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SYNTHESIS OF MODEL COMPOUNDS OF THE NEMATIC POLYESTER POLY(2,2'-DIMETHYL-4,4'-DIOXYAZOXYBENZENEDODECANEDIOYL).

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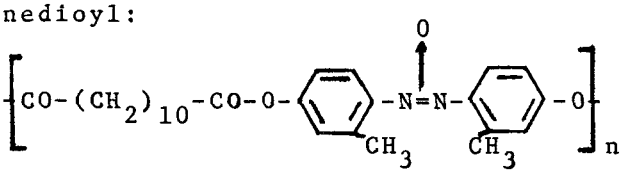
ABSTRACT

We describe synthesis and phase characterization of model compounds of the thermotropic nematic polymer poly(2,2'-dimethyl-4,4'-dioxyazoxybenzene dodecanedioyl), which consists of regularly alternating rigid mesogenic and flexible aliphatic moieties. Models were composed of the following sequences: flexible-rigid-flexible; rigid-flexible-rigid (9-DDA-9); rigid-flexible; flexible-rigid-flexible-rigid-flexible. Only 9-DDA-9 displays a mesophase (monotropic nematic). The appearance of an enantiotropic nematic phase is associated with the development of a polymeric structure (approximately six repeating units are required).

Thermotropic polymers in which a rigid mesogenic core regularly alternates in the main chain with a flexible "spacer" group are currently the focus of active academic and industrial research because of their unique application potential as high strength fibers, films, and coatings. In our laboratory we are investigating the influence of molecular weight and molecular weight distribution on mesophase stability, degree of alignment, and spacer conformation in a series of nematic polyesters. As part of this investigation we describe here the synthesis and preliminary characterization of some model compounds

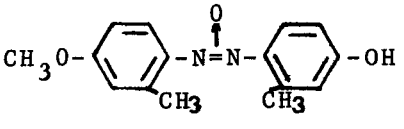
of poly(2,2'-dimethyl-4,4'-dioxyazoxybenzene dodecanedioyl:



This polymer, labelled DDA-9, has moderately low transition temperatures with a nematic stability range of 45-50°C (1). In a sample of $\bar{M}_n$ = 11,700, for example, the phase transitions are K118N162I. Schlieren nematic textures and total miscibility with standard nematics are observed (2). Order parameters in a homogeneously aligned melt were found to be unusually high, for the spacer (3) as well as the mesogene (4) moieties. The extended conformation of the dodecanedioate spacer is confirmed by evidence drawn from x-ray diffraction and calorimetry experiments (5).

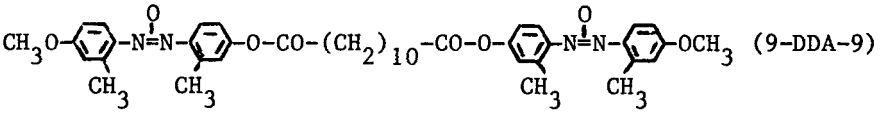
EXPERIMENTAL:

The 2,2'-dimethyl-4,4'-hydroxyazoxybenzene (compound 9) was prepared according to literature procedures (6,7). The symmetrically substituted compounds 2,2'-dimethyl-4,4'-acetoxyazoxybenzene (Ac-9-Ac) and 2,2'-dimethyl-4,4'-lauroyloxyazoxybenzene (DDA-9-DDA) were prepared by acylation of the disodium salt of 9 with acetic anhydride and lauroyl chloride, respectively. The unsymmetrically substituted compound (I), a mixture of 4-methoxy-4'-hydroxy and 4-hydroxy-4'-methoxy structural isomers,



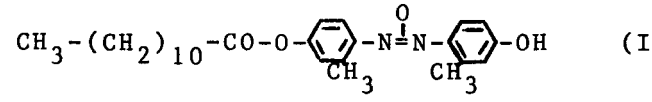
(I) was prepared as follows:

2,2'-dimethyl-4-hydroxy-4'-methoxyazobenzene was obtained by diazotization of 4-methoxy-2-methylaniline and coupling with the sodium salt of m-cresol. Following oxidation with 30% H_2O_2 in glacial acetic acid, isomers (I) were obtained with an 80% yield. Compound (I) was acylated with lauroyl chloride to yield 2,2'-dimethyl-4-methoxy-4'-lauroyloxyazoxybenzene.(9-DDA). Two moles of (I) were acylated with 1 mole of dodecanedioyl chloride to yield 9-DDA-9.



(9-DDA-9)

Acylation of 4-nitro-3-methylphenol with lauroyl chloride, followed by catalytic hydrogenation produced 4-amino-3-methyl phenyl laurate (II), which was diazotized and coupled with the sodium salt of m-cresol to yield 4-hydroxy-4'-lauroyloxy-2,2'-dimethylazobenzene (III). Compound (III) was oxidized to (IV).



