layer was removed to obtain compound(1). $n_d^{20} = 1.4541$ ($n_d^{20} = 1.454$[6]).

4-undecylenoyloxy benzoic acid, (2). 17g (0.123mol) p-hydroxy-benzoid acid dissolved in 100mL of dry pyridine in 250mL three-neck round-bottom flask equipped with a reflux condenser, a drying tube, a droping funnel and a magnetic stirrer. The mixture was stirred at 30℃ for 48h, then was added to 200mL of distilled water. The solution was acidified with 20% aqueous hydrochloric acid until pH = 2, which caused a large numer of light-yellow solid floating on the water. The solid was filtrated at reduced presure and then washed with water till it became neutrality. The crude product was recrystallized twice from dry ethanol, yielding 31g (83.8%) of white plate crystals. m.p. 130-132℃ (131.5-132℃[7]).

4-undecylenoyloxy benzoic acid chloride (3). 3g (6.57mmol) of 4-undecylenoyloxy benzoic acid dissolved in 20mL of $CHCl_3$ and 25ml PCl_3 in 100ml three-neck round-bottom flask equipped with a reflux condenser, a drying tube and a magnetic stirrer. The mixture was stirred for 30h at 30℃. After it was placed motionlessly a few miniutes, the mixture was seperated into two layers: the upper layer was light-yellow liquid while the lower layer was black solid (H_3PO_3). The upper layer was distilled under vacuum to removed solvent and the excess of PCl_3. A few dry benzene was added to the mixture, then the mixture was redistilled under vacuum to remove PCl_3. The resulting residue was light-yellow viscous liquid, and light-yellow solid on cooling. It was compound (3) .

4-(4′-undecylenoyloxy) benzoyl amino benzo-15-crown 5 (6). 4-nitro-benzo-15-crown-5(4) was synthesized according to the precedure of Ungarok[8]. To a stirred solution of

1.5g (4.79mmol) 4-nitro-benzo-15-crown-5 in 20mL of dry dioxane, 0.3g 10% Pd/C was added. The solution was heated to 70℃ with vigorous stirring under H_2 for 12h. The catalyst was filtered. The filtrate was added dropwise to the solution of new-produced 4-undecylenoyloxy benzoic acid chloride (3) dissolved in 20mL dioxane and a few drops of dry pyridine. The mixture was heated to 70℃ with stirring for 48h under a nitrogen atmosphere. After it was placed motionlessly a few miniutes, the mixture was separated into two layers: the upper layer was yellow liquid, the lower layer was brown solid (Pyridinum chloride). The upper layer distilled under vacuum to remove solvent. The residene was red-brown oil liquid, when it became light-yellow globery solid on cooling, the crude product was recrystalled twice from ethanol to obtain compound (6), yielding 1.7790g (64.3%) white crystal. mp. 124.7℃. IR (KBr) 3296.0 (N-H); 1756.0 ($C=O$); 1638.0 (C—NH); 1604.0, 1015.0 (Ph); 986.0 ($CH_2=CH$); MS (m/z) 570(M+1)$^+$; ^{1}HNMR ($CDCl_3$, TMS, ppm) 1.32 (16H m CH_2) 2.54 (16H, S, OCH_2CH_2O); 5.0 (3H, S $CH_2CH=CH_2$ 7.24 (7H, m benzene ring) 8.13 (1H, m, NH); Anal Calcd. for $C_{32}H_{42}O_8N$: C 66.31, H 7.49, N 2.05; Found C 67.49, H 7.56, N 2.46.

