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Communications

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Siloxane Copolymers with Laterally and Terminally Attached Mesogenic Side Chains**

By *G. W. Gray**, *J. S. Hill* and *D. Lacey*

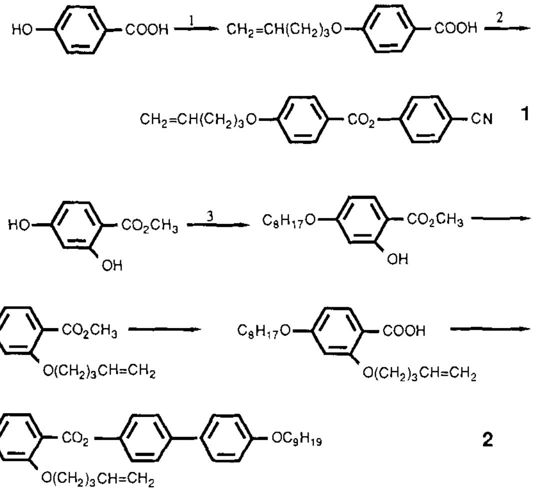
In view of the demand for liquid crystal polymers of different types[1] with certain specific physical characteristics, many workers have considered how this could be met through synthesizing copolymers containing two or more terminally attached mesogenic side chains, and tuning the properties of the polymers by variation of the type and ratio of the side chains. In this way, using the smectic-depressing properties of a lateral methyl substituent, a nematic side-chain polysiloxane with a proportion (but only up to 32%) of terminal cyano-groups and positive dielectric anisotropy was first produced.[2]

Acrylate polymers containing mesogenic groups attached laterally to the backbone were first reported by *Finkelmann*,[3] and analogous polysiloxanes have since been reported by *Gray* et al.[4] and *Keller* et al.[5] These are predominantly nematic materials, and by synthesizing a series of novel siloxane copolymers containing varying amounts of terminally *and* laterally attached mesogenic groups, we now show that a further degree of flexibility is provided for the development of liquid crystal polymers with defined physical characteristics for applications in areas such as integrated optics,[6] optical storage,[1,7] gas liquid chromatography,[1] and NCAP displays,[8] e.g. nematic polysiloxanes containing 80–85% of cyanosubstituted side chains, and having a range of dielectric properties of technological interest.

Experimental

For the precursor of the *terminally* attached moiety we chose the alkene **1**, which gives a crystalline smectic homopolymer with relatively high melting and clearing points. Most laterally attached polysiloxanes which have been prepared to date are nematogenic and have a glass transition. We chose as the *lateral* comesogenic precursor the alkene **2** which has been prepared in our laboratories, and gives a typically low T_g, low T_{N-I} homopolymer.

The synthesis of those compounds using standard procedures is shown in scheme 1.



Scheme 1.

The copolymers were prepared by hydrosilylation of the alkenes in toluene at 70 °C for 18–24 h (Scheme 2), using poly(hydrogenmethylsiloxane) obtained from Wacker Chemie (DP $\sim$46, $\gamma \sim 2.2$); a 1.1 molar excess of the mixture of alkenes was used, with platinum divinyltetramethyl disiloxane as the catalyst. Purification was effected by repeated precipitation of the polymers from dichloromethane solution with 3:2 v:v methanol:ether, and subsequent centrifugation. The pure polymers were dried in vacuo in the isotropic state.

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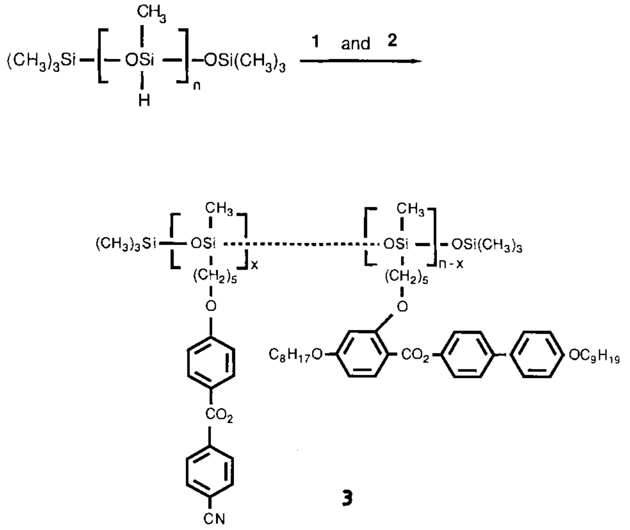
[**] The authors thank the Science and Engineering Research Council for financial support of the research of which this work was a part.



Scheme 2.

The relative proportions of the mesogenic side chains in each polymer were determined by ^{1}H NMR. The terminal-lateral ratio in each copolymer was found to be greater than the ratio of the alkene precursors used in the feedstock for the original reaction. This implies that the overall rate of hydrosilylation is greater for the terminal than for the lateral mesogen, and is probably explained by the greater steric hindrance to the approach of the lateral moiety to the reaction site.

