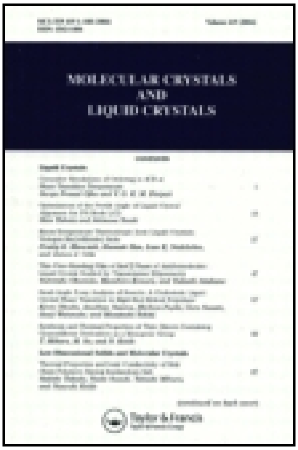
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 19 February 2013, At: 13:06
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

New Mesogenic Polyethers Derived From Benzalazines

Mercedes Marcos [a], Luis Oriol [a], Blanca Ros [a], Jose Luis Serrano [a] & Patrick Keller [b]

[a] Departamento de Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009, Zaragoza, (ESPANA)

[b] Laboratoire de Spectrometrie Neutronique "Leon Brillouin" C.E.N., Saclay, (France)

Version of record first published: 13 Dec 2006.

To cite this article: Mercedes Marcos, Luis Oriol, Blanca Ros, Jose Luis Serrano & Patrick Keller (1988): New Mesogenic Polyethers Derived From Benzalazines, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 155:1, 103-112

To link to this article: http://dx.doi.org/10.1080/00268948808070356

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

Mol. Cryst. Liq. Cryst., 1988, Vol. 155, pp. 103-112
Photocopying permitted by license only
© 1988 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

NEW MESOGENIC POLYETHERS DERIVED FROM BENZALAZINES

MERCEDES MARCOS, LUIS ORIOL, BLANCA ROS, JOSE LUIS SERRANO
Departamento de Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza (ESPAÑA)

PATRICK KELLER
Laboratoire de Spectrometrie Neutronique "Leon Brillouin", C.E.N., Saclay (FRANCE)

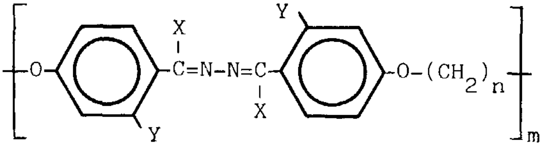
Abstract Four homologous series of flexible main-chain polyethers derived from benzalazines are reported. Enantiotropic nematic phases were found for three of the series. The influence of molecular structure on the mesomorphic properties has been studied. A comparative study is made between their properties and those of the analogous small molecules. The existence of OH group in positions 2,2' of the azine central core made it difficult to synthesize the polymers using the phase transfer catalysis method and consequently a new method was employed.

INTRODUCTION

Many thermotropic liquid crystalline (LC) polymers containing mesogenic segments and flexible spacers in the main-chain have now been synthesized[1-2]. The majority of them have been reported as **polyesters**[2-4] although lately some mesomorphic polyether families have also been reported[5-7].

The aim of this article is to present our preliminary data on synthesis and characterization of four new series of thermotropic main-chain LC polymers whose mesogenic units and flexible spacers are connected by ether groups:

polyethers derived from 4,4'-dihydroxybenzalazine and 4,4'-dihydroxy-α, α'-dimethylbenzalazine (series I, II, III and IV).



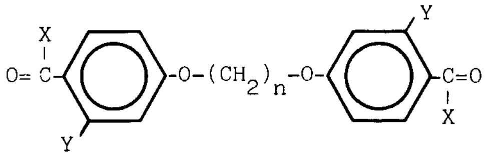
n=6,8,10 and 12

Series	X	Y
I	H	H
II	CH_3	H
III	H	OH
IV	CH_3	OH

The characterization of their phase behaviour was carried out by differential scanning calorimetry (DSC) and optical polarizing microscopy. When the melting points were below the decomposition temperatures the prepared polymers in series I, III and IV show nematic phase, whereas the polymers in series II are not mesogenic.

The polymers in series I and II were prepared by phase transfer catalysed polycondensation. This method, however, proved impossible in the case of the polymers in series III and IV, and for this reason the polymers were synthesised using an alternative method: solution polymerization of monomers (A) with hydrazine hydrate.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013



(A)

n=6,8,10 and 12

Series	X	Y
M-I	H	H
M-II	CH_3	H
M-III	H	OH
M-IV	CH_3	OH

EXPERIMENTAL

SYNTHESIS

Preparation of the monomers

The monomers (A) were prepared using procedures already described by Griffin et al.[5] although several modifications were introduced for the compounds in series M-III and M-IV because of the OH group in ortho-position of the carbonyl groups.