Side-Chain liquid crystalline polymethylsiloxane comtaining 4-(4′undecylenoyloxy) benzoy amino benzo-15-crown-5. 0.5g (8.79 × 10^{-4} mol of compound (6) dissolved in 30mL of anhydrous toluene in a 100mL three-neck round-bottom flask. Siloxane 0.06g (1.93 × 10^{-5} mol of starting polymer, i.g. a 10% excess of monomer over a mole ratio of 1∶1 based upon siloxane hydrogen). The flask was equipped with reflux condenser and the mixtures were protected from moisture and air with a stream of nitrogen. The reaction mixture was heated to reflex with stirring and 100 μl new catalyst solution (1% $H_6PtCl_6 \cdot H_2O$, 1% absolute ethanol, 98% anhydrous THF) was then injected with a syringe. The mixture was reflexed under nitrogen at 110℃ until no Si-H was dectectable by IR spectra (2164cm^{-1}). The solution was then cooled and the solvent was removed under nitrogen. The resulting product, which was white paste, was dissolved into 4mL CH_2Cl_2, then precipitated by the addition of an excess of methanol. The product was collected by centrifugation at 4000rpm for 20min. The supernatant was discarded and the polymer was taken up in CH_2Cl_2 following which it was reprecipitated with methanol and collected once more by centrifugation. The wet gellike material was dried in a $CaCl_2$ dry desiccator under vacuum. After drying, the product (7) was obtained.

Column preparation.

Fused-silica capillary (ϕ0. 25mm × 20m) (Yongnian Optical Fibre Factory, Hebei, China) was used. The capillary was statically coated with a solution of 0. 4% (W/V) compound (7) in dichloromethane. The film thickness was 0. 25μm.

Column evaluation.

The GC spearation were carried out on an SC-7 Gas Chromatograph (Sichuan Analytical Instrument Factory, ChongQing, China) equipped with a flame ionization detector using nitrogen as carrier gas.

RESULTS AND DISCUSSION

The DSC and texture were shown that the monomer (6) did not display mesogenic state. The polymer (7) exhibited nematic state on heat from 115. 605℃ to 142. 399℃ and on cooling from 116. 423℃ to 101. 099℃. Figure 1 showed the texture of ploymer 7.

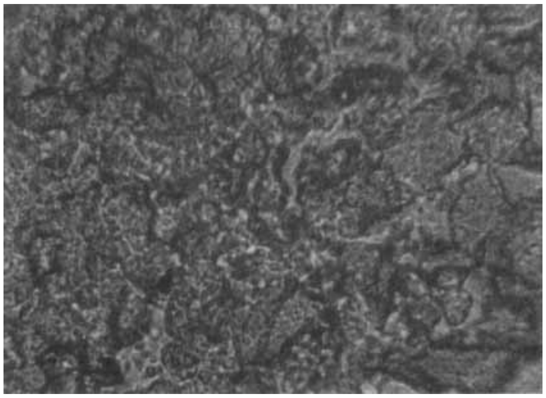


FIGURE 1 Texture of compound (7) on cooling 108℃ (See Color Plate I).

It was found by Finkelmann[9] in 1982 that the polymerization of a mesogenic monomer always stabilized the liquid crystal state. If a nematic monomer was polymeried, the polymer generally exhibited the higher ordered smectic phase. For mesogenic but isotropic monomers, i. g. for monomers, which exhibited a metastablc nematic phase below the melting point, nematic polymers could be obtained. So it was assumed the nonomesogenic monomers could produce mesogenic polymers, as long as the side-chain polymer exhibited a "comb" model, which had the side chain arranged vertially on the main chain. By this way we took advantage of the higher solubility and reaction capacity of the nonmesogenic monomer to avoid the lower solubility and reactionlessness of the mesogenic immediate, 4-(4′-undecylenoyloxy) benxoyl benzoic acid.

The polarities of the stationary phase (7) was expressed by McRkeynolds constants at 120℃ (Table Ⅰ). It was found that the novel stationary phase had moderate polarity between OV 22 and Carbowax -20M and therefore are suitable for seperation of polar and easily polarizable compounds.

TABLE 1 McReynolds constants of the (7) columns

Statornary phase	X′	Y′	McReynolds Z′	Constants U′	S′	TOTAL
Compound 7	133.9	271.8	280.8	251.2	382.6	1320.3
Carbowax-20M[10]	322	536	368	572	510	2308
OV22[10]	160	188	191	283	253	1075

X′=benzene; Y′=1—butanol; Z′=2—pentanone; U′=nitropropane; S′=pyridine

Fig. 2 illustrates chromatogram for a Grob test mixture on stationary phases(7). It was obvious that this (7) fused-silica column had low activity and this column was a neutral column.