The thermal properties of the polymers were determined by differential scanning calorimetry and optical microscopy. The results are summarized in Table 1, and a graphical illustration of these results is given in Figure 1.

Table 1. Transition temperatures (°C) and enthalpies of transition (ΔH, in brackets, cg^{-1}) for polymers of structure **3**

% terminal	% lateral	K$-$S$_A$ maximum	T_g midpoint	S$_A-$I maximum	S$_A-$N maximum	N$-$I maximum
100	0	107		184		
98	2	95.0 (1.18)		174.9 (0.86)		
95	5	62.0 (1.5)		139.8 (0.68)		
92	8		11.5	134.8 (0.56)		
86	14		13.5		130.8	134
84	16		10.8			116.6 (0.4)
80	20		10.9			108.3 (0.31)
70	30		1.9			72.7 (0.26)
58	42		6.3			69.2 (0.17)
44	56		10.7			58.9 (0.11)
19	81		9.9			59.3 (0.20)
0	100		4.8			58.0 (0.17)

K = crystal; S$_A$ = smectic A; N = nematic; I = isotropic liquid

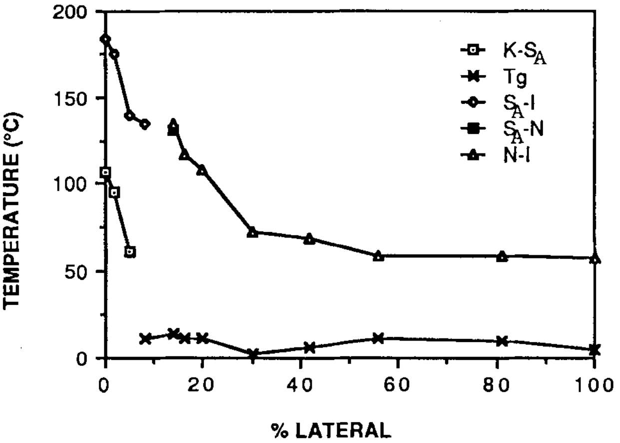


Fig. 1. Thermal properties of siloxane copolymers w.r.t. the proportion of laterally attached mesogens.

The main features of this copolymer system are summarized below.

(a) The introduction of only small amounts of the lateral side-chain component into the predominantly terminally cyano-substituted polymer has been shown for the first time to have very striking effects, whereas introduction of small amounts of the terminal side-chain component into the predominantly laterally substituted polymer has very little effect.
(b) Very low concentrations (2–5%) of the laterally attached side chain decreased both T_m and T_{S-I}, and with $\geq$ 8%, glass transitions were observed.
(c) On increasing the lateral side-chain content to 14%, a narrow range nematic phase appeared to be introduced (DSC) above the S$_A$ phase, and with $\geq$ 16%, the polymers exhibited nematic phases only.
(d) The marked increases in the isotropization temperatures ceased with $\geq$ 30% of lateral side-chain component, and the T_{N-I} values became fairly constant. Apart from minor fluctuations, the T_g values remained about the same for $\geq$ 8% of lateral side-chain component.

X-ray diffraction studies (University of Bristol) and dielectric studies (University of Swansea) are currently being undertaken on these copolymers.

Through this system, we have demonstrated the possibility of tuning the thermal and mesomorphic properties of conventional siloxane polymers with terminally attached side chains by the introduction of a laterally attached comesogenic component. This is exemplified by the introduction of a glass transition, and the change from a purely smectic to a purely nematic polymer system.

At the same time, we have shown that one may introduce both small and large (up to 70%) amounts of mesogenic side chains containing cyano-groups into a laterally attached side chain polymer so that the dielectric properties may be changed considerably without significantly affecting the thermal properties of the original polymer.

This method of using mixed lateral-terminal side-chain copolymers to tune properties may be extended to other side-chain liquid crystal polymer systems such as polyacrylates and condensation polymers.

Received May 11, 1989

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Polymers with a High Refractive Index and Low Optical Dispersion

By *Hans-U. Simmrock, Alfred Mathy, Ligia Dominguez, Wolfgang H. Meyer** and *Gerhard Wegner*

Materials for use in optics are usually characterized in terms of their refractive index n_D and their Abbe number ν_D which describes the wavelength dependence of the refractive index, the optical dispersion ($\nu_D = (n_D - 1)/(n_F - n_C)$ where n_D, n_F and n_C are the refractive numbers of the material at the wavelengths of the spectral lines of Na, F and C respectively).

