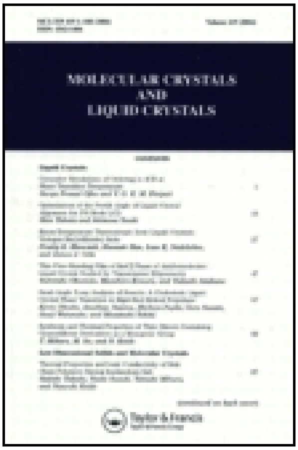

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Synthesis of Segmental Thermotropic Liquid-Crystalline Copolyesters

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SYNTHESIS OF SEGMENTAL THERMOTROPIC LIQUID-CRYSTALLINE COPOLYESTERS

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Abstract. A method of functionalization of a tetramer of α-methylstyrene with 4-hydroxybenzoyl groups has been proposed α,ω-(4-hydroxybenzoyl)-tetra-α-methylstyrene and α,ω-(4-hydroxybenzoyl-4--oxybenzoyl)-tetra-α-methylstyrene were obtained and characterized. Their polycondensation with terephtaloyl chloride or with terephtaloyl-bis-(4-oxybenzoyl)chloride yielded segmental copolyesters consisting blocks of up to seven aromatic rings. It was established that at a given selected structure of the non-mesogenic fragment and a given type of its bonding, the ability for forming LC state is manifested at a length of the polyarylate sequence of seven para-aromatic units.

Thermotropic LC main chain polymers with alternating rigid mesogenic and flexible fragments is one of the principal types of LC polymers. The significance of this type of polymers and its practical prospects for obtaining of high-strength materials have been widely considered in the literature /1/.

When the length of each of the alternating fragments increases to that of a block, it is justified to place these copolymers among the so-called segmental copolymers based on reactive oligomers and employed in practice /2/.

It seems tempting to use the widespread commercially available oligomers for the preparation of LC polymers. It may be said that this experience is partially available. Thus, it is known that when polyethylene and polypropylene glycols have been used as comonomers, LC polyesters were obtained /3/.

When substituents are introduced into the flexible fragments (for example as in polypropyleneglycols) the phase transition temperatures markedly decrease and the solubility of the resulting polyesters icreases.

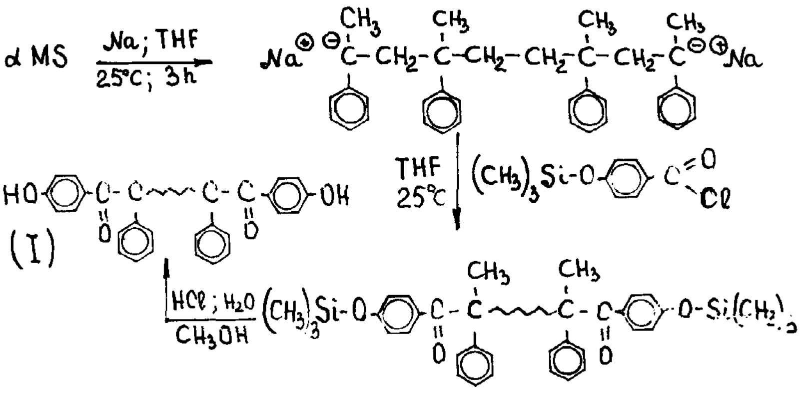
These observations have been carried out for polymers containing mesogenic blocks including at most three phenylene groups. The increase in the length of the mesogenic block and its anisodiametry, should involve a displacement of the range of existence of the anisotropic melt to higher temperatures and an increase in the order of the system.

The synthesis of a mesogenic block of greater length via a complex monomer corresponding to the block length was found to be inconvenient because of the decrease in solubility and excessively high melting temperature of the monomers. We employed a known method of synthesis of copolymers involving the formation of a mesogenic fragment of greater length in course the synthesis of the polymer /4/ and the application of functionalized oligomers containing the elements of the future mesogenic block.

A tetramer of α-methylstyrene (TαMS) which has already been successfully used for the preparation of polymer materials in the form of reactive derivatives /5/ has been chosen as the initial oligomer. The advantage of TαMS is that under certain conditions it can be obtained in the living anionic process as virtually monodisperse /6/. The polydispersity of non-mesogenic fragments plays an important role in the problem of the relationship between the structure and properties of the LC polymers. The second important factor is the presence of methyl and phenyl side groups lowering the phase transition temperatures.

Our aim was to add to the tetramer the elements of the future mesogenic block. 4-Hydroxybenzoyl groups were chosen for this purpose. These functional groups have not previously been introduced into oligomers.

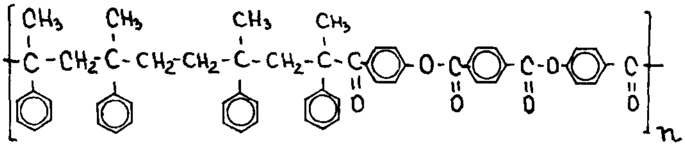
We have previously /7/ proposed a method of functionalization of living polymers by using 4-(trimethylsiloxy)benzoyl chloride.