Each of the precursor compounds (A) was prepared by reaction of 60 mmole of the appropiate carbonyl compound, 60 mmole of base and 30 mmole of the appropiate α,ω-dibromoalkane in a suitable solvent. The resulting mixture was magnetically stirred and refluxed. The product was then isolated and purified. Reaction conditions

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

and purification method are given in Table I. IR and H^1 NMR spectra were consistents with assigned structures.

Preparation of the polymers

The four series were prepared in the same way: condensation of 2.5 mmole of the appropiate monomer with 2.5 mmole of hydrazine hydrate in 160 ml of absolute ethanol. Glacial acetic acid was added to the solution, as catalyst, and the reaction mixture was refluxed under a nitrogen atmosphere for 4.30 hours for the polymers in series I and III, and 90 hours in the case of the polymers in series II and IV.

The polymers were collected by vacuum filtration of the hot solution and were washed with ethanol, ether and chloroform. Air drying of the solid followed by vacuum drying at 100°C afforded the polymeric materials.

TECHNIQUES

The thermal properties of the polymers were studied by optical microscopy using a polarizing microscope (Meiji) fitted with a Mettler FP82 heating stage and FP80 control unit. They were checked by DSC (Perkin-Elmer DSC-2). The heating rate was 10°/min and cooling rate was 20°/min. The apparatus was calibrated with indium (m.p. 156.6°C, ΔH_f 6.8 cal/g) and tin (m.p. 231.9°C, ΔH_f 14.45 cal/g).

All samples were run under a nitrogen atmosphere about 10°C above the isotropization temperature and cooled to room temperature and rerun. The transition temperatures were read during the second heating at the peak maximum positions.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

TABLE I Reagents, reaction conditions and purification method for monomers in series M-I, M-II, M-III and M-IV.

Series	Carbonyl Reagent	Base	Solvent (ml)	Time (hrs)	Purification Method
M-I	4-hydroxybenzaldehyde	K_2CO_3	DMF (50)	5	multiple recrystallization from ethanol.
M-II	4-hydroxyacetophenone	K_2CO_3	DMF (50)	5	multiple recrystallization from ethanol.
M-III	2,4-dihydroxybenzaldehyde	$KHCO_3$	Acetone (400)	140	1-recrystallization from toluene/hexane. 2-column chromatography toluene/Cl_2CH_2 12:1 3-recrystallization from ethanol.
M-IV	2,4-dihydroxyacetophenone	K_2CO_3	DMF (50)	5	1-recrystallization from toluene. 2-column chromatography toluene/Cl_2CH_2 12:1 3-recrystallization from ethanol.

The mesophase was identified by optical microscope studies and miscibility studies with a nematogen compound (4,4'-diethoxy-2,2'-dihydroxy- α , α '-dimethylbenzalazine: C—N 223.3°C; N—I 249.9°C[8]).

Limiting viscosity numbers ([η]) of the polymers were determined at 40°C using methanesulfonic acid as a solvent in a Cannon-Fenske viscometer.

It should be noted that methanesulfonic acid rapidily degrades the polymers. Samples were used immediately after preparation.

The identification of polymers was carried out by IR spectroscopie (KBr disc Perkin-Elmer 283) and elemental analysis (Perkin-Elmer 240 C microanalyzer).

RESULTS AND DISCUSSION

In Table II polymerization yields, limiting viscosity numbers, thermal properties and type of mesophase for polymers in series I, II, III and IV are gathered.

As can be seen, the polyethers in series I, III and IV, with the exception of n=6, exhibited liquid crystalline behaviour whereas compounds in series II did not show mesomorphism.

According to the optical textures observed with microscope and mixcibility studies carried out with a nematogenic compound, the mesophases of these polymers all appear to be nematic. Nematic droplets could be seen in some compounds as the isotropic liquid cooled.

Only melting temperatures (Tm) and clearing points (Ti) are given in Table II but there are often dsc peaks below melting points which disappear when the sample is annealed to a higher temperature than the transition

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

TABLE II Yields, limiting viscosity numbers ($[\eta]$), thermal properties and mesophase (M) of the polymers.

Polymers	n	Yield (%)	$[\eta]$(dl/g)	Tm(°C)	Ti(°C)	M
I-6	6	88	0.11	$269^{dec.}$	---	
I-8	8	59	0.13	266	272	N
I-10	10	80	0.08	219	239	N
I-12	12	65	0.17	217	226	N
II-6	6	70	0.13	270	---	
II-8	8	68	0.20	249	---	
II-10	10	72	0.15	183	---	
II-12	12	78	0.17	217	---	
III-6	6	85	0.64	$344^{dec.}$	---	
III-8	8	88	0.48	302	$305^{dec.}$	N
III-10	10	82	0.48	261	313	N
III-12	12	90	0.59	237	263	N
IV-6	6	49	0.17	$323^{dec.}$	---	
IV-8	8	61	0.13	280	$>325^{dec.}$	N
IV-10	10	54	0.14	260	289^{*}	N
IV-12	12	72	0.16	246	251	N

(*) Optical data.

one and we attributed to solid-solid transitions. However, there are other dsc peaks (e.g. I-8; series I, n=8) which may be associated with melting into the mesophase of a polymorphic solid form.

