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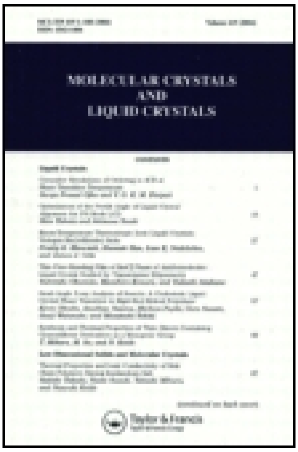

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Synthesis of Liquid Crystalline Polymers with X- and T-Like Mesogenic Fragments Via Diels-Alder Reaction

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SYNTHESIS OF LIQUID CRYSTALLINE POLYMERS WITH X- AND T-LIKE MESOGENIC FRAGMENTS VIA DIELS-ALDER REACTION

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Institute of Macromolecular Compounds of the Russian Academy of Sciences,Bolshoi pr.3I,St.Peterburg, I99004,Russian Federation

Abstract Main chain polymers with a mesogen which contains the residue of muconic acid as the central unit were synthesized.Polymers with a T-like mesogen were obtained by thermal addition of N-substituted maleimides.As a result of reaction with fumaroyl chloride and subsequent reaction with phenols or amines,polymers with X-like mesogen were obtained.

INTRODUCTION

The Diels-Alder(D-A) reaction is very widely used in organic chemistry[I],but has almost not been applied in the synthesis of liquid crystalline(LC) compounds.This is probably due to the fact that classical requirements to the shape of the molecules of the LC compounds are relativly simple.The molecule should be rod-like,and all deviations from this shape,e.g.the broading of the mesogen weaken the mesomorphic properties[2].In contrast,D-A reaction is inevitably related to these changes in the shape of rod-like molecules because the conformation of six-membered reaction product is non planar and also both diene and dienophile should have substituents[I].However,recently new variations of the traditional rod-like shape of LC compounds:discs,crosses, and other more complex molecular shapes have appeared[3].Nevertheless,the synthesis of these compounds is based on traditional approaches,mainly on using consequtive esterification reactions.Therefore,these synthesis are laborious and the variety of resulting compounds is limited.This,in turn, makes it difficult to search for general relationships

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of the structure-properties type in these posystems.In polymers the situation is even more complex because as a result of multistage reactions polymers of very different molecular weight(MW) and with different defects are formed.Therefore, the comparison of their properties is difficalt.The aim of the present paper is to synthesize LC polymers with T- and X-like mesogenic fragments via the chemical modification of one initial polymer.The D-A reaction was chosen as the modificationr reaction,thus,it became possible to obtain a wide range of polymers with T- and X-like mesogens on the basis of a single polymer.

EXPERIMENTAL PART

All reagents and solvents(Sojuzreactiv,USSR),with the exception of I,I,2,2-tetrachloroethane(TCE),Merck,were purified by distillation or by recrystallitation.Muconoyl chloride[4], azophenols[5],and 4-n-heptyloxy-4'-hydroxybiphenyl[6] were prepared according to the literature.

4,4'-(Muconoyldioxy)dibenzoic acid(I):To a solution of 20.92g (0.I47mol) of 4-hydroxybenzoic acid in I60ml of IN NaOH at 0-4°C was added with stirring during 40min a solution of I2.6g(0.07mol) muconoyl chloride in 200ml of carbon tetrachloride and 200ml of IN NaOH.Stirring was continued for another 2h,the residue was filtered off,washed with 200ml of 0.6N HCl and with water,and dried.Yield I6.3g(6I%).

$C_{20}H_{I4}O_8$(379.3) Calc. C 63.27 H 3.69
Found C 63.0I H 3.66

The elemental analysis of I was carried out with a sample obtained by hydrolysis of II.

