Macromol. Symp. ***128,*** *145–154 (1998)*

THE SYNTHESIS OF MESOGENIC POLYMERS PROVOKED BY MOLECULAR MOBILITY. POLYSILOXANARYLENES

Serguei Skorokhodov

Institute of Macromolecular Compounds, Russian Academy of Sciences
Bolshoy pr. 31, St.Petersburg, 199004 Russia

SUMMARY: An approach to the synthesis of potentially thermotropic liquid crystalline polymers based on parallel investigation of their molecular mobility was realized. The initial idea was provoked by the observation that there exists some correspondence of molecular mobility data and the ability of a polymer to form a liquid crystalline phase. Previously this phenomenon was demonstrated on the example of a series of thermotropic main chain polymers with flexible dimethylsiloxane spacers of variable length. The relation between the structure of the main chain and local molecular mobility of different fragments was investigated in a series of regular polysiloxane-silarylenes containing rigid aromatic sequences. Molecular mobility was studied by dielectric spectroscopy in solution and in solid state. The structure of the main chain has been changed by variation of the repeated fragments' length, substituents and joint groups. The data of molecular mobility and their conformity with the chain structure were used for directed synthetic search of desired mesogenic polymers.

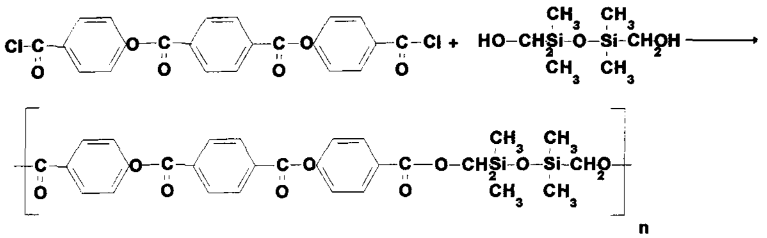
The goal of our study was to develop synthetic strategy of the synthesis of thermotropic rigid flexible (RF) main chain polymers. The synthesis of alternating RF polymers is widely developed. Usually the choice of the structure of mesogenic

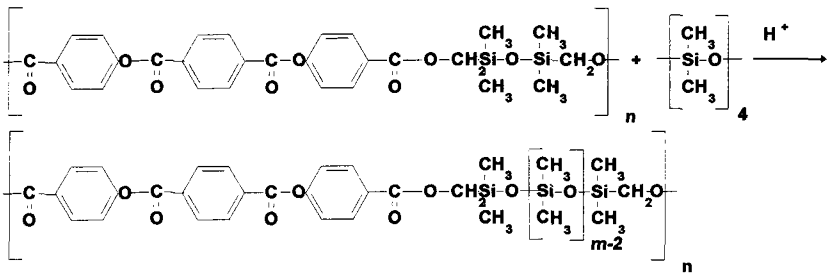
CCC 1022-1360/98/$ 10.00

rigid fragments is based on the assumption that mesogenic ability of the chain rigid fragment correlates somehow with corresponding low molecular weight liquid crystal. The widely used spacers are sequences of methylene, oxyethylene or dimethylsiloxane groups. As a rule, such selection of the structures of polymer chains is a key principle in LC polymer engineering (Refs. 1, 2). This most widespread approach seems to be not sufficient. In the first place, there are difficulties in choosing of an appropriate structure among almost unlimited diversity of possible mesogenic structures. The second limitation of the approach lies in the neglect of kinetic problems of LC ordering formation in polymers which will be controlled by molecular mobility of a polymer.

Thus, our goal was to try to determine the relation between the structure and dynamics of polymer chain and mesogenic ability and to use data obtained for directed synthesis of new mesogenic polymers.

It was necessary to make a rational choice of the most convenient type of polymers and synthesize a series of polymers of variable structure. As an example of basic nematogenic polymer having a typical spacer was synthesized by usual way (Ref. 3).



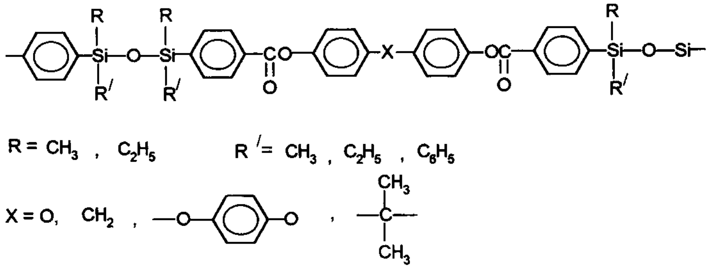


The first variation of the polymer structure was the increase of the spacer length by chemical modification. The reaction of equilibration with cyclic dimethyl-siloxane was performed.