With increasing length of the flexible spacer both the melting and mesophase-isotropic transition temperatures generally decrease although not in a monotonic fashion.

N → I transition normally show wide dsc peaks caused by the dispersion of the molecular species and sometimes in optical microscope transition through a binary system can be observed: N→N+I→I.

If we compare the thermal data of the four series if can be seen that the existence of OH groups in ortho-positions of the azine group (series III and IV) increase the melting and clearing points, which could be attributed to the molecular structure of the polymers where the existence of a hydrogen bond between the ortho hydroxyl groups and the azine nitrogen atoms gives the mesogenic group a rigid central core. As result of this the aromatic rings adopt an almost coplanar orientation and the polarizability of the molecules is increased. This produces a reinforcement of the mesomorphic properties (series II are not mesogenic while series IV are) and an increase in transition temperatures.

The mesogenic behaviour of the polyethers derived from benzalazines is similar to that observed with azines of low molecular weight (used as model compounds) described in previous papers[8-10] in which the presence of OH groups in ortho positions of azine central core stabilized the mesophase. However, low molecular weight compounds with long terminal chains showed smectic phases while polymers show nematic phase.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013

If we make a comparison between the homologous polyesthers of compounds in series II synthesized by Roviello and Sirigu[3] it can be seen that the polyesthers are mesogenic whereas the polyethers do not exhibit mesomorphic properties. This behaviour is also similar to that shown by azines of low molecular weight.

Contrary to what Percec et al.[6,11] observed for polyethers, we found that **polyesters** derived from benzalazines and synthesized by solution polymerization are not soluble in common organic solvents like chloroform, o-dichlorobenzene, THF, tetrachloroethane or nitrobenzene. This makes it difficult to work with them and it was necessary to use more aggressive solvents such as methanesulfonic acid in order to perform the studies of viscosity.

In Table II it can seen that the polymers in series III show higher limiting viscosity numbers than the polymers in the other three series, indicating a higher degree of polymerization for these compounds due to the greater reactivity of the 2,4-dihydroxybenzaldehyde derivatives compared to the other carbonyl compounds used in the other three series.

ACKNOWLEDGEMENTS

One of the authors thanks the Ministerio de Educación y Ciencia (Spain) for the award of a F.P.I. grant which made this research possible.

REFERENCES

1. A. Blumstein, J. Asrar and R. B. Blumstein, Liquid

Crystals and Ordered Fluids (Plenum Press, New York, 1984), Vol. 4, p. 311 and references cited.
2. Ch. K. Ober, J.-I. Jin and R. W. Lenz, Advances in Polymer Sciencie 59 (Springer-Verlag, Berlin-Heidelberg, 1984), p. 103 and references cited.
3. A. Roviello and A. Sirigu, J. Polym. Sci. Polym. Lett. Ed., 13, 455 (1975).
4. R. B. Blumstein, O. Thomas, M. M. Gauthier, J. Asrar and A. Blumstein, Polymeric Liquid Crystals (Plenum Press, New York, 1985), p. 239.
5. A. C. Griffin, T. R. Britt, R. S. L. Hung and M. L. Steele, Mol. Cryst. Liq. Cryst., 105, 305 (1984).
6. V. Percec, T. D. Shaffer and H. Nava, J. Polym. Sci. Polym. Lett. Ed., 22, 637 (1984).
7. P. Keller, Makromol. Chem., Rapid Comm., 6, 255, (1985).
8. M. Marcos, E. Meléndez and J. L. Serrano, Mol. Cryst. Liq. Cryst., 91, 157 (1983).
9. J. L. Alabart, E. Meléndez, B. Ros and J. L. Serrano, Mol. Cryst. Liq. Cryst., 107, 397 (1984).
10. M. Artigas, M. Marcos, E. Meléndez and J. L. Serrano, Mol. Cryst. Liq. Cryst., 130, 337 (1985).
11. T. D. Shaffer and V. Percec, J. Polym. Sci. Polym. Lett. Ed., 23, 185 (1985).

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:06 19 February 2013