4,4'-(Muconoyldioxy)dibenzoyl dichloride(II):6.0g(I7mmol) of I was refluxed with I00ml of thionyl chloride with 3-4 drops of dimethylformamide(DMF) for 4h.The hot solution was filtered off and evaporated.The residue was vacuum-dried and recrystallized from chloroform.Yield 5.Ig(7I%) T_m=232°C

$C_{20}H_{I2}Cl_2O_6$(4I9.2) Calc. C 57.25 H 2.86 Cl I6.9I
Found C 57.4I H 2.8I Cl I6.74

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I

^{1}H NMR(δ ,CDCl$_3$): 8.21(4H,d),7.36(4H,d),AA'XX7.62(2H),6.49 (2H)

Polycondensation:A solution of 2.5mmol of 1,10-decanediol or α,ω -bis-(4-hydrobenzoyl)decane,2.5mmol II,2ml(25mmol) of pyridine in 40ml of TCE was stirred at 100°C in an argon flow for 6h,then the reaction mixture was cooled to 20°C and the solution was poured into 300ml methanol,the precipitated polymer was filtered off,dried,and twice reprecipitated from chloroform or trifluoroacetic acid(TFC) in methanol.Yield 90-95%.

Thermal addition.A sealed tube was filled with 2mmol of polymer III or V,6mmol of dienophile and 20ml of TCE.The tube was placed in a thermostat and heated to 160°C.Thermal addition was continued at this temperature for 48h,the reaction mixture was cooled to 20°C and poured into 200ml of methanol or petroleum ether(for fumaroyl chloride),the precipitated polymer was filtered off and twice reprecipitated from chloroform into methanol or petroleum ether.The yield was quantitative.

α , ω -bis-(4-hydroxybenzoyl)decane IV:2g III(4mmol),0.45g fumaric acid in 10ml of DMF in argon flow was heated at 150°C for 5h and poured into 60ml of water.The resultant crystals were fieltered off,recrystallized from ethanol-water(1:1) and vacuum-dried.Yield 1.04g(65%),T_m=165°C[7].

Chemical modification:

a)with phenols.2mmol polymers VII or XII,6mmol phenol,2ml pyridine in 10ml 1,2-dichloroethane was heated at 70°C for 5h and poured into 100ml of methanol,the precipitated polymer was filtered off,and twice reprecipitated from chloroform into methanol.Yield was quantitative.

b)with anilines.2mmol polymers VII or XII,6mmol of substituented anilines,2ml of pyridine in 10ml of chloroform were stirred at room temperature for 2h and poured into 100ml of methanol,the precipitated polymer was filtered off and twice repricipitated from chloroform into methanol.The yield was quantitative.

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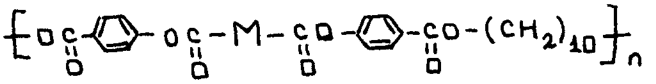
Polymers viscosities were measured in a Ubbelohde viscometer. NMR spectra were recorded on a Bruker AC 200 spectrometer. Polarizing-optical examinations were carried out on a Boethius stage(DDR), and DSC were performed with a DSM-2M instrument(USSR).

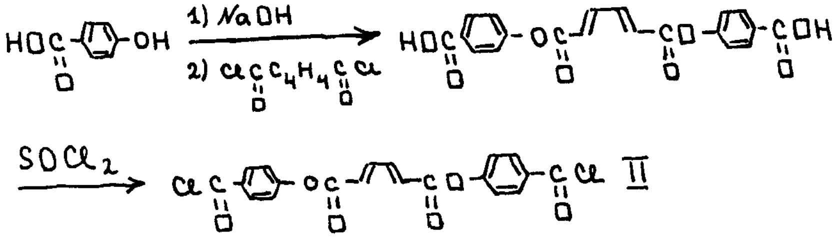
RESULT AND DISCUSSION

In order to facilitate the establishment of the structure-properties relationships of a series of main chain LC polymers, maximally standartisized polymers should be chosen for the investigation:



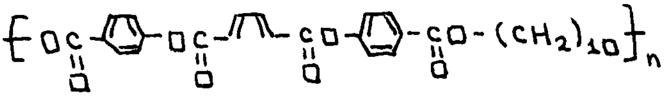
I

Polymers I with a decamehhylene spacer and a mesogenic triad as the rigid block may be used for this purpose[8]. A great number of synthesized LC polymers with this structure facilitate the elucidation of the effect of different structure variations on the LC properties. In order to make these polymers capable of taking part in the D-A reaction, it is sufficient to introduce a cis-butadiene fragment, e.g. a fragment of (E,E)-muconic acid, into the central subunit M. aA relativly convenient method of synthesis of monomer dichloroanhydride containing the potential mesogenic fragment was chosen[9]:



II

High products yields in all stages of synthesis and its relative simplicity make this path very convenient. Chloride II was used in polycondensation with I,IO-decanediol by usual procedure, and polymer III was obtained:



