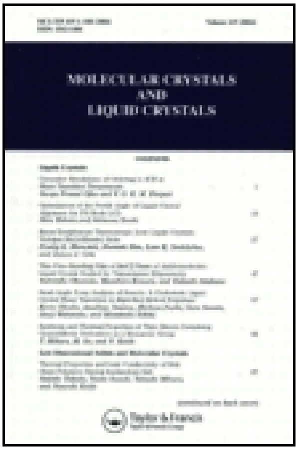

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Synthesis and Study of Polymers Using Complex Monomers

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SYNTHESIS AND STUDY OF POLYMERS USING COMPLEX MONOMERS

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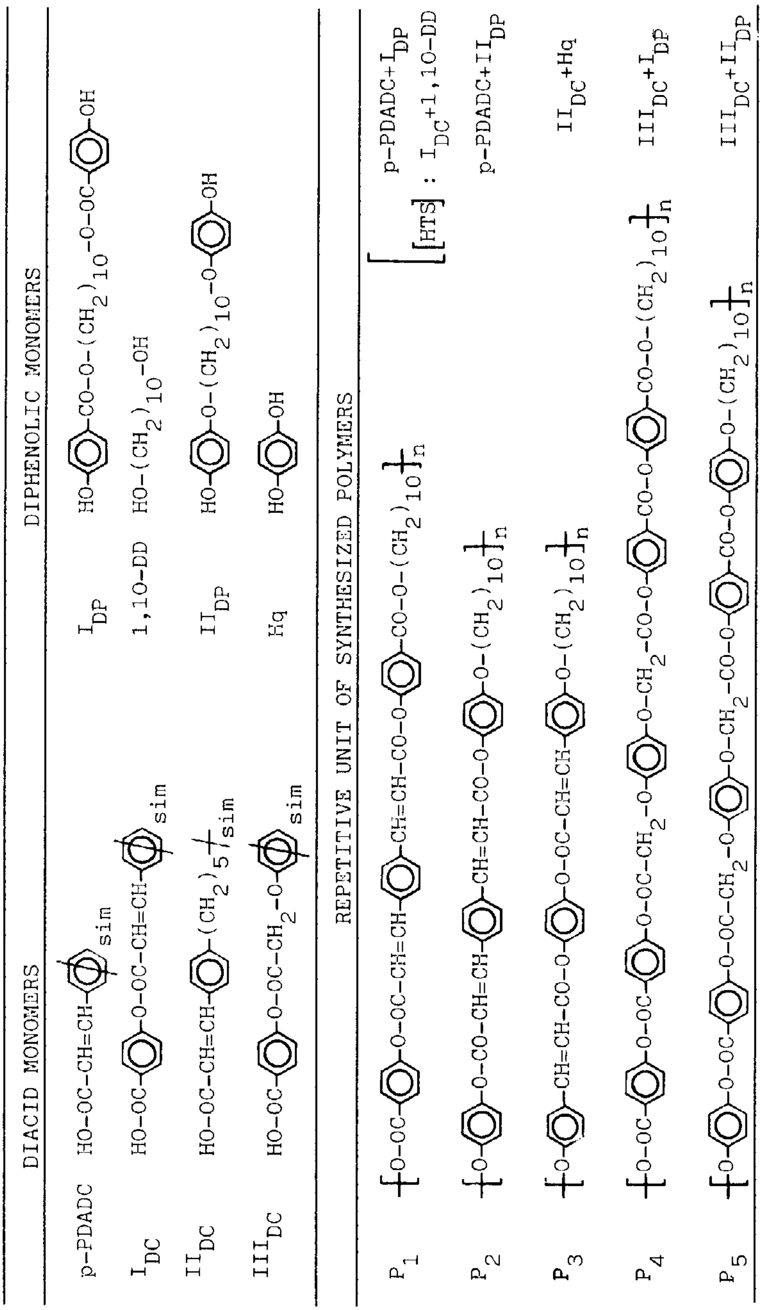
Abstract In this paper the synthesis of five new types of semiflexible thermotropic polymers is described. Complex monomers are used in order to obtain polymers with a regular structure. Of the twelve polymers obtained, one does not exhibit mesomorphic properties, while of the remaining eleven, ten show nematic and one smectic C and nematic phases. A comparative study is made of the four different methods of polymerization: Interfacial Polycondesation, Low Temperature Solution, High Temperature Solution and Melt Transesterification.

INTRODUCTION

Complex monomers have been employed for the construction of thermotropic liquid crystalline polymers with a regular structure[1-4].