In the n_D vs. ν_D diagram the regime of materials which combine high refractive indices with high Abbe numbers used to be exclusively occupied by inorganic glasses. Transparent polymers range from $n_D = 1.33$ to $n_D = 1.73$. However, polymers with high n_D values usually have low ν_D values and vice versa. For example, the data corresponding to two optically extreme polymers are: $n_D = 1.675$ and $\nu_D = 19$ for poly-*N*-vinylcarbazole and $n_D = 1.345$ and $\nu_D = 83$ for Teflon FEP (Fig. 1). Thus, the combination of high refractive index with low optical dispersion in polymers appeared until now to be unachievable.[1]

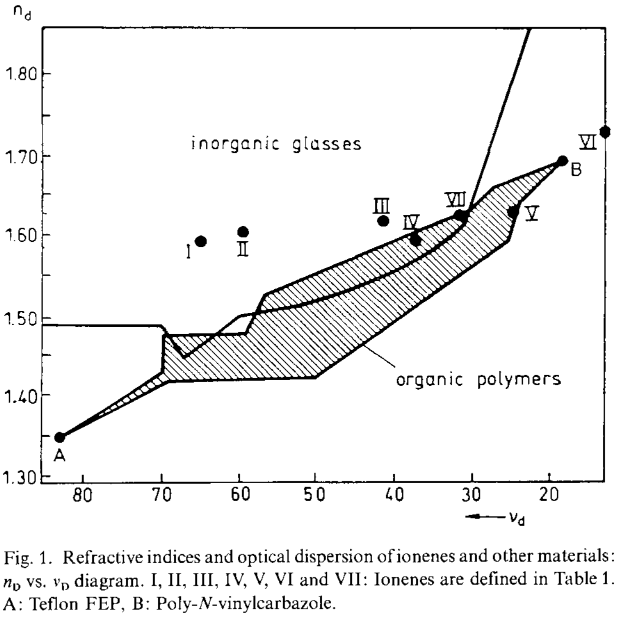

Fig. 1. Refractive indices and optical dispersion of ionenes and other materials: n_D vs. ν_D diagram. I, II, III, IV, V, VI and VII: Ionenes are defined in Table 1. A: Teflon FEP, B: Poly-*N*-vinylcarbazole.

Numerous efforts have been made in the past to extend the polymer regime towards higher indices and lower dispersion. We report here a successful approach using polyelectrolytes, in which the optical parameters can be adjusted by varying the structure of the polymer *and* by the proper choice of the counterions.[2] We use polyelectrolytes of the type **1**, which are also known as "Ionenes" (Io), with the main chain segments R^1, R^2 and the side chains R^3, R^4 being organic moieties (e.g. aliphatic groups), and X = monovalent (q = 1) or divalent (q = 0.5) counterions. The solid state properties of such polyelectrolytes are usually scorned as being "salt-like". Indeed, ionenes with R^1 and R^2 being relatively short aliphatic segments, due to their high charge density, are highly crystalline materials with physical and chemical properties resembling those of inorganic salts.[3]

1 $\left[R^1-N(R^3)_2-R^2-N(R^4)_2 \right]_n 2 \cdot n \cdot q \cdot X$

However, ionenes where R^1 and R^2 are larger organic components with low charge density have more polymer-like properties. They can be processed from the melt or from solution to form glassy films with excellent optical transmission in the visible and near-UV (Fig. 2). In such ionene glasses ionic conductivity has been recently demonstrated.[4]

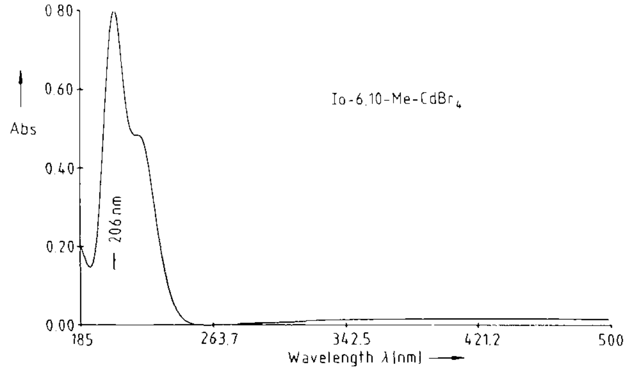

Fig. 2. UV-VIS-Absorption spectrum of a typical ionene-film (thickness: 1 μm; Io-6, 10-Me-CdBr$_4$ defined as in Table 1).

Recrystallization can be suppressed and long-term stability of the glassy state can be obtained by introducing a certain amount of irregularity along the polymeric structure such as in copolymers ($R^1 \neq R^2$) by using isomeric mixtures and by combining rigid and flexible chain segments. By these means the thermal behavior and the processibility of the materials can also be greatly influenced. For example: the glass transition temperature of Io-10-Et-BF$_4$ ($R^1 = R^2 = (CH_2)_{10}$; $R^3 = R^4$ = ethyl; X = BF$_4$) is -22 °C, while that of Io-Do,Pip-Me-CdBr$_4$ ($R^1 = -CH_2-CH=CH-CH_2-$; $R^2 = -$*cyclo*-$NC_5H_9-(CH_2)_3-$*cyclo*-C_5H_9N-; $R^3 = R^4$ = methyl; X = CdBr$_4$) is $+191$ °C. The thermal properties and relaxation phenomena in glassy ionenes have recently been discussed in detail elsewhere.[4]

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