III

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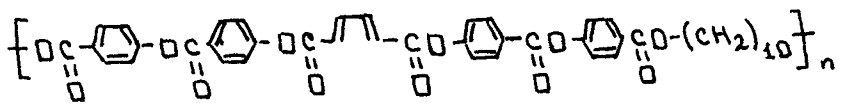
Polymer III does not exhibit LC properties because of the E,E-configuration of the central unit. This polymer is soluble in chloroform, I,2-dichloroethane, TCE, and upon heating also in o-dichlorobenzene, DMF, and diphenyl oxide which makes it possible to use it as a substrate in thermal D-A reaction.

Usually the procedure for imparting LC properties to the polymer consists of the lengthening of the potential mesogenic fragment[8]. In this work polymer V was sythesized by reaction II with α,ω-bis-(4-hydroxybenzoyl)decane IV:



V

The well-known method of synthesis IV by using protecting groups is multistage and laborious[7]. In this work a new method of itssynthesis has been developed by using a polymer derivative as the intermediate. It has previously been observed that under certain conditions of thermal D-A reaction between diethyl muconate and maleic or fumaric acids the products is unstable and decomposes with the formation of carbon oxide and dioxide. By heating polymer III with a twofold excess of fumaric acid in DMF in an argon flow diol IV was obtained in 60-70% yield. This method greatly simplified the synthesis enabling us to use a very narrow reagents range and only few stages.

Polyester V($[\eta]$=0.7-I.0dl/g, TFA, 25°C) is the thermotropic, its T_m=I50-I60°C and $T_i \geqslant 300$°C. The precise determination of isotropization temperature is prevented by polymer V degradation at temperatures exceeding 250°C. Polymer V is soluble in TFA and, on heating, in TCE.

The cis-configuration of double bonds in (E,E)-muconic acid favours the cycloaddition but the presence of the carbonyl groups greatly deactivate this enophilic component[I]. Hence, only active dienophiles, e.g. those with accepting sub-

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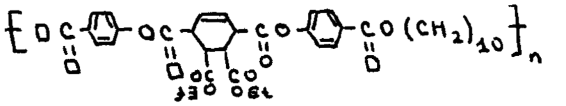
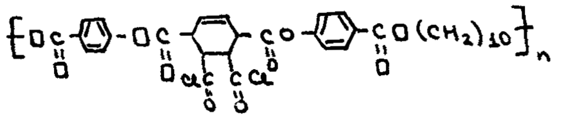
stituents,should be used for thermal addition.Fortunatlly, COCl is the most activating group[I].Therefore,it is possible to use the polymers obtained by D-A reaction for furthern chemical modification.

Diethyl fumarate,fumaroyl chloride and N-phnylmaleimidewere used as dienophiles.The optimal conditions of D-A reactions in these systems are as follows:48h at I60°C in a sealed tube at a three-fold excess of dienophile component in TCE solution.Under these conditions quantitative addition takes place.The introduction of copper powder excluded the reactions of free-radical crosslinking.No thermal degradation of polymers and no decrease in MW take place in these conditions.This has been determined from end groups content by ^{I}H NMR spectroscopy.

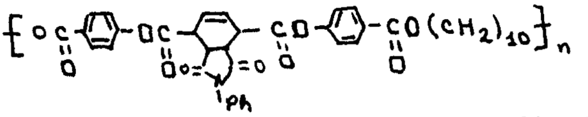
Polymers VI-VIII containing fragment of substituted cyclohexene as the central unit were obtained:in



VI $T_m = 113^\circ$C



VII $T_m = 94^\circ$C



VIII $T_m = 76^\circ$C

Initial polyester III used in modification has[η] =0.35-0.40dl/g in chloroform at 25°C,e.g. $\bar{M}_W$~ I5000,which exceeds the limit necessary for the absence of MW dependence of phase transition temperature[IO].

We expected to reveal the LC behaviour of these polymers,because polyesters containing the trans-I,4-cyclohexane fragment as central unit have a highly stable mesophase[II]. The most stable conformation of cyclohexene is half-chair[I2], which ensures the trans configuratin of carbonyl groups of the muconic acid residue in the resulting cyclohexene.This also formally favours the LC behaviour.