The use of complex monomers as precursors of thermotropic polymers has certain advantages. In the first place they make the synthesis of polymers with a regular structure easier and secondly, the use of complex monomers avoids drastic conditions of synthesis in which such undesirable side reactions as branching and crosslinking may be unavoidable.

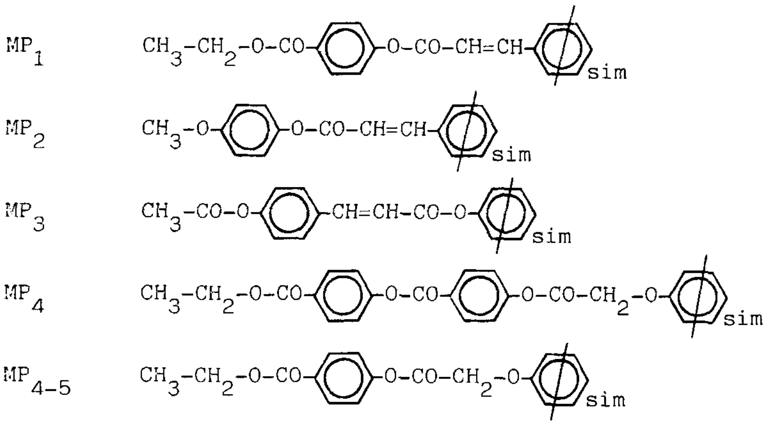
This paper describes the synthesis of complex monomers, dicarboxylic diacids, I_{DC}, II_{DC}, III_{DC} and their dichlorides


DIACID MONOMERS
DIPHENOLIC MONOMERS
p-PDADC
I_{DC}
II_{DC}
III_{DC}
I_{DP}
1,10-DD
II_{DP}
Hq
sim
REPETITIVE UNIT OF SYNTHESIZED POLYMERS
P_1
P_2
P_3
P_4
P_5
p-PDADC+I_{DP}
[HTS] : I_{DC}+1,10-DD
p-PDADC+II_{DP}
II_{DC}+Hq
III_{DC}+I_{DP}
III_{DC}+II_{DP}

SCHEME-I

and the preparation of thermotropic liquid crystalline polymers with a regular structure, P_1 to P_5 (SCHEME-I).

Low-molecular-weight liquid crystalline compounds are useful for making comparisons with their high-molecular-weight analogues. For this reason, model compounds representing the repeating units of the polymers were prepared and their properties compared with those of the analogous polymers (SCHEME-II).



SCHEME-II

Most of the complex monomers, thermotropic polymers and model compounds described in this paper have not been reported so far.

We prepared polymers P_1 to P_5 by high and low temperature solution polycondesation methods ([H.T.S.] and [L.T.S.]) and by interfacial [I] and melt transesterification [T] of diacids and diacetates of diphenols in order to make a comparative study of these methods of synthesis for this type of polymers.

RESULTS AND DISCUSSIONS

SYNTHESIS OF COMPLEX MONOMERS AND POLYMERS

We prepared complex monomers dicarboxilic diacids I_{DC}, II_{DC}, III_{DC} in a single step reaction avoiding the blocking and deblocking procedures of the functional groups, which would have complicated the preparation considerably (see experimental).

The method of synthesis and the characteristic properties of the polymers are summarized in TABLE I.

High temperature melt transesterification of dicarboxylic diacids with diacetates of diphenols was not a suitable procedure for the preparation of polymers P_1 to P_5. Firstly, the monomers used as precursors contained ester bonds and it is an accepted fact that the transesterification of this type of monomer[5] does not yield polymers with a definite structure. Secondly, the precursors of the polymers were based on p-phenylenediacrylic acid and unfavourable gelation due to thermal crosslinking could result[6,7]. However, we made an experiment with diacid II_{DC}, wich has not ester bonds and is based on p-hidroxycinnamic acid whose homopolyester has been obtained by high temperature melt transesterification of the p-acetoxycinnamic acid without evidence of crosslinking[8]. We transesterificated diacid II_{DC} with diacetate of hidroquinone in order to obtain P_3[T], which was not mesomorphic and had the highest melting point of all the polymers synthesized. Later transesterifications of diacid II_{DC}, with diacetates of asymmetrically subtituted hydroquinones yielded thermotropic liquid crystalline polymers. The results will be reported in forthcoming publications.