(IV)

Two moles of (IV) were acylated with one mole of dodecanedioyl chloride to yield bis 4-(4'-lauroyl-2,2'-dimethylazoxybenzene) dodecanedioate and two other structural isomers (DDA-9-DDA-9-DDA).

Azoxy compounds were isolated by column chromatography using Woelm SiO_2 with a chloroform-ethanol solvent system. They were checked for purity by elemental analysis and NMR spectroscopy; molecular weights were determined by mass spectrometry. The relative

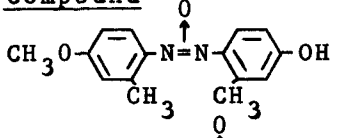
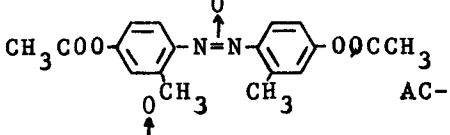
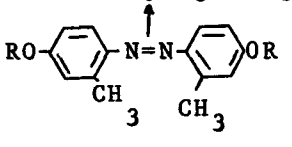
proportions of structural isomers were calculated from 90-MHz proton NMR spectra of 9-DDA and the shift reagent $Eu(fod)_3$, following a procedure described by Rondeau, et. al. (8). Similar results can be achieved without a shift reagent by using a 100 MHz instrument.

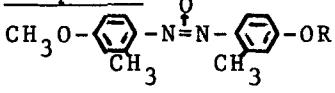
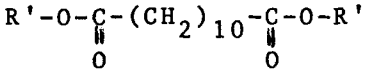
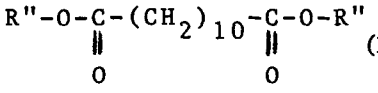
Textures of the materials were studied using a Leitz Ortholux polarizing microscope equipped with a Mettler hot stage and temperature programmer. Thermal analysis was performed with a Perkin Elmer 2C Differential Scanning Calorimeter. In order to provide a consistent thermal history, each material studied was first heated to at least 20 degrees above the crystal to isotropic transition. DSC traces were obtained by cycling the sample between this temperature and 240°K. The heating and cooling rates were 10 degrees/min.

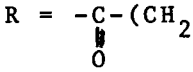
RESULTS AND DISCUSSION:

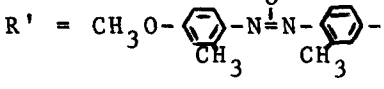
Phase transition temperatures of model compounds are listed in Table I.

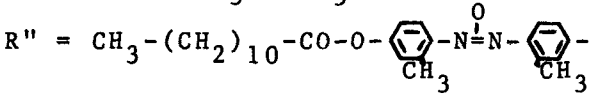
Table I PHASE TRANSITIONS OF MODEL COMPOUNDS

Compound	Symbol	Molecular Weight (g/mole	T_{KI} (°K)	T_{IN} (°K)
	I	272.3	(decomposition) ~383	
	AC-9-AC	342.3	424	
	DDA-9-DDA	622.8	350	

Compound	Symbol	Molecular Weight (g/mole)	T_{KI} (°K)	T_{IN} (°K)
	9-DDA	454.6	333	
	9-DDA-9	738.8	395	373
	$(DDA-9)_2$-DDA	1075.4	343.2	

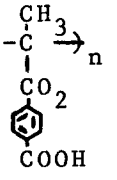
R = 

R' = 

R" = 

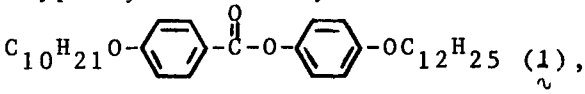
Structures derived from the unsymmetrically substituted compound (I) were mixtures of structural isomers: 9-DDA, for example, was found to be a mixture of the 4-methoxy-4'-lauroyloxy and 4-lauroxy-4'-methoxy isomers in about 55/45 ratio. Compound 9-DDA-9 is the only one for which a mesophase was observed, a monotropic nematic phase appearing at 100°C. upon cooling from the isotropic melt. This nematic phase is supercooled to room temperature but cold crystallization is observed at 36°C. upon heating. Fig. 1a shows the ringed spherulites developed by cold crystallization. Fig. 1b shows the development of the monotropic nematic phase upon cooling from the isotropic melt. DDA-9-DDA-9-DDA is not mesomorphic; indeed, of the systems which we have investigated to date, the smallest molecular weight

to display an enantiotropic nematic phase is an oligomer fraction of M_n = 2,700, containing approximately six repeating units per chain. We are therefore dealing with a system in which the monomer and the repeating unit are not mesomorphic and in which the appearance of a nematic phase is associated with the development of a polymeric structure. It is interesting to note that we have obtained similar results with poly(methacryloyloxybenzoic acid), a vinyl polymer in which the rigid mesogenic units are attached to the flexible backbone as side-chains. The polymer

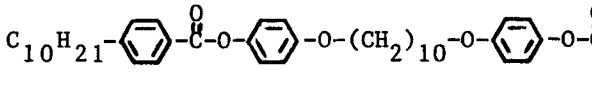


(PMBA) forms a smectic glass (9) but neither the monomer nor the dimeric model compound are mesomorphic. On the other hand, oligomeric fractions containing an average of 4-6 repeating units per chain were found to display smectic organization (10).

