This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 19 February 2013, At: 10:33

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered

office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/gmcl17

Side Chain Polymers Containing 4 - (5-Alkylated 2-Thienylcarbonyloxy) Benzoic Acid

G. Kossmehl ^a & C. Pithart ^a

^a Institut für Organische Chemie, Freie Universität Berlin, Takustr. 3, D-1000, Berlin, 33, FRG Version of record first published: 22 Sep 2006.

To cite this article: G. Kossmehl & C. Pithart (1990): Side Chain Polymers Containing 4 - (5-Alkylated 2-Thienylcarbonyloxy) Benzoic Acid, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 193:1, 167-170

To link to this article: http://dx.doi.org/10.1080/00268949008031821

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst. 1990, Vol. 193, pp. 167–170 Reprints available directly from the publisher Photocopying permitted by license only © 1990 Gordon and Breach Science Publishers S.A. Printed in the United States of America

SIDE CHAIN POLYMERS CONTAINING 4-(5-ALKYLATED 2-THIENYLCARBONYLOXY) BENZOIC ACID

GERHARD KOSSMEHL, CORNELIA PITHART Institut für Organische Chemie, Freie Universität Berlin, Takustr. 3, D-1000 Berlin 33, FRG

Abstract The synthesis of a series of (5-substituted 2-thienylcarbonyloxy)benzoic acid is reported. Their mesomorphic behaviour investigated by DSC and polarizing microsindicating schlieren textures. Esters of copy, the above compounds with ω-alkenyl with poly(hydrogenmethylsients are reacted to give alkylated side chain poly(methylsiloxane)s, which are investigated by the The alkylated poly(methylsilomethods. with long spacers have schlieren texxane)s tures.

In the recent years a large number of studies been made concerning liquid crystalline side chain polymers with phenyl benzoate moieties1-5). We investigating analogous compounds exchanging benzene to a thiophene system. Ιn this paper, report the syntheses and the mesomorphic behaviour 4-(5-alkylated 2-thienylcarbonyloxy)benzoic acids. Their esters with ω -alkenyl substituents have been reacted with poly(hydrogenmethylsiloxane).

SYNTHESIS

The 4-(5-alkylated 2-thienylcarbonyloxy)benzoic acids have been synthesized from 2-alkylthiophene

by lithiumation/carboxylation to the 5-substituted thiophenecarboxylic acid⁶), formation of the acid chloride and esterification with 4-hydroxybenzoic acid $(\underline{1}-\underline{3})$:

R
$$+ BuLi$$
 $+ CO_2$ $+ H_2O$ $- LiOH$ R $- S$ $- COOI$
 $+ SOCl_2$ $- SO_2$, $- HCl$ R $- S$ $- COOH$
 $+ HO$ $- COOH$
 $+ HCl$ R $- S$ $- COOH$
 $+ R = H$
 $+ R = CH_3$
 $+ R = CH_3$
 $+ R = CH_3$
 $+ R = CH_3$

The side chain poly(methylsiloxane)s $\underline{4}$ - $\underline{7}$ have been prepared by the reaction of poly(hydrogenmethylsiloxane) and the allylester or the undecenylester of $\underline{2}$ and $\underline{3}$ in the presence of hexachloroplatinic(IV) acid⁷).

$$(H_{3}C)_{3}Si - O = \begin{pmatrix} CH_{3} & 1 & 4 & R = CH_{3}, n = 3 \\ -Si & -O = Si & (CH_{3})_{3} & 5 & R = C_{4}H_{9}, n = 3 \\ -(CH_{2})_{n} & 6 & R = CH_{3}, n = 11 \\ -(CH_{2})_{n} & 7 & R = C_{4}H_{9}, n = 11 \\ -(CH_{2})_{n} & 0 & -C = C + C_{1} & -C_{2} & -C_{2} & -C_{3} & -C_{4} & -C$$

RESULTS

4-(5-alkylated 2-thienylcarbonyloxy)benzoic All (1-3) have a schlieren texture studied polarizing microscopy and DSC measurements. thermal transitions are listed in Tab. I. The compounds decompose before they become isotropic. Although $\underline{1}$ has no substitution in the position 5 of the thiophene ring, it has mesomorphic behaviour. The allylester, the undecenylester of 2 and 3 and the polymers $\underline{4}$ and $\underline{5}$ do not have liquid crystalline behaviour by either calorimetric or microscopic examination. The side chain poly(methylsiloxane)s 6 and 7 that have a spacer with eleven methylene units have mesogenic behaviour. They have a schlieren texture.

TABLE I: Thermal transitions* [°C]

No.	transition temperature			
<u>1</u>	С	224	sch	dec
<u>2</u>	C	195	sch	dec
<u>3</u>	c	136	sch	dec
<u>4</u>	g	?	i	
<u>5</u>	g	-35	i	
<u>6</u>	g	-37	sch	21 i
7	g	-50	sch	-25 i
			·	

^{*} by DSC and polarizing microscopy;

c = crystalline, g = glassy, sch = schlieren
texture, i = isotropic, dec = decomposed

comparison with the known polysiloxanes phenyl benzoate mesogens3,8-10) our polysiloxanes the thienylcarbonyloxybenzoic acids 0° C temperature below and the phases are at lower temperatures as the analogous aromatic polysiloxanes. Besides, our side poly(methylsiloxane)s are only liquid crystalline, if they have a long spacer with eleven methylene units. Polymers having a spacer with three methylene units do not have mesogenic behaviour.

REFERENCES

- H.Finkelmann, H.Ringsdorf, J.H.Wendorff, <u>Makromol. Chem.</u>, <u>179</u>, 273 (1978)
- 2. H.Finkelmann, G.Rehage, <u>Makromol. Chem., Rapid.</u>
 Commun., 1, 31 (1980)
- 3. M.Mauzac, F.Hardouin, H.Richard, M.F.Achard, G.Sigaud, H.Gasparoux, Eur. Polym. J., 27, 137 (1986)
- H.Ringsdorf, A.Schneller, <u>Makromol. Chem.</u>, <u>Rapid Commun.</u>, <u>3</u>, 557 (1982)
- R.Zentel, H.Ringsdorf, <u>Makromol. Chem., Rapid.</u>
 <u>Commun.</u>, <u>5</u>, 393 (1984)
- G.Κοβmehl, D.Budwill, Z. Naturforsch., 38b, 1669 (1983)
- G.Nestor, M.S.White, G.W. Gray, D.Lacey,
 K.J.Toyne, <u>Makromol. Chem.</u>, <u>188</u>, 2759 (1987)
- 8. P.Keller, <u>Mol. Cryst. Liq. Cryst.</u>, <u>157</u>, 193 (1988)
- H.Richard, M.Mauzac, H.T.Nguyen, G.Sigaud, M.F.Achard, F.Hardouin, H.Gasparoux, Mol.Cryst.Liq.Cryst., 155, 141 (1988)
- 10. B.Krücke, M.Schlossarek, H.Zaschke, <u>Acta Polymerica</u>, <u>39</u>, 607 (1988)