The prepared in this manner homologic series of polymers was investigated by dielectric spectroscopy method. It was shown that at a certain length of the spacer the polymer looses its mesogenity and isotropization temperature predicted from T_i plot on spacer lengths was found to be lower than Tg (Refs. 3, 4).

This result leads to principal conclusion of the necessity of sufficient molecular mobility level for transition of a polymer into LC state.

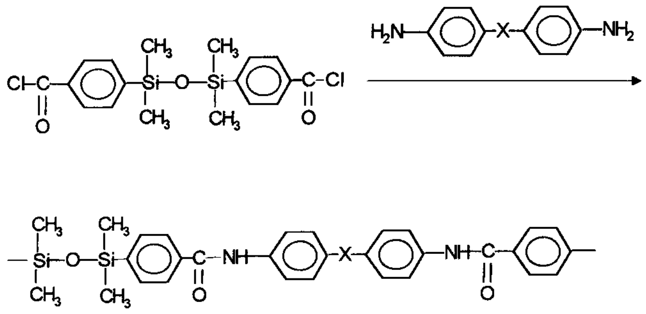
To get more detailed information on dynamic behaviour of polymer chain and in search on new silicon containing polymers a new family of polymers was synthesized. The monomeric unit of polymers consists of siloxanesilarylene sequences as it is shown in formula:



Similar polymers were synthesized by Dvornik and Lenz (Ref. 5) and Inoue (Ref. 6). The synthesis of a series of polyesters was prepared through low temperature acceptor polycondensation of dichloroanhydride known siloxane containing dicarboxylic acid and diphenols. All synthesized polymers turned out to be nonmesogenic (Ref. 7). Nevertheless this series of polysiloxanesilarylene polyesters was investigated by dielectric spectroscopy methods in solution and in bulk. The aim of this investigation was to determine the role of every chain fragment including separate parts of composite rigid fragments. The influence of substituents was also traced. The results can be summarized as follows (Ref. 8).

The dynamic behaviour of the polymer chain was described satisfactory. The factors affecting kinetic flexibility and mechanism of local mobility were estimated. the "loading" of rigid fragment by substituents leads to the increase of relaxation times and hindering of internal rotation in the fragment. The peripherical phenylene group attached to Si-atom was moving more free than the central part of rigid fragment. The change of the mobility in rigid fragment influenced the rotation in spacer (in solution). The variation of substituents at Si-atom produces small but noticeable influence on the mobility of the chain and local mobility of the fragments.

In general the results of dynamic characteristics measurements manifest the coupling of rotating elements sequence corresponding to certain groups bound by polar joints. The next variation of the structure included the change of an ester group by an amide group illustrated by the scheme of the synthesis and the table containing data on the properties of polymers.



X = — (1)

-O- (2)

$-O(CH_2)_2O-$ (3)

$-O(CH_2)_3O-$ (4)

$-O(CH_2)_4O-$ (5)

Properties of polyamides

	Yield	η, dl/g, 25°C	Temperature of phase transitions, °C
1	85	0.81	non meltable
2	81	0.35	Tg 160
3	73	0.47	Tg 120
4	76	0.94	190 N 280
5	74	0.58	170 N 300
PE*	57	0.46	205 LC 220

* model polyesters X = $-(CH_2)_4-$

The idea of this structure variation was based on well known effect of amide groups in a mesophase formation. They increase intermolecular hydrogen bonds and dipole-dipole interactions. The series of polyamides was prepared by variation of rigid fragment. The Si-containing spacer remained constant. Polyamides were synthesized by polycondensation of corresponding amines and standard dichloranhydride. The polyamides without spacers could not form liquid crystalline phase. They were crystalline and had high melting temperature. The IR spectra have confirmed of intra- and intermolecular hydrogen bonds formation. The additional relaxation process reflecting the mobility of amide groups involved in intermolecular interactions by hydrogen bonds was demonstrated (Refs. 9, 10). The investigation of dipole moments of the polymers in solution exposed the formation of intramolecular H-bonds in a part of macromolecules and the correlation factor of interaction between polar amide groups was determined. However, thermotropic mesogenity did not appear (Ref. 10).