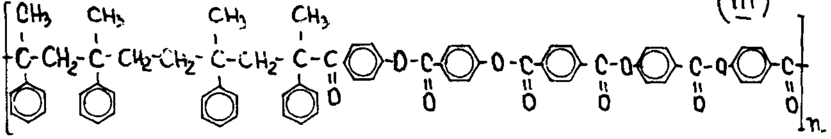
The reaction of di-Na-TαMS with 4-(trimethylsiloxy)-benzoyl chloride proceeds under mild conditions in quantitative yield. The protection of the hydroxyl group made it possible to avoid secondary reactions with its participation.

If it is assumed that TαMS is quantitatively only a tetramer, then its MW is 714. The experimental value of M_n 680 is in a good agreement with the expected one. The functionality was 1.92 calculated on the theoretical MW. The structure of the diphenol synthesized (I) was confirmed by IR and NMR spectra.

The condensation of the functionalized tetramer with terephtaloyl chloride or with a complex mesogenic monomer, terephtaloyl-bis-(4-oxybenzoyl chloride, TOBC) proposed by Bilibin and co-workers /3/ yielded copolymers with the following structures:



(II)



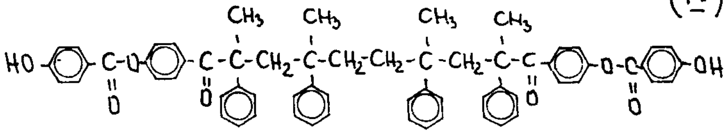
(III)

Copolymers II and III are readily dissolved in most common organic solvents. According to the data of polarizing microscopy, copolymers II and III pass into an isotropic melt at 170–175°C and 175–180°C, respectively. For II, the transition at 135–140°C from the solid to the viscous state persisting to 170°C is observed. It may probably be explained by the predominant influence of the α-MS-block in the copolymer.

The absence of the LC phase in melts II and III may result from the insufficient length and bulkiness of the side groups of the non-mesogenic fragment, which does not ensure the mutual arrangement and ordering of the mesogenic blocks.

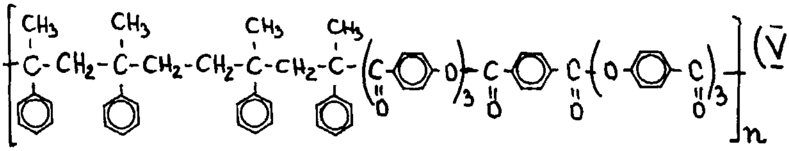
In order to study the effect of these factors it was decided to increase only the length of the mesogenic fragment. For this purpose, a TαMS with 4'-oxybenzoyl-4-oxybenzoyl groups was obtained similarly to I

(IV)



The M_n of diphenol I determined by vapor osmometry was 790 and the calculated value was 954. The functionality according to the calculated MW was 1.85. The structure of the product was confirmed by IR and NMR spectroscopy.

The reaction of α,ω-(4'oxy-benzoyl-4-oxybenzoyl)-TαMS (IV) with TOBC gave a copolymer with the following structure:



(V)

The spectral characteristics of copolymer V are in good agreement with the supposed structure. According to the data of polarizing optical microscopy, in the 200-285°C range the copolymer

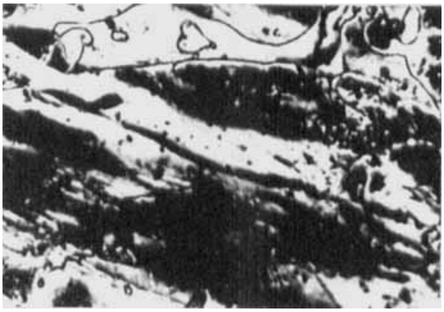


FIGURE 1. Nematic texture of copolymer V at 250°C.

is in the LC state. The existence of a typical thread-like texture indicates that the resulting mesophase is probably of the nematic type(Fig.1).

At relatively low M_n of the copolymers, the type of the end groups (or end blocks) of the multi-block copolymers probably profoundly affects the properties of the copolymer.

Hence, these data show that it is possible to obtain thermotropic segmental copolymers with sterically loaded non-mesogenic fragments rigidly bonded to the mesogenic fragments.

The relationships between the structure and the mesogenic ability assumed for the LC polymers evidently have wider limits than is usually considered.

EXPERIMENTAL

1. A bis-Na-tetramer of α-methylstyrene was obtained similarly to /6/. The reagent used and the reaction conditions had to meet the requirements typical of the living anionic polymerization /8/.

2. α, ω -(4-hydroxybenzoyl)-TαMS.

