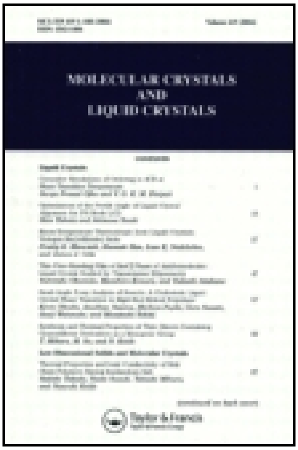

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Electroactive Mesomorphic Side-Chain Polymers from Cationic Polymerization of Polar End-Group Liquid Crystal Monomers

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Electroactive Mesomorphic Side-Chain Polymers from Cationic Polymerization of Polar End-Group Liquid Crystal Monomers

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We report preliminary results dealing with the preparation of highly ordered side-chain polymers $(-\underset{\substack{| \\ R}}{C}=N-)_n$ from a special class of mesogenic nitriles, $R-C\equiv N$ in which the cyano group is electrically and mechanically decoupled from a rigid aromatic core. The polymerization process consists of heating the complexes formed between $R-C\equiv N$ and a transition-metal halide, such as $ZnCl_2$. These complexes form highly ordered smectic phases and their transition temperatures make it possible for polymerization to occur within an oriented mesophase phase. In the polymers, the conjugated main chain induces an electroactive character, which allows the formation of a conducting system upon doping. We specially stress the possibility of obtaining crystalline and/or mesomorphic properties with appropriate R groups.

Keywords: side-chain polymers, electroactive polymers, liquid crystals, smectic mesophases

INTRODUCTION

The production of conjugated polymers of the $(-\underset{\substack{| \\ R}}{C}=N-)_n$ structure from the cationic polymerization of nitriles is well known.[1,2,3,4] Theoretical predictions of ionization potentials, gaps and bandwidths[5] allow us to conclude that such materials could exhibit electroactive behavior (*i.e.*, they should be able to generate an electronic conductor upon doping) for a range of R substituents.

In addition to their electroactive properties, $(-\underset{\substack{| \\ R}}{C}=N-)_n$ polymers could exhibit some properties resulting from the R side chains attached to the conjugated $(-C=N-)_n$ backbone. If R happened to be a mesogenic unit, highly ordered polymers could be expected. In this paper we describe the results of an exploratory study carried out with this goal in view.

Another feature of interest in the study of polynitriles is the technique of polymerization itself. The $C\equiv N$ triple bond is activated through a complex with a Lewis acid, and is then polymerized by heating. If the complex is a mesophase, it can provide an oriented medium for the polymerization. This is not an essential condition for the production of a mesomorphic polymer, but clearly, the better the alignment of monomer units before polymerization, the more likely the production of a polymer of high quality.[6]

Our first attempts at polymerizing nitriles were with conventional molecules (R = $—C_6H_5$ and $—C_7H_{15}$). We obtained brown-black polymers, infusible at T ≤ 300°C, insoluble in usual solvents and closely similar to the corresponding products described in the literature.[7,8] In agreement with theoretical calculations, they were able to form charge transfer complexes having an electrical conductivity after treatment with oxidizing agents such as iodine.[9]

Once we had established the electroactive potential of polynitriles, we attempted to proceed with the synthesis of $(\underset{\underset{\displaystyle R}{|}}{—C}=N—)_n$ polymers for which R is a mesogenic moiety. The present paper reports their mesomorphic and electrical properties. It also includes a brief description of the monomers and the conditions of polymerization.

1. MONOMERS

We have prepared two polar end-group liquid crystals which we shall refer to as M_1 and M_2. M_1 has two polar end-groups whilst M_2 possesses a non-polar aliphatic chain and only one polar terminal $—C\equiv N$ group. Their chemical structures are given Figure 1.

