

SYNTHESIS OF SIDE-CHAIN LIQUID CRYSTALLINE POLYSILOXANE CONTAINING SCHIFF'S BASE MESOGENS WITH NO₂-END GROUP AND ITS BEHAVIOR IN A DC ELECTRIC FIELD

XIE Ping (谢萍) SUN Limin (孙立民) and ZHANG Rongben (张榕本)

(Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing, 100080)

ABSTRACT

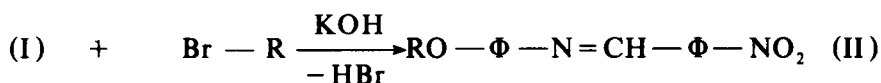
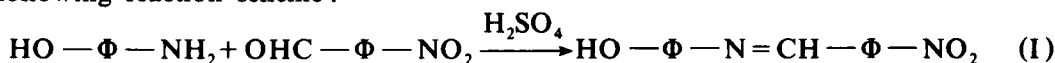
A side chain liquid crystalline copolysiloxane, which would show electro-optic effects as known from low mass liquid crystal, was synthesized by hydrosilylation reaction, and the two homologous monomers with different length spacers containing Schiff's base mesogen with —NO₂ terminated group were grafted to a polysiloxane main chain. Residual monomer in crude product is effective in reinforcing the response to an electric field over that of pure polymeric liquid crystal.

INTRODUCTION

Owing to the dipole anisotropy, some liquid crystal polymers can be easily oriented by an electric field as it is known for low mass liquid crystal compounds^[1,2]. We report here some preliminary results of investigation on the synthesis and electro-optic behavior of side chain liquid crystalline polysiloxanes containing Schiff's base mesogens with —NO₂ end group in a D.C. electric field. Copolymerization of two monomers with different length spacers and the remained monomers are effective in reducing the melt viscosity and in increasing the response to an electric field.

EXPERIMENTAL

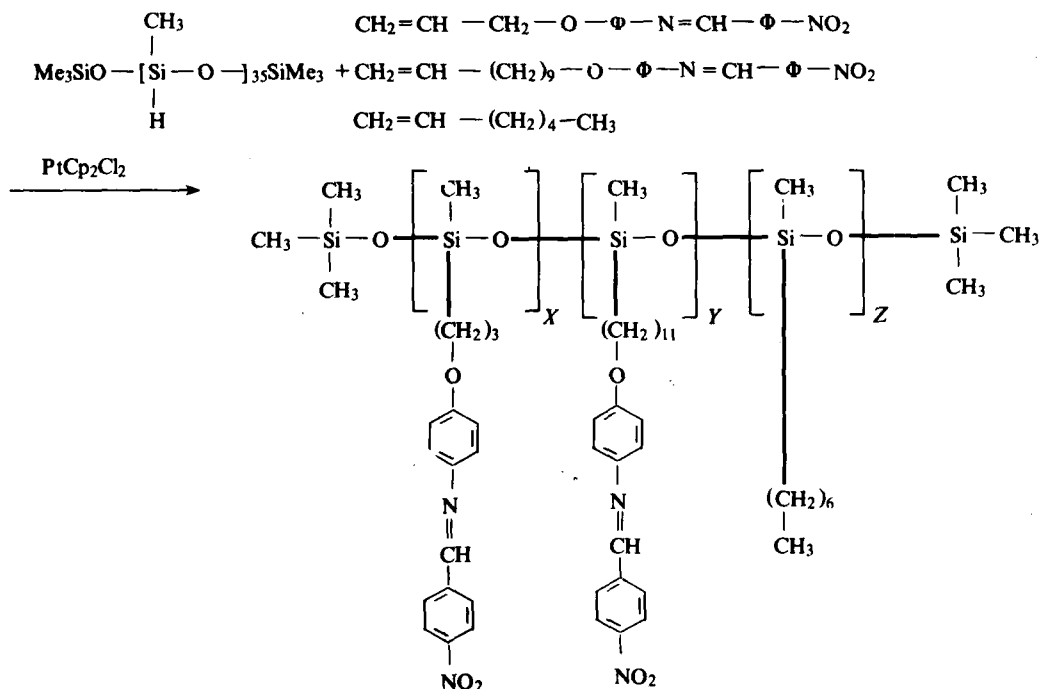
Synthesis of monomers and low mass model compounds is summarized in the following reaction scheme.^[3]



where R: $\text{CH}_2 = \text{CH} - (\text{CH}_2) -$ M-3
 $\text{CH}_2 = \text{CH} - (\text{CH}_2)_9 -$ M-11
 $\text{C}_4\text{H}_9 -$ LM-4
 $\text{C}_{12}\text{H}_{25} -$ LM-12

p-Hydroxyphenyl-p-nitrophenylimine (I) was synthesized by condensation of p-aminophenol and p-nitrobenzaldehyde. Monomers with vinyl-terminated group

and low mass model compounds (II) were synthesized by dehydrohalogenation of (I) and alkenyl bromide, alkyl bromide respectively. Monomer M-3 or M-11 was grafted to a polysiloxane main chain by hydrosilylation reaction in the presence of a platinum catalyst with the monomer in excess (mole ratio of monomer to Si-H is 1 : 1), 1-heptene was finally used to react with the remained Si-H.



Crude polymer product was purified by repeating procedures of dissolving in toluene and then precipitated with methanol until no low mass substances were detected by TLC. Element analysis result is: N: 5.12, C: 54.5, H: 7.02. Approximate estimation was made for x+y: 35%, z: 18% and the remained low mass monomers: 56%. No Si-H was detected by IR or NMR. Absence of Si-H may be attributed to hydrolysis or crosslinking.

The structure analysis and thermal properties of synthesized compounds are shown in Table 1 and Table 2.

