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Liquid Crystalline Polyethers Based on Conformational Isomerism. 1. Quasi-Rigid Polyethers Containing Methyleneoxy Units

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ABSTRACT: This paper presents the first series of experiments which demonstrate that the synthesis of main-chain liquid crystalline polymers does not require rigid rodlike mesogenic groups. Mesomorphic behavior can be obtained for polymers containing flexible structural units which exhibit conformational isomerism when their most stable conformer adopts an extended linear conformation. The examples described here are based on quasi-rigid polyethers and copolyethers based on methyl- and/or phenylhydroquinone and *trans*- and/or *cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane. The methylene ether units inserted within the polyether backbone exhibit anti (extended) and gauche (kinked) as the two most thermodynamically stable conformers which are in dynamic equilibrium. The ratio between these two conformers allows the overall conformation of the polymers to be extended, and therefore they exhibit thermotropic liquid crystallinity.

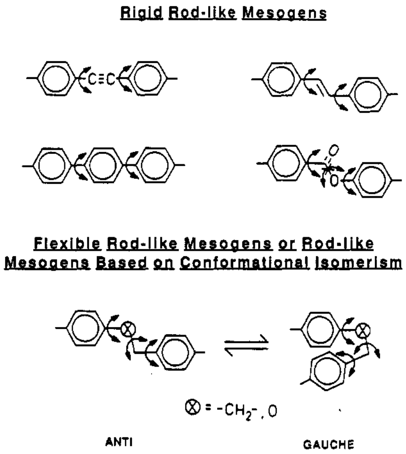
Introduction

In the past 25 years, the relationship between the chemical structure and the properties of low molar mass liquid crystals underwent such a dramatic development that in recent years organic chemists could safely state: "Contrary to the theoretician's belief, the constituent molecules of liquid crystals are neither rigid nor cylindrically symmetric".[1] This relationship has been extensively discussed and reviewed.[1-12]

The traditional pathway to synthesize low molar mass liquid crystals implies the interconnection of two similar or dissimilar aromatic, *trans*-cyclohexane, bicyclooctane, etc. rings through a rigid interconnecting group. The interconnecting group should provide a linear and eventually planar conformation to the resulting compound. Therefore, again aromatic, *trans*-cyclohexane, bicyclooctane, and *trans*-2,5-dioxane, -dithiane, or -dioxathiane groups are preferred, although linking units containing multiple bonds about which freedom of rotation is restricted (for example, $-C{\equiv}C-$, $-CH{=}N-$, $-N{=}N-$, $-(C{=}C)_n-$, and $-CH{=}N-N{=}CH-$) are frequently employed. The last group of multiple bonds can conjugate with the phenylene rings, enhancing the anisotropic polarizability. This function increases the molecular length and maintains rigidity. The ester linkage is also effective since it has a planar trans conformation and since resonance interactions impart double-bond character on its $-C({=}O)O-$ bond restricting rotational motions. Therefore, in all these examples, the extended conformation of a certain molecule is accomplished and maintained through the rigidity and linearity of its constituents, i.e., its rigid rodlike character (Scheme I).

The transplant of this concept from low molar mass liquid crystals to macromolecular liquid crystals led to the presently accepted pathway used in the synthesis of both main-chain[13-17] and side-chain liquid crystalline polymers.[12]

Scheme I
Rigid Rodlike Mesogens and Flexible Rodlike Mesogens or Rodlike Mesogens Based on Conformational Isomerism



An alternative solution to the creation of an extended conformation of a molecule can be considered when the ester group from the previously described structures is replaced with flexible ethane and methyleneoxy units. Although ethane and methyleneoxy units can adopt an extended conformation which is similar to the trans one provided by an ester unit, they are flexible and therefore undergo free rotation leading to a number of different conformational isomers which are in dynamic equilibrium. The two most stable conformational isomers are anti and gauche (Scheme I). The anti conformer has an extended conformation similar to that exhibited by a molecule containing an ester interconnecting unit and, therefore, is expected to display liquid crystallinity. The gauche conformer is similar to a "kinked" unit which is occasionally introduced within the structure of main-chain liquid crystalline copolymers to depress phase transition temperatures.[13] The anti and gauche conformers are in dynamic equilibrium. Therefore, the insertion of flexible units capable of giving rise to extended and kinked conformers, as for example, 1,2-diphenylethane, benzyl ether, and methyleneoxy, within the main chain of a polymer is expected to provide a liquid crystalline polymer having a dynamic composition.

It was only recently that the idea of replacing ester groups with methyleneoxy groups within the structure of mesogenic units was pursued by organic chemists working in the field of low molar mass liquid crystals.[18-30] Methyleneoxy units were successful in stabilizing the mesophase, particularly when they were used to interconnect two cycloaliphatic units or an aromatic and a cycloaliphatic unit. Low molar mass liquid crystals containing a methyleneoxy unit in between two aromatic groups were reported only in 1985.[25,30]

In contrast to mesogenic units where the linearity and planarity of the molecule is realized and maintained through their rigid rodlike character, in the second class of mesogens the rodlike character is realized through the conformational isomerism and maintained through the dynamic equilibrium between different conformers.

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Therefore, in this case, we can use the name *liquid crystals* or *rodlike mesogenic units based on conformational isomerism.*

The first examples of liquid crystal polymers containing mesogenic units based on conformational isomerism belong to the class of thermotropic side-chain liquid crystalline polymers and were recently reported from our laboratory.[31-33]

The goal of this paper is to introduce the conformational isomerism-based liquid crystallinity concept to the synthesis of thermotropic main-chain liquid crystalline polyethers without flexible spacers, i.e., quasi-rigid polyethers. The examples described here are aromatic–aliphatic thermotropic polyethers based on methyl- and/or phenylhydroquinone and *trans*- and/or *cis*-1,4-cyclohexanedimethanol.

Experimental Section

Materials. Methylhydroquinone (99% from Aldrich) was recrystallized once from toluene to yield a product with 99.9% purity as determined by HPLC; mp (DSC, 20 °C/min) 126 °C. Phenylhydroquinone, mp (DSC, 20 °C/min) 90–101 °C from Aldrich, was placed in a Soxhlet and extracted with hexanes under nitrogen atmosphere. The product that crystallized from the hexanes has purity of 100% (HPLC); mp (DSC, 20 °C/min) 107 °C.