In order to experiment with the high temperature solution

TABLE I Method of Synthesis, Yields, LImiting Viscosity Numbers, Thermal Properties, Mesophase Type of the Polymers

POLYMER	METHOD OF SYNTHESIS	YIELD(%)	η(dl.g^{-1})	Tm(°C)	Ti(°C)	ΔT(MESOPHASE TYPE)
P_1[LTS]	SOLUTION (LOW TEMPERATURE)	84	0.32	217	287	70 (N)
P_1[I]	INTERFACIAL POLYCONDENSATION	87	0.66	222	312	90 (N)
P_1[HTS]	SOLUTION (HIGH TEMPERATURE)	98	1.08	196	320	124 (N)
P_2[LTS]	SOLUTION (LOW TEMPERATURE)	90	0.35	279	318	39 (N)
P_2[I]	INTERFACIAL POLYCONDENSATION	85	0.44	278	330	52 (N)
P_3[LTS]	SOLUTION (LOW TEMPERATURE)	91	0.24	219-S_C-249-N-305		20 (S_C), 56 (N)
P_3[I]	INTERFACIAL POLYCONDENSATION	15	0.19	198	258	60 (N)
P_3[T]^a	TRANSESTERIFICATION	95	0.36	---	332	-----
P_4[LTS]	SOLUTION (LOW TEMPERATURE)	87	0.38	190	217	27 (N)
P_4[I]	INTERFACIAL POLYCONDENSATION	91	0.51	202	237	35 (N)
P_5[LTS]	SOLUTION (LOW TEMPERATURE)	92	0.43	218	241	23 (N)
P_5[I]	INTERFACIAL POLYCONDENSATION	93	0.48	210	262	52 (N)

a) P_3 T show Tg Transition at 128°C

polymerization method the diacid I_{DC}, was prepared and condensed with 1,10-decanediol at high temperature in solvents with high boiling points. This method of polycondensation was chosen to obtain P_1 [HTS] polymer, with a yield, viscosity and mesomorphic range higher than that of the polymers obtained by other methods of polycondesation, because the rate of reaction is much higher than that of the competing and side reactions. There was no evidence of thermal crosslinking during the process of synthesis, so this method of synthesis for the preparation of these polymers will be the subject of our forthcoming studies.

Low temperature solution and interfacial polycondensation methods of synthesis were used to prepare P_1 to P_5 polymers with reasonably high yields and viscosities. With the exception of P_3 [I] all the polymers synthesized by interfacial polycondensation had higher viscosities than those of the polymers obtained by the low temperature solution method. A correlation between viscosities and mesophase range was observed for polymers P_1 to P_5 prepared by these two methods, the higher mesophase ranges corresponding to the polymers with the highest viscosities.

Under a nitrogen atmosphere and at temperatures below 300°C, a slow crosslinking process was detected during DSC studies for polymers P_1 and P_2. When P_1 and P_2 polymers were heated below 300°C under an atmosphere with oxygen a quicker crosslinking process was observed on IR studies. A weakening of the absorptions (due to $\nu_{C=C}$ at 1620 cm^{-1}) was detected, indicating a decrese in unsaturated bonds. Polymer P_3 [LTS] forms the most ordered phase (a S_C phase) of all the polymers synthesized.

The behaviour of polymer P_3 [I] is obviously very different from that of P_3 [S] in that the former does not exhibit a smectic mesophase. The poor yields obtained for polymer P_3 [I] and its low viscosity values indicate the problems which arise during polimerisation. Consequently, polymer P_3 [I] has a low degree of polymerisation and a high degrae of dispersion, which may account for its different thermal properties.

MODEL COMPOUNDS

Multiple transitions were observed for all the model compounds on DSC analysis (TABLA II). All the compounds proved to be polymorphic and enantiotropic, crystal ---> crystal transitions were observed on DSC curves of heating runs. With the exception MP_{4-5}, all the model compounds formed a nematic phase on melting. The fact that model compounds MP_{4-5} did not exhibit mesomorphic properties suggested that the anisotropic unit of P_4 and P_5 polymers was built-in during the polymerization process and that the polymer precursor was not mesomorphic

TABLE II Transition temperatures (°C) for the five model synthesized.

	C	-----	C'	----	N	----	I	ΔT
MP_1 [a]	.	196.9	.	216.5	.	339.2	.	112.7
MP_2	.	113.1	.	185.2	.	309.8	.	124.6
MP_3	.	204.6	.	237.4	.	330 desc.		90
MP_4	.	142.7	.	185.0	.	193.4	.	8.4
MP_{4-5}	.	-----	.	-----	.	154.9	.	-----

a) This compound had two C-►C' transitions a lower temperatures (171.4 and 175.3°C) in itself, and so could be considered a spacer between mesomorphic units bis (p-oxybenzoate).

Comparisons of the microscopic observations and transition temperatures showed that there was a correspondence in phase transition temperatures, mesomorphic range and mesophase type for polymers and model compounds analogues.