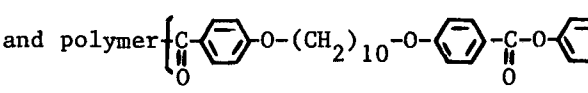
In what is to our knowledge the only other study of models of liquid crystalline polymers, Griffin and Britt (11) have compared the behavior of 4-alkoxyphenyl-4'-alkoxybenzoate



(1), the model prepolymer



(2), and polymer



(3)

Compound (1) has a rigid central core with flexible tails similar to the flexible-rigid-flexible sequence found in DDA-9-DDA; compound (2) has a flexible-rigid-flexible-rigid-flexible sequence similar to that of DDA-9-DDA-9-DDA. In contrast to our results, however, the authors report a continuum of nematic behavior from compound 1 to polymer 3. It is clear that in the case of the DDA-9 system the nematic phase appears as the result of cooperativity between successive repeating units. In order to delineate the transition from low molecular weight to polymeric liquid crystal we are currently investigating order parameters and degree of extension of the flexible spacer units, as a function of molecular weight.

Figure 1a. Ringed spherulites formed during cold crystallization of 9-DDA-9. Magn. 320x.

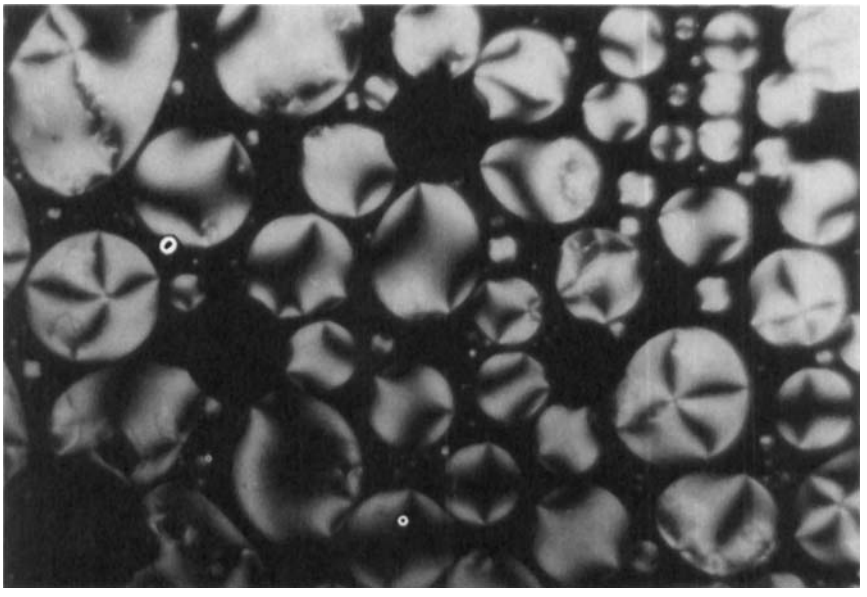


Figure 1b. Monotropic nematic phase formed upon cooling of 9-DDA-9. Magn. 320x.

ACKNOWLEDGEMENT:

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REFERENCES:

1. A. Blumstein and S. Vilasagar, Mol.Cryst.Liq. Cryst. (Letters), 72, 1(1981).

2. J. Billard, A. Blumstein, and S. Vilasagar, Mol. Cryst.Liq.Cryst. (Letters), 72, 163(1982).

3. A.F. Martins, J.B. Ferreira, F. Volino, A. Blumstein, and R.B. Blumstein, Macromolecules (Submitted for Publication).

4. F. Volino, A.F. Martins, R.B. Blumstein and A. Blumstein, C.R.Acad.Sci. (France), 292, II, 89(1981).

5. A. Blumstein, S. Vilasagar, S. Ponrathnam, S.B. Clough, and R.B. Blumstein, J.Polymer Science, (Polymer Physics), 20, 877(1982).

6. N.J. Leonard and J.W. Curry, J.Org.Chem., 17, 1071(1952).

7. R.A. Raphael and E. Vogel, J.Chem.Soc., Pt.2, 1958(1952).

8. R.E. Rondeau, M.A.Berwick, R.N.Steppel, and M.P. Serve, J.Am.Chem.Soc., 94,4(1972).

9. A. Blumstein,S.B. Clough, L.Patel, R.B.Blumstein and E.C.Hsu, Macromolecules, 9, 243(1976).

10. E.M. Stickles and R.B.Blumstein, unpublished results.

11. A.C. Griffin and T.R. Britt, J.Am.Chem.Soc., 103, 4957(1981).