Triphenylphosphine (99%), *o*-dichlorobenzene (99%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), 4-methoxyphenol (98%) (all from Aldrich), 1,4-cyclohexanedimethanol (practical, isomeric mixture containing about 70% trans and 30% cis) (Kodak), *trans*-1,4-cyclohexanedimethanol (98% trans) (Kodak), and all other reagents were used as received.

Synthesis of *trans*- and *cis*-1,4-Bis((methylsulfonyl)methyl)cyclohexane. *trans*-1,4-Bis((methylsulfonyl)methyl)cyclohexane was synthesized according to a literature procedure[34] for the mesylation of *trans*-1,4-cyclohexanedimethanol. Methanesulfonyl chloride (26.21 g, 0.229 mol) was added dropwise to an ice-water-cooled solution of *trans*-1,4-cyclohexanedimethanol in 100 mL of dry pyridine. The reaction mixture was stirred for 2 h and then left in a refrigerator overnight. The product was precipitated into 700 mL of ice water, filtered, and washed successively with water, 5% aqueous hydrochloric acid, water, 5% aqueous sodium bicarbonate, and water. The product was recrystallized from 1500 mL of 2:1 (v/v) methanol/acetone to yield 29.3 g (93.8%) of white needles: mp (DSC, 20 °C/min) 158 °C (lit.[34] mp 158 °C); decomposition temperature (DSC, 20 °C/min) 210 °C; ^{1}H NMR ($CDCl_3$, TMS, ∂) 1.07 (4 protons, $-CH_2-$ axial, m), 1.61 (2 protons, $>CH-$, m), 1.91 (4 protons, $-CH_2-$ equatorial, d), 3.01 (6 protons, $-OSO_2CH_3$, s), 4.05 (4 protons, $-CH_2OSO_2-$, d). According to the ^{1}H NMR spectrum this product is 100% trans isomer.

Alternatively, *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane was prepared by the mesylation of the cis/trans mixture of 1,4-cyclohexanedimethanol followed by fractional crystallization from a 1:1 (v/v) mixture of acetone/methanol. The second recrystallization gives a product containing 92.6% trans and 7.4% cis isomers. Successive evaporations of the solvent followed by crystallizations yielded: for the third fraction 7% trans and 93% cis, for the fourth fraction 5% trans and 95% cis, and for the fifth fraction 1.7% trans and 98.3% cis. The composition of all fractions was determined by ^{1}H NMR spectroscopy. The fractions containing 93.0–98.3% *cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane were used over the entire work as the cis isomer: mp (DSC, 20 °C/min) 68 °C (lit.[34] mp 69 °C); ^{1}H NMR ($CDCl_3$, TMS, ∂) 1.41–1.71 (8 protons, $-CH_2-$, equatorial and axial, m), 2.00 (2 protons, $>CH-$, m), 3.02 (6 protons, $-OSO_2CH_3$, s), 4.13 (4 protons, $-CH_2OSO_2-$, d). No unreacted alcohol groups were detected by ^{1}H NMR spectroscopy in the *trans*- and *cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane, and therefore, we consider the purity of the mesylated products to be 100%.

Synthesis of *trans*-1,4-Bis(bromomethyl)cyclohexane. *trans*-1,4-(Bromomethyl)cyclohexane was previously synthesized by the nucleophilic displacement of the tosyl groups from *trans*-1,4-((tolylsulfonyl)methyl)cyclohexane with lithium bromide.[34] We have synthesized it by the direct bromination of *trans*-1,4-cyclohexanedimethanol with triphenyldibromophosphorane according to a literature procedure used for the synthesis of primary alkyl bromides.[35-37] A solution of triphenyldibromophosphorane was prepared by adding bromine (17.9 g, 0.112 mol) dropwise to an ice-water-cooled solution of triphenylphosphine (29.4 g, 0.112 mol) in 150 mL of dry acetonitrile. A solution of *trans*-1,4-cyclohexanedimethanol (7.7 g, 0.053 mol) in 50 mol of dry acetonitrile was added to the reaction mixture which was stirred under nitrogen overnight. The solvent was evaporated to yield a golden oil which crystallized on standing. The solid was finely dispersed in hexanes and filtered to remove the triphenylphosphine oxide. The hexane solution was evaporated on a rotary evaporator to a clear oil which crystallized on standing. The product was recrystallized from methanol to yield 11.4 g (79.2%) of white crystals: mp (DSC, 20 °C/min) 53 °C lit.[34] mp 55 °C); ^{1}H NMR ($CDCl_3$, TMS, ∂) 1.07 (4 protons, $-CH_2-$ axial, m), 1.61 (2 protons, $>CH-$, m), 1.95 (4 protons, $-CH_2-$ equatorial, d), 3.30 (4 protons, $-CH_2Br$, d); purity (^{1}H NMR), 100%.

Synthesis of *trans*-1,4-Bis(chloromethyl)cyclohexane. This compound was not reported previously in the literature. Attempts to chlorinate the *trans*-1,4-cyclohexanedimethanol with thionyl chloride led to a mixture of isomers which was not identified. A successful chlorination was accomplished by using triphenylphosphine/carbon tetrachloride as a halogenation reagent.[38,39] To a solution of *trans*-1,4-cyclohexanedimethanol (10.0 g, 0.068 mol) in 200 mL of dry carbon tetrachloride was added triphenylphosphine (47.3 g, 0.18 mol). Triphenylphosphine oxide began to precipitate from solution after 1 h of reflux; however, the reaction mixture was stirred under reflux and nitrogen atmosphere for three more hours. The reaction mixture was allowed to cool to room temperature, and 200 mL of hexanes was added to the reaction flask after which the precipitated triphenylphosphine oxide was filtered and washed with additional hexanes. The filtrate was evaporated to yield a colorless liquid which was redissolved in hexanes and eluted through a chromatographic column containing 150 g of neutral alumina. The solvent was evaporated again, and the resulting liquid was distilled at 84 °C and 1.0 mmHg to yield 9.0 g (71.4%): ^{1}H NMR ($CDCl_3$, TMS, ∂) 1.07 (4 protons, $-CH_2-$ axial, m), 1.61 (2 protons, $>CH-$, m), 1.93 (4 protons, $-CH_2-$ equatorial, d), 3.40 (4 protons, $-CH_2Cl$, d); purity (GC) 99.3%.