In both cases, the polymerizable $C\equiv N$ groups are mechanically and electrically decoupled from the rigid parts of the molecules, by being located at the end of an aliphatic chain. This decoupling of the cyano group means that, in the polymer, the rigid parts of the side-chains will be linked to the main chain through a flexible spacer. Such a linkage is necessary for the liquid crystalline organization. Here the spacer is a six-carbon aliphatic chain containing for both M_1 and M_2.

Our choice was also influenced by the aim of obtaining mesomorphic behavior at high temperature, so that the polymerization could be carried out in an oriented medium. Molecules quite similar in architecture to M_1 and M_2 but with no polar groups are known to exhibit smectic S_A and S_B phases at high temperature.[10]

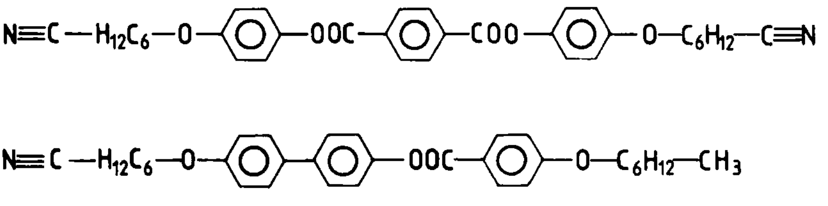

FIGURE 1 Chemical architecture of monomers.

M_1 and M_2 have been prepared by conventional techniques[11] and identified in the usual way by IR spectra and microanalysis (M_1:C% calc 71.83, fnd 71.75; H% calc 6.34, fnd 6.33; 0% calc 16.90, fnd 16.99; N% calc 4.93, fnd 4.85 – M_2:C% calc 77.19, fnd 77.38, H% calc 7.60, fnd 7.68; 0% calc 12.48, fnd 12.37; N% calc 2.73, fnd 2.62). The mesomorphic behavior has been studied by D.S.C. and optical polarizing microscopy.

Below the nematic phase, M_2 exhibits two smectic phases S_1 and S_2. S_2 is monotropic and is only observed on lowering the temperature. S_1 forms a focal conic fan texture and at the S_1 to S_2 transition the fans are covered by transient striations. This behavior is typical of a $S_A \rightarrow S_B$ transition.[12] D.S.C. measurements agree well with a first order $S_1 \leftrightarrow S_2$ transition.

Concerning M_1, below its nematic phase only one smectic phase is observed. This has a texture similar to that of S_1, with which it is miscible.

The smectic phase S_1 is assumed to be a S_A phase and the S_2 a S_B phase. The phase transition temperatures are given Figure 2.

We have previously described the mesomorphic behavior of molecules containing a highly dipolar end-group mechanically and electrically decoupled from the rigid moiety and we have studied the influence of the decoupling on the observed mono- and bi-layered arrangements.[13] X-ray investigations are in progress to characterize the S_1 and S_2 phases of M_1 and M_2 and to reveal the nature of the lamellar arrangement of such compounds.

2. PRIOR POLYMERIZATION, ACTIVATION OF THE C≡N BOND BY COMPLEXATION

2.1. General considerations

A convenient way of obtaining a polymer with a conjugated —C=N— main chain from a nitrile, consists of heating at high temperature (200 to 300°C), the complex formed between the nitrile and a transition-metal halide, usually $ZnCl_2$ or $TiCl_4$.[1,2,3,4] Such complexes are, in general, crystallized substances with a well-defined stoichiometry.[14]

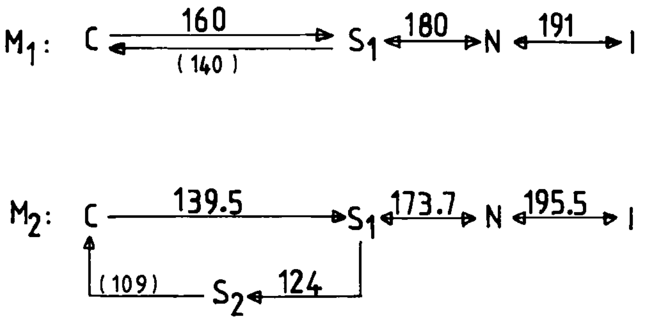

FIGURE 2 Mesomorphic behavior of monomers. S_1 and S_2 are assigned respectively as S_A and S_B phases.