A reaction vessel filled with the prepared solution of trimethylsiloxybenzoyl chloride in THF was charged with a bis-Na-TαMS solution a thin stamless steel needle with the aid of argon pressure. The reaction was carried out at 25°C. The trimethylsilyl protection group was removed by addition of an aqueous-methanol solution of hydrochlorid acid. The product was isolated by dissolving at selectively in chloroform and benzene and twice lyophilized from benzene.

Found: % C 84.53; H 7.02; OH 4.56; M_n 680

Cald.: %: C 84.03; H 7.00; OH 4.76; MW 714.

3. Trimethylsilyl-4-(trimethylsiloxy)benzoate was obtained by the silylation of 4-hydroxy-

benzoic acid with hexamethydisilazane /9/. The product was isolated by fractional distillation collecting the fraction with $T_{B.p.}$ 102°C (2mHg) the yield was 90%, n_D^{20}=1.4845.

Found: %: C 55.12; H 7.62; Si 19.65.

Calc. %: C 52.27; H 7.85; Si 19.89.

4. 4-Trimethylsiloxybenzoyl chloride was obtained according to /10/.

5. 4'-hydroxybenzoyl-4-oxybenzoic acid (4-HOBA) was obtained by the modified procedure described in /11/ from 4-hydroxybenzoic acid. The structure of the product was confirmed by NMR spectra.

K_M 255°C $\xrightarrow{LC}$ I 277-282°C with decomposition.

6. Silylation of 4-HOBA was carried out with hexamethyldisilazane similarly to that described above (p.3).

7. 4'-trimethylsiloxy-4-benzoyl-oxybenzoyl chloride was prepared by the chlorination of a bis-silyl ester of 4-HOBA with thionyl chloride in benzene at 80°C and isolated by treatment with dry benzene. The yield was 85-90%.

K 64°C $\xrightarrow{LC}$ I 74°C.

Found %: C 59.80; Si 8;26; H 5;15; Cl 10.13.

Calc. %: C 58.54; Si 8.03; H 4.88; Cl 10.19.

8. α,ω-(4'-hydroxybenzoyl-4-oxybenzoyl)-TαMS was obtained by the reaction of corresponding chloroanhydride with di-Na-TαMS in THF by the method described above (p.2.) The product was isolated by selective dissolution in chloroform and benzene and lyophilized twice from benzene. The content of OH (reffered to the theoretical MW) %:

found 3.32, calc. 3.56, T_{melt} 127-130°C.

9. The synthesis of copolymers was carried out by two methods: a) acceptor-catalytic low-temperature (20°C) condensation and b) acceptorless high-temperature condensation in solution. Triethylamine was used as the catalyst and acceptor of hydrochloric acid. At high-temperature condensation, the side products were "flushed out" with an argon stream. The solvents used were chloroform for the low-temperature process and diphenyloxide for the high-temperature one. The polymers were purified by repeated repricipitation $[\eta]$ dl/g ($CHCl_3$, 20°C) for II 0.16 (method a, b), for III 0,3-0,5 (methods "a" and "b", for V $[\eta]$=0.33 dl/g ($C_2H_2Cl_4$, 20°C) method "b".

10. Methods of analysis. Content of hydroxyl groups was determined by acetylation.
Molecular weights of oligomers were determined by Hitachi-Perkin-Elmer md. 115 osmometer.

The NMR spectra of the products were obtained with a JEOL-60 Spectrometer.

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REFERENCES

1. Ober Ch.K., Jin J.I., Lenz R.W. Adv.Pol.Sci., 1984, N 59, p.103.
2. Van Berkel R.W.N., de Graaf S.A.F., Huntjens C.M.F., Developments in Block Copolymers -

1. Ed. by I.Goodman, Appl.Sci. Publish., London & N.Y., 1982, p.261.

3. Bilibin A.Yu., Tenkovtsev A.V., Pyraner O.N., Skorokhodov S.S., Vysokomol.Soedin., 1984, t.26, N 12, p.2570.

4. Bilibin A.Yu., Shepelevsky A.A., Frenkel S.Ya., Skorokhodov S.S., Vysokomol.Soedin., 1980, t.22B, N 10, p.739.

5. Weber L., Makromolek.Chem., Makromolek.Symp., 1986, N 3, p.317.

6. Richards D.H., Williams R.L. J.Polym.Sci., Polym.Chem. Ed. 1973, N 11, p.89.

7. Skorokhodov S.S., Korshun A.M., Asinovskaya D.N., Abstr.Euchem.Conference on the Synthesis of Polymers and Polymer Liquid Crystals, Lahti, Finland, 1986, p.30.

8. Szwarc M., Carbonions Living Polymers and Electron Transfer Processes. N.Y., John Wiley, 1968.

9. Choby E.C., Jr., Neuworth M.B., J.Org.Chem., 1966, N 31, p.633.

10. Schwarz G., Alberts H., Kricheldorf H.R., Liebigs Annalen der Chemie, 1981, N 7, p.1257.

11. Fischer E., Freudenberg K., Ann., 1910, N 372, p.45.