Synthesis of Polyethers and Copolyethers. Scheme II outlines the synthesis of polyethers and copolyethers. Conventional liquid–liquid (organic solvent–NaOH aqueous solution) phase-transfer-catalyzed polyetherification reaction conditions were used for the preparation of all polyethers and copolyethers reported in Tables I and II. The polyetherifications were carried out at 80 °C in *o*-dichlorobenzene–NaOH aqueous solution (10 times molar excess of NaOH versus phenol groups; 12 N aqueous NaOH was used for the polyetherifications in Table I except for polymers 40/60 trans/cis and 30/70 trans/cis which were prepared with 10 N NaOH; 10 N NaOH solutions were used for the polyetherifications reported in Table II). TBAH was used as the phase-transfer catalyst (10 mol % based on the concentration of phenol groups). The ratio between the nucleophilic monomer(s) and the electrophilic monomer(s) was 1.2:1.0 (mol/mol) for the polymerizations in Table I except for polymers 40/60 and 30/70 which used a nucleophile/electrophile molar ratio of 1.0:1.2. A nucleophile/electrophile molar ratio of 1.0:1.1 was used for the polymerizations reported in Table II. An example of one of these polyetherifications is as follows: *o*-dichlorobenzene (10.0 mL) and 12 N NaOH (6.7 mL) were added to a 25 mL round-bottom flask equipped with magnetic stirred and reflux condenser. The mixture was bubbled with nitrogen while stirring. Methylhydroquinone (0.5000 g, 4.028 mmol) followed by *trans*-1,4-bis(methylsulfonyl)methyl)cyclohexane (1.008 g, 3.3564 mmol) and TBAH (0.2735 g, 0.8055 mmol) was added to the flask. The reaction mixture was heated to 80 °C and stirred under nitrogen for 6 h at a stirring rate of 1100 rpm. Afterward, 0.2 g of 4-methoxyphenol was added to the reaction mixture which was stirred for an additional hour at 80 °C. The organic and aqueous layers were diluted with *o*-dichlorobenzene and water, respectively, and separated. The organic layer was washed three times with water and once with dilute hydrochloric acid. The polymer solution

Table I
Synthesis and Characterization of Polyethers and Copolyethers Based on Methylhydroquinone and *cis*- and/or *trans*-1,4-Bis((methylsulfonyl)methyl)cyclohexanes[a]

trans/cis (mol/mol)	yield, %	M_w (GPC)	M_w/M_n	heating				cooling				
				T_g	T_{kk}	T_{kn}	T_{ni}	T_{in}	T_{nk}	T_{kk}	T_g	$\Delta H_i/\Delta S_i$
100/0[b]	76.1	5300	1.9	46	130	182	257	253	156	101	42	0.92/1.80
90/10	66.1	12600	2.6	50	146	196	242	232	165	123	44	0.46/0.91
80/20	74.1	12100	2.4	50	146	198	248[g]	222	166	132	46	0.15/0.30
75/25	70.3	10150	2.1	53	152	195	230[g]	214	164	135	46	0.07/0.14
50/50	78.6	16800	2.1	55	130	177[d]			156[e]	119	50	
40/60		14300	1.8	55		129[d]			92[e,f]		49	
30/70		7500	2.4	42								
7/93	59.3	4700	1.5	34							30	

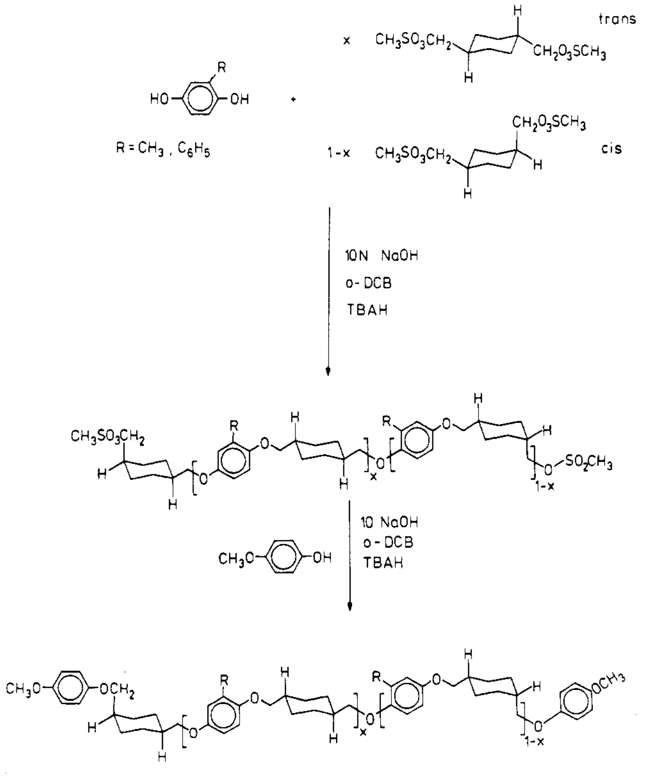
[a] Polymerization conditions: 4.028 mmol of methylhydroquinone, 6.7 mL of 12 N NaOH, 6.7 mL of *o*-dichlorobenzene. [b] 10.0 mL of *o*-dichlorobenzene. [c] mru = mole repeat unit. [d] $T_{kn} = T_{ki}$. [e] $T_{nk} = T_{ik}$. [f] From heating scan. [g] Determined by optical microscopy at 20 °C/min. [h] ΔH in kcal/mru; ΔS in cal/(mru K).