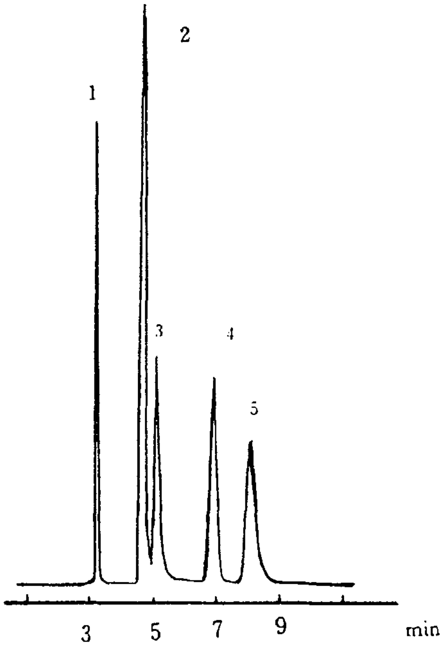


FIGURE 2 Chromatogram of Grob test mixture on the 7 stationary phase. Column temperature: 120℃

Peaks 1=2-octanone; 2=1-octanol; 3=aniline; 4=naphthalene; 5=phenol

The properites of liquid crystal column were usually measured by the capicity of operation of anthrancene and phenanthrene. Fig. 3 showed the chromatogram of anthrancene and phenanthrene on the (7) column. Table I listed the R values of anthrancene and phenanthrene, from which it was chear that the (7) staionary phase had a higher selectcity for anthrancene and phenathrene.

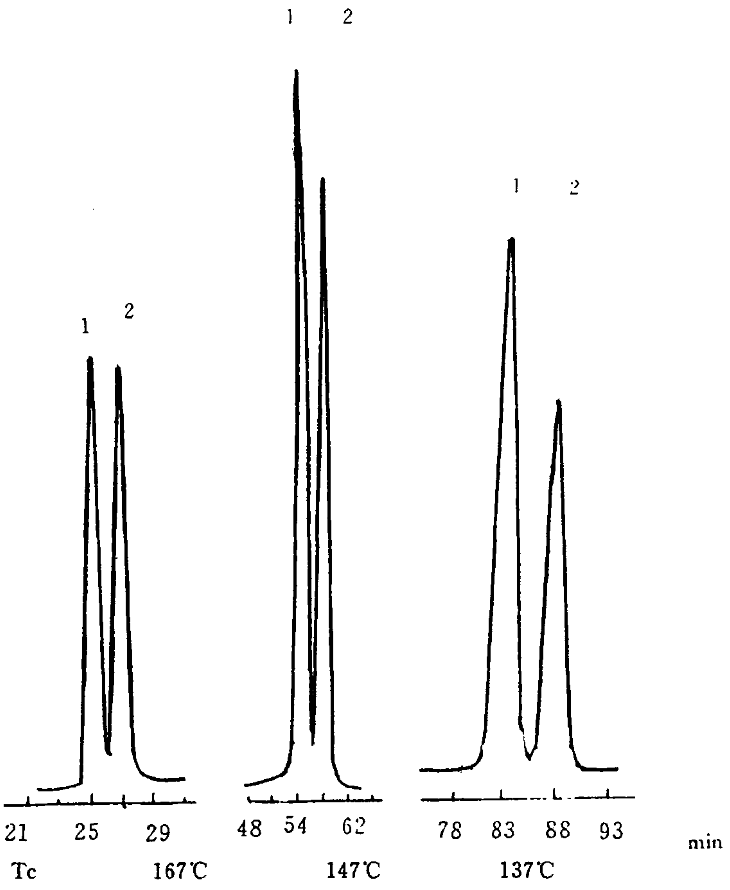


FIGURE 3 Chromatograms of anthrancene and phenanthrene on the stationary phase (7)

linear gas velocity 12. 47cm/s

1 phenanthrene 2 anthrancene

TABLE I R Values of anthrancene and phenanthree

Tc(℃)	106.0	112.0	127.5	137.0	147.0	156.0	167.0
R	1.76	1.73	1.54	1.33	1.17	1.14	1.12