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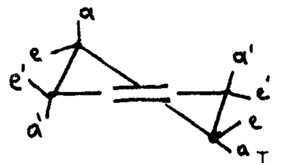
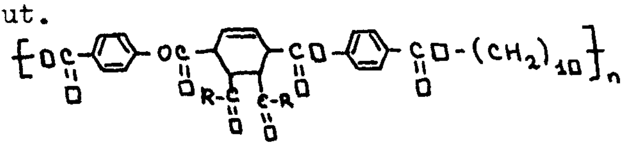


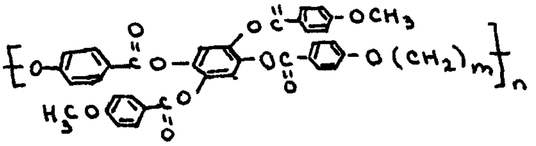
I

Since D-A reaction is stereospecific,the initial configuration of diene and diedophile is retained in the addition product.However,these polymers do not exhibit the LC behaviour.This may be attributed to the presence of bulky substituentes which decrease the anisometric ratio of mesogen[2]. Hence,this result is on thewhole expected.The presence of reacting chloroanhydride groups in polymers VII easily makes it possible to obtain polymers with an X-like mesogen by by reactios with the corresponding p-substituented anilines or phenols,because during D-A reaction trans-configuration of chloroanhydride groups is retained.This synthesis was carried out.



IX

All polymers IX are not LC(Table I).This result is unexpected to a considerable extent because,for example polymers X synthesized by Ringsdorf at al.[I3] with a similar structure,have a highly stable mesophase(for example for m=6,T_g=60°C,T_i=2I7°C,m=9,T_g=54°C,T_i=2I4°C).



X

The absence of the LC behaviour for polymers IX may be due to the high conformational lability of the cyclohexene fragment,which is much higher than that for cyclohexane[I2]. As already mentioned,the conformation lability of the central unit of polymer I has a negative effect on the possibility of the mesomorphism[I3].

An attemt to render polymers IX mesomorphic was made: polymers in which the length of the arm of cross-like meso-

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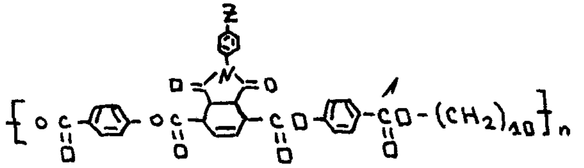
gen is greatly increased.were synthesized by reacting polymer VII with p-aminoazobenzene and p-aminoazotoluene(Tab.I). However,neither these polymers were LC polymers.

Polymer V was allowed react with a series of N-phenyl maleimides substituented on the nucleus:



XI

TABLE I Properties of polymers IX

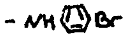
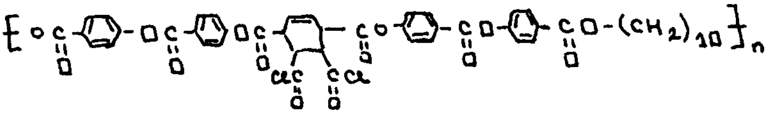
R						
T_m °C	85	I20	80	I00	II2	I05

TABLE 2 Properties of polymers XI

Z	H	CH_3	OCH_3	$O\text{-}n\text{-}C_3H_7$	Cl	Br	NO_2
T_m °C	95	94	9I	90	95	93	I00
T_i °C	I26	I22	I20	II9	I23	I22	I2I

The properties of polymers XI are given in Table 2.All of them have low temperatures of melting and isotropization and these temperatures are similar regardless of the substituent Z.On the whole the effect of the substituent on the phase behaviour of polymers XI is close to that observed by Lenz for polyester I[I5] and shows that for polymers with a bulky side substituent in the mesogenic fragment the steric interaction play the main rolein the determination of mesophase stability,whereas all other contribution are minor. The mesophase type for polymers XI was not determined.

The reaction of polymer V with fumaroyl chloride yields polymer XII(T_m=70°C, T_i=II5°C).