Table II
Synthesis and Characterization of Polyethers and Copolyethers Based on Methylhydroquinone (MHQ) and/or Phenylhydroquinone (PHQ) and *trans*-1,4-Bis((methylsulfonyl)methyl)cyclohexane[a]

MHQ/PHQ (mol/mol)	yield, %	M_w (GPC)	M_w/M_n	heating				cooling				
				T_g	T_{kk}	T_{kn}	T_{ni}	T_{in}	T_{nk}	T_{kk}	T_g	$\Delta H_i/\Delta S_i$
100/0	69.5	6100	1.97	59	168	196	267	259	177	138	57	0.76/1.43
90/10	90.6	5300	1.58	61	129	168	232	229	133	97	56	0.58/1.13
75/25	84.3	8600	2.00	65	165	204[d]	230[f]	202	128	98	59	0.54/1.13
50/50	69.2	6300	1.69	72	151	222[d]			167[e]	129	66	
0/100[b]	100	6700	2.11	69	145	224[d]			159[e]	111	64	

[a] Polymerization conditions: 2.6851 mmol of hydroquinone, 5.4 mL of 10 N NaOH, initial volume of *o*-dichlorobenzene 3.0 mL with additional *o*-DCB added in 1–2-mL increments to keep polymer in solution as reaction proceeds. [b] Initial *o*-dichlorobenzene = 5.0 mL. [c] mru = mole repeat unit. [d] $T_{kn} = T_{ki}$. [e] $T_{nk} = T_{ik}$. [f] Determined by optical microscopy at 20 °C/min. [g] ΔH in kcal/mru; ΔS in cal/(mru K).

Scheme II
Synthesis of Polyethers and Copolyethers Based on 1,4-Bis((methylsulfonyl)methyl)cyclohexanes and Methyl- or Phenylhydroquinone



was precipitated into methanol to yield 0.6355 g (76.1%) of polymer powder. The polymer was further purified by successive precipitations from *o*-dichlorobenzene into acetone and finally methanol. All the polymerizations in Tables I and II were performed in a similar manner with the exceptions to experimental procedure noted in the footnotes to each table.

Techniques. ^{1}H NMR (200-MHz) spectra were recorded on a Varian XL-200 spectrometer. All spectra were obtained in CDCl$_3$ solutions at room temperature using TMS as an internal standard.

A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS Data Station Model 3600 was used to determine the thermal transitions. Heating and cooling rates were 20 °C/min in all cases. Crystalline–crystalline (T_{kk}), crystalline–nematic (T_{kn}), nematic–crystalline (T_{nk}), nematic–isotropic (T_{ni}), isotropic–nematic (T_{in}), crystalline–isotropic (T_{ki}), and isotropic–crystalline (T_{ik}) transitions were read at the maximum of the endothermic or exothermic peaks. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. After the first heating scan the samples were annealed at about 10 °C above the isotropization temperature for about 5 min. All the heating and cooling scans after the first heating scan produced perfectly reproducible data. The transitions reported were taken from the second or third heating or cooling scans.

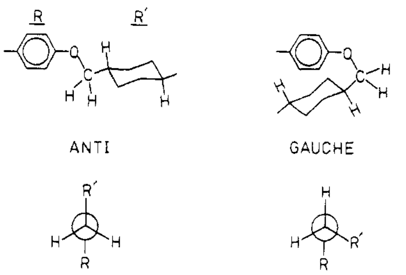
A Carl Zeiss optical polarizing microscope (magnification 100×) equipped with a Mettler FP 82 hot stage and a Mettler central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[40]

Molecular weights were determined by gel permeation chromatography (GPC). High-pressure liquid chromatography (HPLC) and GPC analyses were carried out with a Perkin-Elmer Series 10LC equipped with a LC-100 column oven, LC 600 auto sampler, and a Sigma 15 Data Station. The measurements were made by using the UV detector, chloroform as solvent (1 mL/min, 40 °C), a set of PL gel column of 10^2, 5×10^2, 10^3, 10^4, and 10^5 Å, and a calibration plot constructed with polystyrene standards.

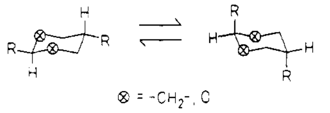
Results and Discussion

Main-chain thermotropic liquid crystalline polyethers were synthesized for the first time in our laboratory[41] and their synthesis both by phase-transfer-catalyzed polyetherification and by cationic ring-opening polymerization was recently reviewed.[17,42] Phase-transfer-catalyzed polyetherification of mesogenic bisphenols with bielectrophilic spacers seems to represent the most convenient method for the preparation of main-chain polyethers containing flexible spacers,[41-43] although they also can be synthesized by cationic ring-opening copolymerization of bridged bicyclic ethers with cyclic ethers.[45] Nevertheless, until now main-chain thermotropic polyethers without

Scheme III
Conformational Isomerism of Cycloaliphatic–Aromatic Mesogens Containing Methyleneoxy Linkages



Scheme IV
Conformational Isomerism of *trans*-1,4-Disubstituted-cyclohexanes or *trans*-2,5-Disubstituted-1,3-dioxanes



flexible spacers were prepared only by cationic ring-opening polymerization of bridged bicyclic ethers.[45,46]

The use of the conformational isomerism-based extended conformation concept opens a number of novel and interesting synthetic avenues unexploited previously for the synthesis of thermotropic liquid crystalline polymers without flexible spacers, i.e., quasi-rigid liquid crystalline polymers. In this first study, we have selected the cycloaliphatic–aromatic methyleneoxy unit as the group responsible for the conformational isomerism (Scheme III). This unit is inserted within the structure of the polymer backbone by the polyetherification of trans- or a mixture of *trans*- and *cis*-1,4-bis(chloro-, bromo-, or (methylsulfonyl)methyl)cyclohexane with methylhydroquinone and with different mixtures of methylhydroquinone and phenylhydroquinone (Scheme II).