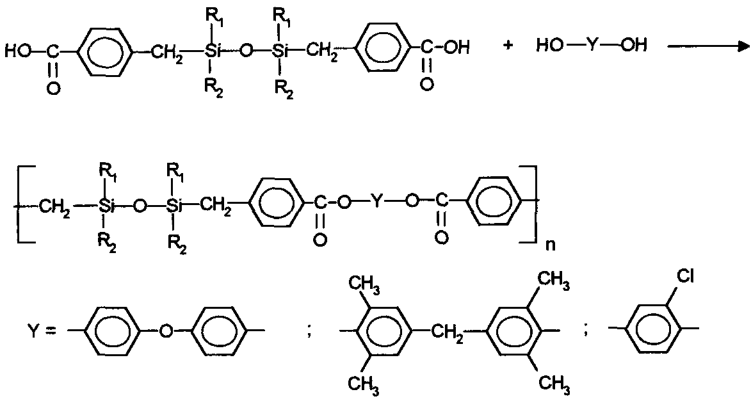
Going from high rigidity of aromatic polyamide rods we tried to lower rigidity by introducing of the flexible oxyalkylene spacer into the rigid fragment. At the same time the ordering of the ends of newly-formed mesogenic fragments attached to the spacer was to be facilitated. The polyamides were prepared by the reaction of corresponding α,ω-aminophenyloxyalkanes and standard dichloranhydride (cf. scheme of the synthesis).

It was established by POM, DSC and X-Ray data that the polymers prepared and having the even number of methylene groups in the spacer do form smectic phase. The polyamide with the odd number of methylene groups was nonmesogenic. For the comparison the analogous polyester with -O$(CH_2)_4$-O- spacer was synthesized and the formation of LC phase of a relatively narrow interval of existence was observed. These results indicate the possibility of LC ordering on the contrary to overcrowding of the second end of the mesogenic fragment by Si-atom substituents. The approach used appears to be valid both for polyamides and polyesters.

The results obtained provoked the next structural variation with the aim to exclude hindering of rotation between Si-atom and peripheric aromatic core of the mesogenic fragment. This fragment of the polymer chain seems to play the key role in ordering of rigid mesogenic fragments. Simultaneously the length of the Si-containing spacer would be increased.

The new monomer containing methylene group between Si-atom and phenylene core was prepared. The newly synthesized corresponding dicarboxylic acid was transformed to dichloranhydride, which was condensed with a number of diphenols by acceptor low temperature polycondensation. The Higashi method was also used (Ref. 11). Special precautions are recommended for the synthesis to prevent the distortion of the unstable -Si-C_{aliph}- bond. Special notice on synthetic complications with compounds containing silbenzylidene groups is given in recent monograph (Ref. 12).

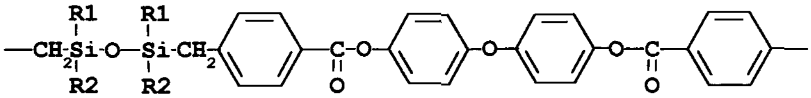
A series of polysilbenzylidene esters was prepared.



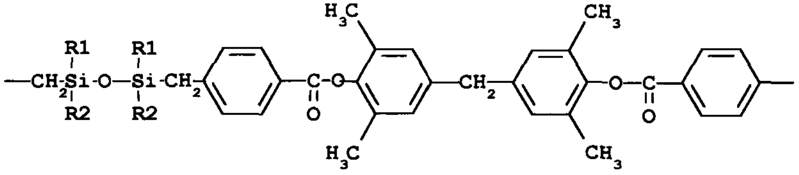
(1) (2) (3)

R_1; R_2 = Me; Et; Ph

All polymers of the series I are highly crystalline and decompose before melting. Introduction of four methyl substituents in rigid fragment must lead to lowering of melting points and ordering. Nevertheless polymers of the series II and III are both thermotropic liquid crystals. This conclusion is based on the data of polarization microscopy and DSC traces.

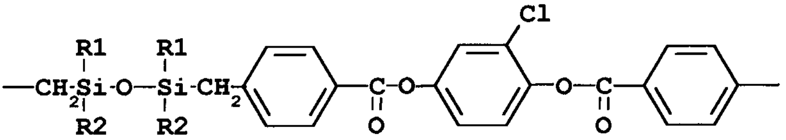


$R_1 = CH_3$; C_2H_5 $R_2 = CH_3$; C_2H_5 ; C_6H_5 not melt. , not sol. , cryst.