XII

A wide range of polymers XIII was obtained by the reaction of this polymer with various phenols and amines.It can be esealy seen that all polymers XIII(Table 3) obtained

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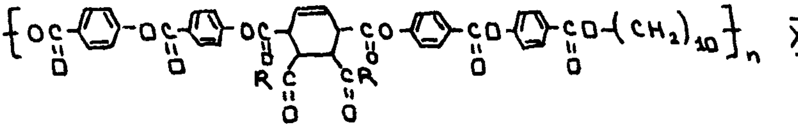
during the reaction of mononucleus compounds are not LC. This is probably due to the fact that in usual main chain



XIII

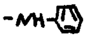
LC polymers the effect of two arene substituents is incomparably higher than that of one arene substituent.If the mesogenic fragment contains two arene substiutents,these linear polymers usually do not exhibit LC behaviour,even in the case of polyarylates[16].

The situation changes drastically if dinuclear phenols or amines are used in the reaction.POlymers XIII obtained in this way are LC.It is interest that the azophenol substituents exhibit the stabilazing effect of lateral substituet on the mesophase which is characteristic of low molecular wheight nematics[2].

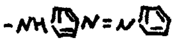
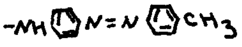
$$OCH_3 > CH_3 > OC_2H_5 > Cl \approx Br$$

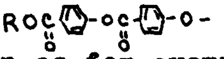
According to the textures detected under the polarizing microscope all polymers XIII have the nematic phase.

TABLE 3 Properties of polymers XIII

R						
Tm °C	95	I25	IOO	II2	95	II5
T_i °C	not LC	not LC	Not LC	not LC	not LC	not LC

R					
T_m °C	I20	I05	95	88	90
T_i °C	I63	I32	I60	I73	I57

R				
T_m °C	IIO	I20	I40	IIO
T_i °C	I43	I44	not LC	I6I

These series of polymers allow the formulation of the main requirements for the appearance of the thermotropic mesomorphism of polymers with an X-like mesogen:each arm of the cross should be able to play the role of mesogenic fragment in low molecular wheight compounds.In our case in the main chain this is  and side substituents are typical mesogen as,for example .

The conditions of LC appearance formulated by us for polymer XIII with an X-like mesogen conside completely with the theoretical predictions:each arm of the cross should consist of molecules capable of being mesogens in low molecular wheight compounds[I7].

REFERENCES

I. W.Carruthers,*Cycloaddition Reactions in Organic Synthesis* (Pergamon Press,New York,I990).
2. H.Kelker and R.Hatz,*Handbook of Liquid Crystals*(Verlag Chemie,Weinheim,I980).
3. D.Demus,*Liq.Cryst.*,*5* ,728(I988).
4. D.B.Taylor,K.P.Callahan and I.Shikh,*J.Med.Chem.*,*I8*,I088 (I974).
5. *Organikum*(VEB Deutscher Verlag der Wissenschaften,Berlin, I976).
6. T.Nakono,T.Hasegava and Y.Okamoto,*Macromolecules* ,*26*, 5494(I993).
7. C.K.Ober,J.I.Jin and R,W.Lenz,*Polymer J.*,*I4*,9(I982).
8. C.K.Ober,J.I.Jin and R.W.Lenz,*Adv.Polym.Sci.*,*59*,I04(I984)
9. A.Yu.Bilibin,A.V.Tenkovcev,O.N.Piraner and S.S.Skorokhodov,*Vysokomollek.Soedin.,Ser.A*,*26*,2570(I984).
I0.R.BBlumstein,E.M.Stickles and A.Blumstein,*Mol.Cryst.Liq. Cryst.Lett.*,*82*,205(I982).
II.K.Clausen,J.Kops,K.Rasmussen,K.H.Rasmussen and J.Sonne, *Macromolecules*,*20*,2660(I987).
I2.J.M.Lambert and D.E.Marko,*J.Am.Chem.Soc.*,*I07*,7978(I985).
I3.S.Berg,V.Krone and H.Rngsdorf,*Makromol.Chem.Rapid Commun.* *7*,38I(I986).
I4.A.Yu.Bilibin,A.V.Tenkovcev and O.N.Piraner,*Makromol.Chem.* *I92*,30I3(I99I).
I5.R.W.Lenz,*J.Polym.Sci.Polymer Symp.*,*72*,I(I985).
I6.H.R.Kricheldorf,G.Schwarz,A.Domschke and V.Linzer,*Macromolecules*,*26*,5I6I(I993).
I7.D.Braun,M.Reubold,M.Wegmann,J.H.Wendorf,*Makromol.Chem. Rapid Commun.*,*I2*,I5I(I99I).

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