The 1,4-bis(electrophilic methyl)cyclohexane monomer was selected since it is known from the literature on thermotropic polyesters that the use of *trans*-1,4-cyclohexanedicarboxylic acid instead of its parent aromatic acid (terephthalic acid) leads to an important depression of the polyester melting temperature.[47-53] This seems to be the result of at least three factors. The linear but not planar conformation of the 1,4-disubstituted cyclohexane unit; the conformational isomerism exhibited by the trans-1,4-disubstituted unit; i.e., the two substituents can flip between their axial or equatorial positions without changing the linear conformation of the compound (Scheme IV); and, the acid-induced trans–cis and cis–trans isomerization of the 1,4-cyclohexanedicarboxylates and 1,4-cyclohexanedicarboxylic acid which leads to a thermodynamic equilibrium between the cis and trans isomers of 66 ± 2% trans in isotropic liquids at 300 °C and of 100% trans content in a crystalline phase.[52] The replacement of the ester unit with a methylene ether unit eliminates the cause of the acid-induced trans–cis isomerization of the 1,4-disubstituted unit and replaces it with the conformational isomerism effect of the methyleneoxy unit.

In addition, the copolymers based on mixtures of *trans*- and *cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane and methylhydroquinone and copolymers based on mixtures of phenyl- and methylhydroquinone and *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane were synthesized in attempts to enhance the solubility of the polymers in comparison to that of the parent homopolymers.

Before going into the discussion of any quantitative results, we have to mention briefly some preliminary scouting experiments which led us to the polyetherifications summarized in Tables I and II.

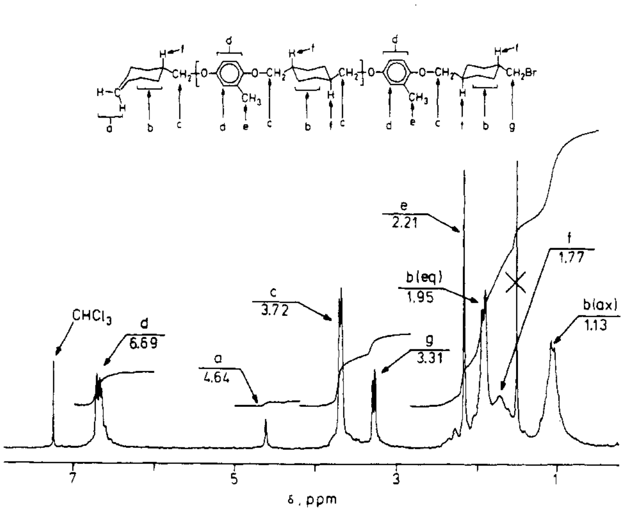


Figure 1. 200-MHz ^{1}H NMR spectrum (CDCl$_3$, TMS) of a polyether obtained from methylhydroquinone and *trans*-1,4-bis(bromomethyl)cyclohexane ($\bar{M}_n$ = 1200).

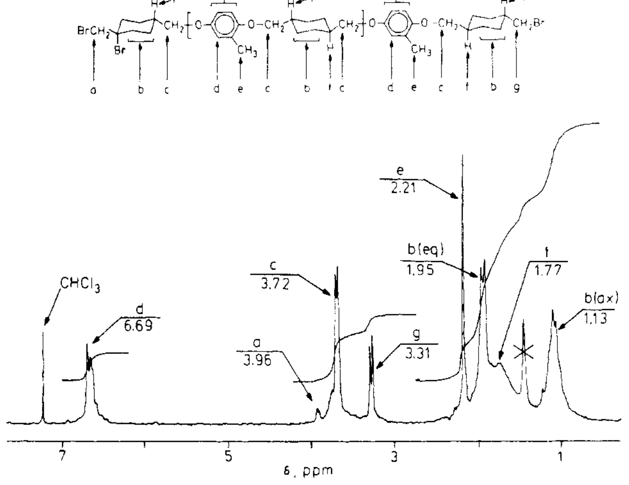


Figure 2. 200-MHz ^{1}H NMR spectrum (CDCl$_3$, TMS) of the polyether obtained from methylhydroquinone and *trans*-1,4-bis(bromomethyl)cyclohexane ($\bar{M}_n$ = 1200) after bromination in the NMR sample tube. Same sample as in Figure 1.

The polyetherifications of *trans*-1,4-bis(chloromethyl)cyclohexane and *trans*-1,4-bis(bromomethyl)cyclohexane with methylhydroquinone led to low conversions and polymers with number average molecular weights below 1200. Figure 1 presents a representative ^{1}H NMR spectrum of a polyether ($\bar{M}_n$ = 1200) obtained from *trans*-1,4-bis(bromomethyl)cyclohexane and methylhydroquinone, together with the assignment of its protonic resonances. Most of the resonances are self-explanatory. Nevertheless, this polymer contains both bromomethyl (doublet at 3.31 ppm) and olefinic (singlet at 4.64 ppm) chain ends. The chemical shift of the protonic resonance due to the olefinic chain end agrees well with the chemical shift of other exocyclic olefins reported in the literature,[54] and after its electrophilic bromination in the NMR sample tube, this signal shifts upfield as expected (Figure 2). Therefore, with both *trans*-1,4-bis(bromomethyl)cyclohexane and *trans*-1,4-bis(chloromethyl)cyclohexane, there is competition between nucleophilic displacement and elimination reactions and this limits the degree of polymerization of the resulting polymers. It could be that elimination takes place either at the interface or within the organic phase, in the second case being induced by the onium hydroxide transferred into the organic phase.[55]

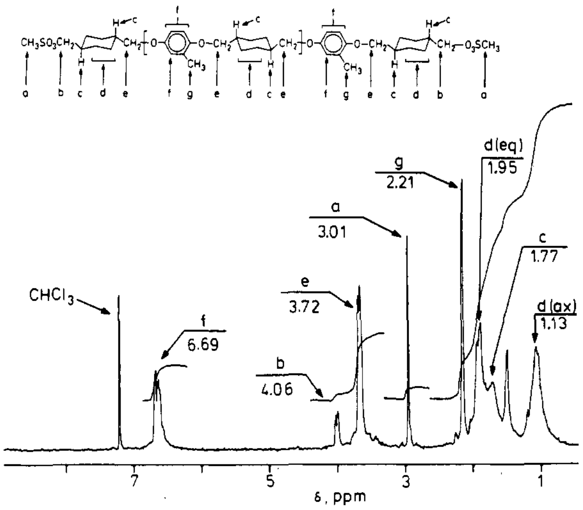


Figure 3. 200-MHz ^{1}H NMR spectrum (CDCl$_3$, TMS) of the polyether obtained from methylhydroquinone and *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane (sample 100/0 from Table I) before end capping.