Fig 4. showed the curve of logarithm of the adjusted retention time t_R'v.s. recipocal absolute temperature for xylene isomers. There were two turning points at the upper and lower transition temperatures of mesogenic state, which showed there were two phase changes in the heating process. It was shown that this column possessed the charatoristics of liquid crystal column.

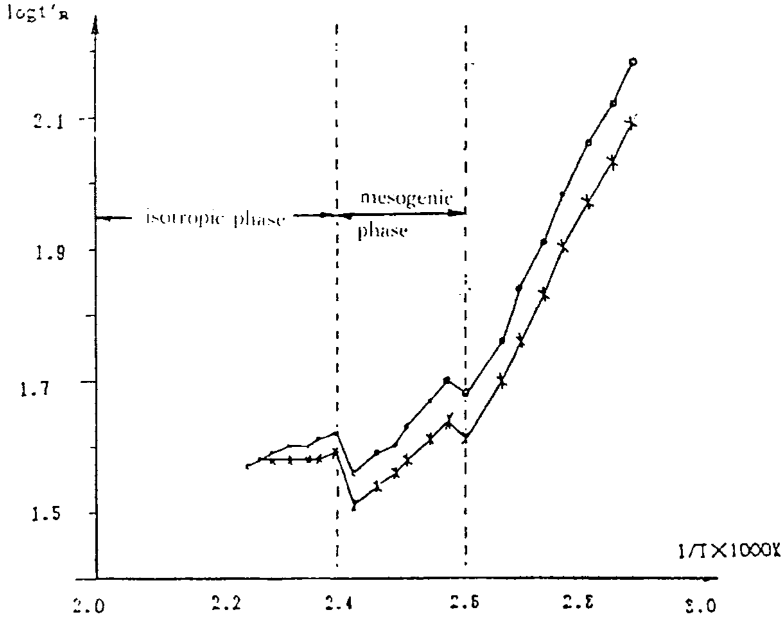


FIGURE 4 Curve of logarithm of the adjusted retention time t_R' VS. recipocal absolute temperature for xylene isomers.

○ o-xylene × m-xylene

CONCLUSION

An amido side-chain liquid crystalline polymethylsiloxane containing benzo crown ether unit was synthesized. The polymer was a novel liquid Crystalline crown ether polymer. When it used as stationary phase for capilliary column, it belonged in neutral column and possessed moderate polarity, hight effciency and unique selectivity for positional isomers.

ACKNOWLEDGMENT:

This work was supported by the National Natucal Sicence Foundation of China

REFERENCES

1. R. N. Fu, P. Jing, J. Cu, Anal. Chem. 6,93 (1993)
2. H. Chun, R. N. Fu, Z. F. Huang, Chromatogr. (China), 12(1),50 (1994)
3. R. N. Fu, I. Q. Zhang, Anal. Chem. (China),19(11),1238 (1991)
4. Y. H. Jin, R. N. Fu, Z. X. Guan, J. S. Gong, B. G. Li, J. Chromatogr 483, 394(1989)
5. R. Mojingo, Org. Syn., Coll. Vol. 3,685(1955)
6. CRC Handbook of chemistry and Physics, 69Th Edition, 1988-1989, C-538:14670
7. H. Fiedler, Arch. Pharm., 291,330(1958)
8. R. Ungaro, B. Elhaj B., J. Sinid, J. Am. Chem. Soc. 98(17),5198(1976)
9. H. Finkelmann, G. Rehage, Macromol. Chem. Rapid Commun., 864(3),859 (1982)
10. W. O. McReynolds, J. Chromatogr. Sci. 8,685(1970)