The poling experiments were carried out with film samples of thickness 10 — 17 μm sandwiched between two transparent conductive glass plates. The sample thickness was controlled by polycarbonate spacer. The sample was tempered on a hot stage. Electro-optic behavior was observed between crossed polars.

RESULTS AND DISCUSSION

The side chain liquid crystalline polysiloxane in which mesogens are substituted in the para-position by polar substituent — NO₂ should desirably possess a positive dielectric anisotropy. Homopolymer appears to be too sticky to have effective response to the external electric field. Therefore the two homologous monomers M-3 and M-11 with different length spacers have been copolymerized. As expected, copolymer P-3-11 exhibited lower melt viscosity

and was favourable to investigation of electric effect. In the synthesis, the monomers with strong polar end-group NO_2 can not be added to siloxane main chain on the basis of stoichiometric reaction. The reactivity of the vinyl group in another end may be affected by polar group $-\text{NO}_2$ and spacer length, so the exact ratio of two monomers in the final copolymer cannot be assured. The crude product was a mixture including high molecular weight LC polysiloxane, unreacted LC monomers and trace of catalyst. The presence of low mass LC monomers in the mixture resulted in reducing viscosity and increasing response to an electric field, compared with purified high molecular weight LC polysiloxane. A rapid response time would be expected for this mixture system of monomeric-polymeric liquid crystals. At lower temperature and moderate voltage

regions, rapid homeotropic transition could be realized and initial texture could be recovered immediately after the electric field was turned off. But the response time for purified polymeric liquid crystal is much longer. In the higher temperature region, turbulence (like "boiling") occurred for the mixture system as well as for the purified copolymer. The "boiling" became much stronger as the voltage increased. Additional phenomenon for the mixture system was the apparent conduction behavior. The mechanism of this conductivity phenomenon is not clear. It may be attributed to electron mobility. With the aid of intermolecular interaction, the retardation of electron mobility would be reduced, so the electric conduction



Fig.1 Induced textural change (dark area) upon the application of a 60v dc electric field across copolymer P-3-11 at 144 °C in contrast to the scattering textures at left-lower corner.

would be related to molecular orientation and temperature. Strong polar NO_2 end group may act as electron acceptor and trace of Pt-ion may be as mobilizing electron donor. It was found that the current decayed with time, especially at higher temperature it decayed very quickly. The preliminary results are summarized in Tables 3, 4 and 5.

Table 1 Structure analysis of monomers and model compounds.

Sample	Element anal. found (calc.)	IR (cm^{-1})	^1H NMR (ppm) (CDCl_3 , TMS)
M-3	N 9.79 (9.93)	$-\text{CH}-\text{N}-$ 1576	$-\text{CH}-\text{N}-$ 8.56 (s)
	H 4.83 (4.96)	$-\text{NO}_2$ 1339	$-\text{CH}_2\text{O}-$ 3.39
	C 67.88 (68.08)	853	(t or d)
M-11	N 6.99 (7.11)	$-\text{CH}-\text{N}-$ 1576	$-\text{CH}-\text{N}-$ 8.54 (s)
	H 7.89 (7.61)	$-\text{NO}_2$ 1341	$-\text{CH}_2\text{O}$ 4.47 (t)
	C 72.85 (73.10)	853	
LM-4	N 9.35 (9.39)	$-\text{CH}-\text{N}-$ 1583	$-\text{CH}-\text{N}-$ 8.57 (s)
	H 6.05 (6.08)	$-\text{NO}_2$ 1340	$-\text{CH}_2\text{O}-$ 4.00 (t)
	C 68.06 (68.44)	854	
LM-12	N 6.69 (6.82)	$-\text{CH}-\text{N}$ 1576	$-\text{CH}-\text{N}-$ 8.57 (s)
	H 7.53 (8.35)	$-\text{NO}_2$ 1341	$-\text{CH}_2\text{O}-$ 3.96 (t)
	C 72.53 (73.14)	852	

Fig.1 shows the induced homeotropic transition upon the application of a D.C electric field .

Table 2 Thermal properties of monomers , model compound and copolymer

Sample	T_m (°C)	T_{CI} (°C)	Texture
M-3	106		no LC
M-11	67.1	81	fan , marbly
LM-12	64.1	90.2	S _A , fan
P-3-11	93.7	160	focal-conic

Table 3 Poling conditions and behavior of purified copolymer in a DC electric field . (Distance holder is about 10 μ m) .

Poling condition T_{oven} (°C) V_{th} (v)		Phenomenon
170	20 — 30	light turbulence
	≥ 50	stronger turbulence
157	45	turbulence
	> 70	homeotropic (reversible)
135	40	homeotropic and the initial texture is not easy to be recovered .
120	60 — 90	
< 100	140 — 160	light homeotropic

Table 4 Poling conditions and behavior of crude copolymer system (monomeric-polymeric liquid crystal mixture)

Poling condition T_{oven} (°C) V_{th} (v)		Phenomenon
69	> 190	homeotropic
82	40 — 78	homeotropic, DC current
93	> 20	turbulence, DC current
104	≤ 5	turbulence (The current rapidly decayed)

Table 5 Apparent electric conduction of crude copolymer in a DC electric field .

T_{oven} (°C)	R_{appear} (V_{meas}/I_{meas})
< 70	no current
79	$10 - 14 \times 10^6$
82	$8 - 10 \times 10^6$
93	$2 - 3 \times 10^6$
103	$1.7 - 10^5$ *
≥ 110 **	

* : The current can not be stable for longer .

** : It is not possible to get linear relations of V-I , and when $V > 60v$ I_{meas} decayed rapidly .

Keywords: Liquid Crystalline Polysiloxane; Schiff's base Mesogens; Electro-optic

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