I. $R_1 = CH_3$ $R_2 = C_6H_5$ $[\eta] = 0.37$ dl / g DSC $C \xrightarrow{220} LC \xrightarrow{260} I$

II. $R_1 , R_2 = C_2H_5$ $[\eta] = 0.41$ dl / g DSC $C \xrightarrow{230} LC \xrightarrow{260} I$



I. $R_1 = CH_3$ $R_2 = C_6H_5$ $[\eta] = 0.46$ dl / g DSC $C \xrightarrow{290} LC \xrightarrow{400^*} I$

II. R_1 , $R_2 = C_2H_5$ $[\eta] = 0.43$ dl / g DSC $C \xrightarrow{270} LC \xrightarrow{400^*} I$

$[\eta]$ in $CHCl_3$, 25°C *decomposition

The polymer of the series 2 (R_1=CH_3, R_2=C_6H_5) was studied by dielectric spectroscopy method. The most important result is the estimation of relaxation time increase characterizing the rotation in the sequence - Si-CH_2-C_{ar}, which is a key group in ordering as follows from the data considered before. The effect of T_{rel} increase is in contradiction with expected rotation freedom increase owing to the increasing of the spacer length and the distortion of an electronic conjugation between aromatic core and Si-atom. This observed hindering of rotation can be explained by the existence of an electronic effect reflecting interaction between π-electrons of the aromatic nucleus and d-orbitals of Si-atom through the methylene group like hyperconjugation.

As a summary of the investigations carried out we would like to make some statements.

1. The synthesis of the system of a series of alternating rigid flexible polymers with predetermined structure of polysiloxanesilarylene type and parallel investigation of their molecular mobility by dielectric method were carried out.
2. The precise analysis of the local molecular mobility of separate chain fragments including both rigid and flexible fragments and their parts revealed the correlation of movements of certain chain sections.
3. This correlation being estimated for all series starting from the first one was applied for the choice of the structure at every next synthesis stage in connection with ordering ability of the polymer, especially LC ordering.
4. Some electronic characteristics of joint bonds could be deduced from the parameters of the correlated movements observed.
5. A new family of polysilarylenes having good solubility, film forming properties and thermostability and ordering can be perspective for new materials design.

6. The proposed approach seems to be of general significance and can be used in polymer synthesis more widely.

ACKNOWLEDGEMENT

The lecture was based on the research work carried out in cooperation with associates of several laboratories of the Institute of Macromolecular Compounds RAS.

Synthetic preparations - D.Asinovskaya, G.Smirnova, V.Zuev, A.Osadchev.

Hydrodynamic, dinamooptic and conformational properties - V.Tsvetkov, L.Andreeva, E.Astapenko, S.Bushin, E.Beliajeva.

Dielectric investigations - T.Borisova, L.Burshtein, S.Zhukov, V.Malinovskaya, N.Nikonorova, T.Stepanova.

Spectroscopy - A.Koltsov, B.Volchek, A.Purkina, V.Denisov, A.Gribanov, V.Shamanin.

X-Ray and DSC measurements - A.Grigor'ev, N.Andreeva, V.Volkov, S.Lukasov, I.Ivanova.

This work was supported by Russian Foundation for Basic Research, grant No 96-03-33849.

REFERENCES

(1) N.A.Platé, *Ed.Liquid Crystal Polymers.* Plenum Press, New York 1993, Ch.5

(2) S.S.Skorokhodov, A.Yu.Bilibin, *Makromol.Chem. Macromol.Symp.* **26**, 9 (1989)

(3) V.V.Zuev, G.S.Smirnova, N.A.Nikonorova, T.I.Borisova, S.S.Skorokhodov, *Makromol.Chem.* **191**, 2865 (1990)

(4) T.I.Borisova, *Macromol.Symp.* **90**, 153 (1995)

(5) P.R.Dvornik, R.W.Lenz, In: *"High Temperature Siloxane Elastomers".* Hütig & Wepf Verlag 1990, p.136

(6) K.Matssuwaka, H.Inoue, *J.Polym.Sci. Polym.Lett.* **28**, 13 (1990)

(7) S.S.Skorokhodov, D.N.Asinovskaya, A.I.Grigor'ev, S.V.Lukasov, A.D. Savenkov, S.N.Zhukov, *Polym.Sci.* **35A**, 237 (1993)

(8) L.L.Burshtein, T.I.Borisova, V.P.Malinovskaya, S.V.Zhukov, T.P.Stepanova, D.N. Asinovskaya, S.S.Skorokhodov, *Polym.Sci.* **38A**, 12 (1996)

(9) L.L.Burshtein, T.I.Borisova, V.P.Malinovskaya, S.V.Zhukov, T.P.Stepanova, D.N. Asinovskaya, S.S.Skorokhodov, *Polym.Sci.* **38**, 1127 (1996)

(10) L.L.Burshtein, T.I.Borisova, V.P.Malinovskaya, A.Yu.Osadchev, S.S. Skorokhodov, *Polym.Sci.* **38**, 1737 (1996)

(11) F.Higashi, N.Akiyama, I.Takahashi, T.Koyama, *J.Polym.Sci. Polym.ChemEd.* **22**, 1653 (1984)

(12) H.R.Kricheldorf, Ed. Silicon in Polymer Synthesis. Springer-Verlag, Berlin-Heidelberg 1996, p.157