In order to avoid the elimination reaction, we used a much better leaving group, i.e., mesylate. The ^{1}H NMR spectrum in Figure 3 shows that the polyethers obtained from *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane and methylhydroquinone contain only methanesulfonyl chains ends. The reason for the formation of polyethers containing only electrophilic chain ends was detailed elsewhere.[55] However, as we have reported in the experimental part, the *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane undergoes thermolysis at 210 °C, releasing methanesulfonic acid. Since at this temperature most of these polymers are in their nematic mesophases, they undergo a very fast cationic decomposition which is initiated by the methanesulfonic acid resulting from the thermolysis of the polymer chain ends. This reaction can be easily followed on the hot stage of the optical polarized microscope where upon heating above 210 °C, the nematic mesophase starts to transform into an isotropic melt. In order to avoid this depolymerization reaction, all the synthesized polymers were end-capped with methoxyphenoxy chain ends as the ^{1}H NMR spectrum in Figure 4 shows. Trace amounts of unreacted methanesulfonyl groups are still present in some samples, however, they do not provide enough methanesulfonic acid to induce cationic depolymerization during the time scale required for the thermal characterization of the polymers. Although for the purpose of this study the thermal reactivity of these polymers is not desired, it might have some useful applications. To our knowledge it represents the first example of cationic-induced depolymerization which takes place in a nematic mesophase. A series of polyetherifications were performed with different ratios between the nucleophilic and electrophilic monomers (i.e. 1.1/1.0, 1.0/1.0, 1.0/1.2); however, no significant changes in the polymer molecular weights were observed. This let us speculate that the limited solubility of the polymers is one factor that controls the upper limit of their molecular weight. Even the synthesized copolyethers based on either *cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane or phenylhydroquinone was still not soluble enough to be obtained with controllable molecular weights.

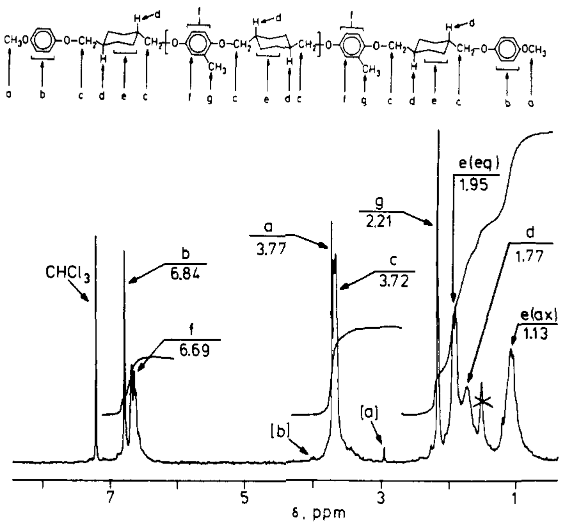


Figure 4. 200-MHz ^{1}H NMR spectrum (CDCl$_3$, TMS) of the methoxyphenoxy end-capped polyether obtained from methylhydroquinone and *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane (sample 100/0 from Table I. [a] and [b] signals correspond to a and b from Figure 3.

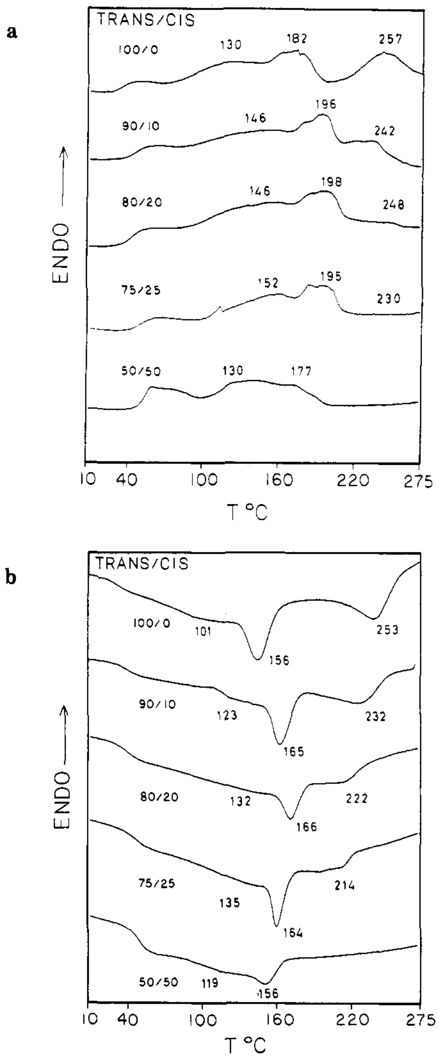


Figure 5. Representative heating (a) and cooling (b) DSC thermograms of the polyethers and copolyethers based on methylhydroquinone and *trans*- and/or *cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane (sample compositions correspond to those in Table I).

The thermal behavior of the polyethers and copolyethers based on *trans*- and *cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane and methylhydroquinone will be discussed on several representative heating (Figure 5a) and cooling (Figure 5b) DSC thermograms. The polyether obtained from *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane and methylhydroquinone (sample trans/cis = 100/0 from

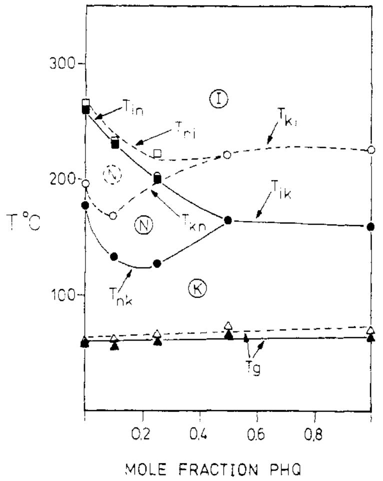


Figure 6. Thermal transitions (T_g, T_{kn}, T_{nk}, T_{ki}, T_{ik}, T_{ni}, and T_{in}) for the polyethers and copolyethers based on methylhydroquinone and *trans*- and/or *cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane (data from Table I; —, cooling scan; - - -, heating scan).