EXPERIMENTAL PART

TECHINIQUES AND APPARATUS

The solution viscosities of the polymers were mesaured at 50±1 °C using a Cannon-Fenske viscosimeter in phenol/TCE (weight ratio 6:4).

A polarizing microscope (Meiji) fitted with a Mettler FP82 heating stage and FP80 control unit, and a DSC analyzer (Perkin-Elmer DSC-2) calibrated with tin and indium as standards, were used for the study of the thermal properties of the polymers and model compounds. The heating rate was 10 °/min and cooling rate was 20 °/min.

Studies of miscibility with a suitable nematogen compound were carried out for the identification of the mesophase type.

All the monomers were characterized by IR and H^1 NMR spectroscopies and elemental analysis. All the polymers were characterized by IR and elemental analysis. IR spectra were obtained by using a Perkin-Elmer 283 spectrometer, and elemental analysis by using a Perkin-Elmer 240C microanalyzer.

SYNTHESIS

Synthesis of monomers

Synthesis of Diphenol Monomers

Complex diphenol monomers (I_{DP} and II_{DP}) were prepared according to the methods described on the literature[9,10].

1,10-Decanediol (1,10-DD) and hidroquinone (Hq) were commercials. 1,10-DD was purified by distillation. Hq was purified by recrystallization from water/sodium hidrogen sulfite.

Synthesis of Diacid Dichlorides Monomers

The dichlorides of p-phenylendiacrylic diacid (monomer of polymer P_1 and P_2 and precursors to the complex monomer I_{DC}) and p-phenylendioxyacetic diacid were prepared using Cl_2SO[10] and were recrystallized from n-hexane.

4,4'-diformyl-1,10-diphenoxydecane precursor to complex monomer II_{DC} was prepared by the method described in the literature[11].

Synthesis of 4,4'-(p-phenylenediacryloyloxy)dibenzoyl dichloride (I_{DC})

To a solution of 13.8g of 4-hydroxybenzoic acid dissolved in 100ml of 2M NaOH, vigorously stirred, a solution of 12.5g of p-phenylenediacrylic diacid dichloride in 40ml of Cl_3CH was added dropwise. After 30 min of stirring the white precipitate was filtered, washed with water, 1M HCl, acetone and dried to yield 20g (87%) of dicarboxylic diacid I_{DC} wich, without further purification, was refluxed with thionyl chloride for 5 h. The hot solution was then filtered and the precipitate collected was recrystallised from toluene (m.p. 226.1). Yield 75%.

Synthesis of 4,4'-(1,10-decanediyl-bis(oxy))bis(cinnamoyl chloride) (II_{DC})

A mixture of (25g) dialdehyde (4,4'-diformyl-1,10-diphenoxydecane) and malonic acid (20g) and piperidine (1g) in pyridine (100ml) was heated with stirring at 100 C for 5h. The hot solution was filtered and the white precipitate collected, washed successively with acetic acid, water and acetone and recristallised from DMF to obtain 18g of dicarboxylic diacid II_{DC} (58%) (m.p. 275.1) which was then refluxed with thionyl chloride until disolution. The thyonil chloride was evaporated and the residue was recrystallised from toluene (m.p. 215.8). Yield 73%.

Synthesis of 4,4'-(p-phenylenedioxyacetyloxy)dibenzoyl dichloride (III_{DC})

To a solution of 13.8g of 4-hydroxybenzoic acid in a mixture of 50ml of 1,4-dioxane and 50ml pyridine, cooled with ice and stirred, 13g of p-phenylenedioxyacetyl dichloride in 15ml of 1,4-dioxane was added dropwise. After 24h of stirring the white precipitate was filtered, washed first with water, then with acetone, dried and recrystalised from 1,4-dioxane to yield 15g (65%) of dicarboxylic diacid III_{DC} (m.p. 295 °C) which was refluxed with thionyl chloride was evaporated and the residue was recrystallised from Cl_3CH. Yield 78%.

Polymerization Methods

High Temperature Solution Polycondensation

Polymer P_1 [HTS] was prepared following the method described by Bilibin et al[1-4].

Low Temperature Solution Polycondensation

Solvents: 1,1,2,2-Tetrachloroetane (TCE) and pyridine. Conditions: 24h under a N_2 atmosphere.

Interfacial Polycondensation

All the polymers were prepared following the method used by Griffins and Havens[10].

High Temperature Melt Transesterification

Conditions: 30min at room temperature, 265°C for 45min, 280 °C for 45min, 310 °C for 30min, 310 °C and 2mmHg for 15 min. The polymer was extracted with acetone.

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