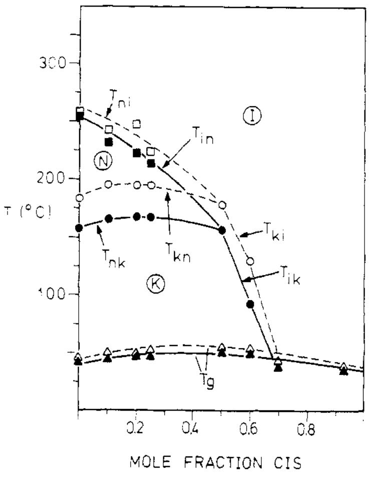


Figure 7. Thermal transitions (T_g, T_{kn}, T_{n5}, T_{ki}, T_{ik}, T_{ni}, and T_{in}) for the polyethers and copolyethers based on *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane and methyl- and/or phenylhydroquinone (data from Table II; —, cooling scan, - - -, heating scan).

Figure 5a) exhibits on the heating scan a glass transition, T_g = 46.4 °C, crystalline–crystalline transition T_{kk} = 129.7 °C, a crystalline–nematic transition T_{kn} = 182.2 °C, and an isotropization transition T_{ni} = 256.6 °C. On the cooling scan the isotropization transition is supercooled with only 3.8 °C, while the crystallization is supercooled with 26.0 °C. This result is in agreement with thermodynamically controlled isotropic–nematic transitions and kinetically controlled nematic–crystalline transitions. A quick inspection of the thermal behavior of thermotropic polyesters based on *trans*-1,4-cyclohexanedicarboxylic acid and chloro- or methylhydroquinone[47,48,53] shows that they exhibit quite similar DSC thermograms with those of the homologous polyethers. The major difference consists in the fact that, in the case of the polyesters, the isotropization transition is above the decomposition temperature of the polymer. Besides this difference, both polyethers and polyesters exhibit crystalline–crystalline transitions and a melting into a nematic mesophase. Of interest is the fact that all the polyethers and copolyethers crystallize very fast even when the polymer is quenched from the isotropic melt. This crystallization behavior can be explained by a three-dimensional positional long-range order which is rotationally disordered with respect to rotations about the long axes of rodlike macromolecules; as Wendorff et al.[56] have suggested, this crystallization leads to so called "rotationally disordered crystals". However, at this time we cannot make any additional comments on this subject. The isotropization enthalpies of these polyethers are within the range of values expected for a nematic mesophase (Table I) and are quite low because of the low molecular weight of the polymers (Table I). As previously discussed for other classes of liquid crystalline polymers, both phase transitions and their thermodynamic parameters are strongly molecular weight dependent at least below a number average molecular weight of about 10 000–12 000.[43,44]

The insertion of a certain amount of cis units within the copolymer structure decreases the isotropization temperature and enthalpy until the polymer containing 50 mol % trans units is only crystalline. Nevertheless, since the copolymers are more soluble than the homopolymers, their degrees of polymerization are higher and this can explain the increase of the melting transition with the increase of the cis units content (Figure 5, Table I). The copolymer containing 30 mol % trans units is amorphous as is the "pure cis" homopolymer (containing 7% trans units) (Table I). The phase diagram containing T_g, T_{kn}, T_{nk}, T_{ki}, T_{ik}, T_{in}, and T_{ni} plotted as a function of copolymer composition is presented in Figure 6. From it we can see even more clearly the influence of the molecular weight on the phase transitions, particularly by following the increase of the T_g by increasing the amount of cis content. This result is certainly an artifact introduced by the increase in copolymer molecular weights since the pure cis polyether has a lower T_g than the pure trans polyether.

The other series of copolymers was synthesized from *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane and different mixtures of methyl- and phenylhydroquinone. The characterization of these polymers is presented in Table II. The polyether from *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane and phenylhydroquinone is only crystalline. The polyester prepared from a thermodynamically equilibrated mixture of 1,4-cyclohexanedicarboxylic acid and phenylhydroquinone is amorphous while the polyester obtained with 100% *trans*-1,4-cyclohexanedicarboxylic acid is liquid crystalline.[52]

Copolyethers containing up to 50 mol % phenylhydroquinone are enantiotropic liquid crystals. The copolyethers containing 50 or more mol % phenylhydroquinone are only crystalline (Table II). The phase diagram for this set of copolymers is presented in Figure 7.

As previously mentioned, all the polyethers and copolyethers exhibiting thermotropic mesomorphism are nematic. Figure 8 presents a representative optical polarized micrograph showing the characteristic schlieren nematic texture exhibited by all these liquid crystalline polymers.

The first conclusion resulting from this series of experiments is that the synthesis of main-chain liquid crystalline polymers does not require that rigid rodlike mesogenic units be present in their structure. The conformational isomerism based extended conformation concept can be used in the synthesis of quasi-rigid thermotropic liquid crystalline polyethers. These polymers are of particular interest from a theoretical and practical point of view since they might exhibit both random-coil and extended conformations in solution as well as in the melt. From a preparative polymer chemistry point of view, this result is important since it is well-known that random coil and rigid rodlike macromolecules are not miscible and therefore it is difficult to perform reactions between the chain ends of these two types of macromolecular segments in order to insert them within the structure of a block

Figure 8. Schlieren nematic texture exhibited by the homopolymer based on methylhydroquinone and *trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane (sample 100/0 from Table II). Sample was heated to 215 °C and annealed for 10 min (magnification 200×).

copolymer.[53] A liquid crystalline polymer that exhibits both extended and random-coil conformations could theoretically solve this problem since while it is in its random coil conformation, it can be reacted with a random-coil flexible polymer. At the same time, these polymers are useful models to study the influence of a mesophase on the dynamic equilibrium between the anti-extended and gauche-kinked conformers. This represents a fundamental problem of physical chemistry, since it has been predicted that when rodlike or linear conformations are in dynamic equilibrium with random coil conformations, the rodlike conformation is preferred in the nematic phase.[57-59] Therefore, we can speculate that the ratio between the anti and gauche conformations will be affected by a mesomorphic phase.

We have also demonstrated that the extended conformation-based liquid crystallinity can be applied to the synthesis of thermotropic main-chain liquid crystalline polymers containing flexible spacers. In this case the "mesogenic unit" is created through the conformational isomerism of a flexible unit. The results of this work represents the subject of the next paper in this series of publications.

While the preparation of this paper was in progress, we learned that a similar concept has been used for the synthesis of thermotroic main-chain liquid crystalline polyesters.[60,61]

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Registry No. (MHQ)(*cis*-1,4-bis((methylsulfonyl)methyl)cyclohexane)(*trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane) (copolymer), 116076-51-8; (MHQ)(*trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane) (copolymer), 115506-11-1; (MHQ)(PHQ)(*trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane) (copolymer), 115506-10-0; (PHQ)(*trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane) (copolymer), 115506-12-2; (PHQ)(*trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane) (copolymer, SRU), 115516-27-3; (MHQ)(*trans*-1,4-bis((methylsulfonyl)methyl)cyclohexane) (copolymer, SRU), 115516-28-4.

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Functional Derivatives of Poly(phenylacetylenes)

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ABSTRACT: Methyl *p*-ethynylbenzoate was polymerized at room temperature in toluene using WCl_6/Ph_4Sn as catalyst, giving high molecular weight poly(methyl *p*-ethynylbenzoate) with a predominantly trans structure. Lithium trimethoxyaluminum hydride reduction and subsequent oxidation with dimethyl sulfoxide/oxalyl chloride gave poly(*p*-ethynylbenzyl alcohol) and poly(*p*-ethynylbenzaldehyde), respectively. Yields for the above reactions were 90%, 97%, and 89%, respectively. Insoluble cis polymers of *p*-ethynylbenzaldehyde and *p*-ethynylbenzyl alcohol were also produced in lower yields by direct polymerization of the monomers using higher catalyst concentrations.

Introduction

Polyacetylenes[3a] are a unique class of polymers in that the polymer chain contains conjugated double bonds. Such extended conjugation reduces the gap between the bonding and antibonding molecular orbitals. In polyacetylene, this gap is approximately 1.4 eV, producing interesting semiconducting properties in the parent hydrocarbon and simple derivatives.

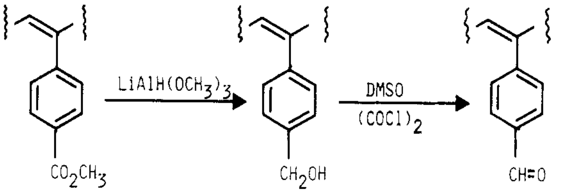
Polyacetylene can be produced in two forms, cis and trans, having conductivities of about 10^{-10} and 10^{-6} $(\Omega\ \text{cm})^{-1}$, respectively. The trans polymer is photoconducting.[3b] The conductivities can be raised to about 10^3 by doping with such materials as iodine and AsF_5.[3c]

Phenylacetylene can be polymerized with a variety of catalysts, most commonly tungsten and molybdenum compounds, yielding polymers of fairly high molecular weight.[4] When tungsten compounds are used, the polymer chain contains predominantly trans double bonds, which allow the overlap needed for extended conjugation. These polymers are red. On the other hand, molybdenum compounds give a high cis content, resulting in yellow polymers with minimal conjugation due to steric hindrance. Furthermore, the red trans polymers are amorphous and soluble in a variety of solvents, whereas the yellow cis polymers are crystalline and insoluble.[4] These crystalline polymers have been assigned a cis–cisoidal microstructure, while the cis–transoidal form, obtained under certain conditions of Ziegler–Natta catalysis, is amorphous and soluble.[5a] Furlani et al. have produced a soluble, yellow, stereoregular polymer which is presumably the cis–transoid form by using a Rh(I) catalyst.[5c] Under certain conditions, cyclohexadiene structures are also present.[5a,b]

Although the unique structure of these compounds, together with the favorable solubility properties of the transoid polymers, should make them good candidates for further study, the number of functional derivatives reported has been limited to *p*-methoxy, *p*-methyl, *p*-chloro,[6] fluoro- and trifluoromethyl,[7] nitro,[8] and alkyl and chloro on the chain.[9] A few sulfur- and nitrogen-containing derivatives form the basis of a Japanese patent.[10]

In contrast to semiconducting parent polyacetylenes, poly(phenylacetylenes) are insulators. The latter have been shown, however, to have other interesting properties attributable to the conjugated polymer chain. For example, photoconductivity which is especially sensitive to long wavelength light has been demonstrated.[11]

Scheme I
Conversion of Poly(methyl *p*-ethynylbenzoate) to Poly(*p*-ethynylbenzyl alcohol) and Poly(*p*-ethynylbenzaldehyde)



1 2 3

In this paper, we describe the preparation of poly(methyl *p*-ethynylbenzoate) **1** (Scheme I); poly(*p*-ethynylbenzyl alcohol), **2**; and poly(*p*-ethynylbenzaldehyde), **3**. These derivatives give new properties to the polymers and provide reactivity that should allow further modification of the polymer side chains.

Results and Discussion

Our primary interest was in the formyl derivative, **3**. However, numerous initial attempts to polymerize *p*-ethynylbenzaldehyde and its dimethyl acetal using the conditions of Higashimura et al.[4] failed. Similar attempts to polymerize *p*-ethynylbenzyl alcohol also failed. Finally, it was found that methyl *p*-ethynylbenzoate would polymerize if a higher concentration of catalyst was used, giving the brick-red polymer characteristic of the trans structure. Later experiments using carefully purified monomer showed that polymerization would occur at room temperature using catalyst amounts similar to those of Higashimura et al., giving 90% yield.

When even higher concentrations of catayst were used, the aldehyde and alcohol also polymerized but gave insoluble yellow polymers (presumably cis–cisoid). Their insolubility made them unsuitable for our purposes. Thus, it was necessary to convert the methyl ester into the al-

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