As a complexing agent, we have used $ZnCl_2$ capable of forming complexes with a range of organic electron donators including nitriles.[15] These [R—C≡N, $ZnCl_2$] complexes have a 4 fold tetrahedral coordination and their stoichiometry is usually 2:1 (*i.e.*, formula $ZnCl_2$, $(RCN)_2$).[16]

To achieve the polymerization of R—C≡N it is not necessary to use the stoichiometric quantity of $ZnCl_2$. The metal chloride produced by the dissociation of a polymerized complex can form a new complex with free nitriles and induce further polymerization.[17] Bearing this in mind, we have attempted to vary somewhat the amount of $ZnCl_2$ in such a way as to produce both a catalytic effect on the polymerization process and the stabilization of the smectic phase of the system at the temperature of polymerization.

2.2. Mesomorphic properties of the complexes between $ZnCl_2$ and M_1 or M_2

It is interesting to note that, in the absence of moisture, the binary systems [M_1 – $ZnCl_2$] and [M_2 – $ZnCl_2$] form stable mesophases – Direct I ↔ S transitions are observed (with no nematic phase being observed). In both cases (M_1 and M_2) the thermal stability range of the smectic phases is appreciably enhanced with respect to the corresponding pure M_1 and M_2 compounds.

These "induced" smectic phases occur with a maximum stability for a molecular ratio [nitrile:$ZnCl_2$] equal to 2:1 – Deviations from this composition are possible (up to 4:1) but they cause a drastic lowering of the S–I transition temperature and they give a very large biphasic region. Thus, despite the fact that the concentration of $ZnCl_2$ does not matter very much for catalytic purposes, a ratio of 2:1 is used because it is its optimum for giving polymerization within a lamellar phase. Our description of the liquid crystalline properties of the complexes will hence concern this special case.

In such systems, $ZnCl_2$ interacts with the C≡N groups, leading to a head-to-head association of the molecules.[18] Since the rigid cores of the "dimers" are decoupled from the C≡N by the aliphatic chains, a stabilization of the molecules within a lamellar arrangement occurs. The strength of the Cn – $ZnCl_2$ interactions, however, is modified by the mobility of the C≡N groups; this point will be discussed elsewhere.

For the [$(M_2)_2$, $ZnCl_2$] complex, only one smectic phase, S_1 is observed. This forms a focal conic fan texture. A smectic phase with similar texture is also observed for [$(M_1)_2$, $ZnCl_2$] which also forms another smectic phase S_2. The appearance of non-transient concentric arcs across the fans is an indication that this is a smectic E type. Such a type of smectic arrangement would be in perfect agreement with both the tetrahedral organization around the Zn atoms and the layered order of the mesophase. An orthorhombic organization of crystalline $ZnCl_2$-nitriles complexes has been observed, *e.g.* in [$(CH_3CN)_2$, $ZnCl_2$].[16] The thermotropic behavior of [$(M_1)_2$, $ZnCl_2$] and [$(M_2)_2$, $ZnCl_2$] is given in Figure 3.

From microscope observations we have not been able to ascertain the miscibility of the S_1 phases of the complexes with the S_A phase of the corresponding monomer by the contact method with any degree of certainty. X-ray investigations are therefore necessary to determine the molecular arrangement in the smectic phases of

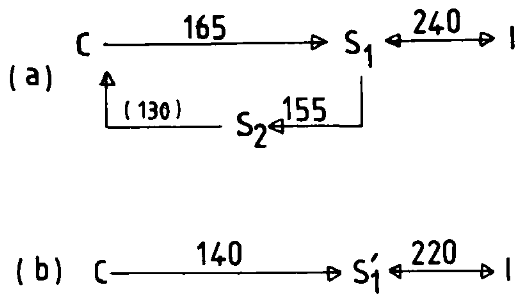

FIGURE 3 Phase transition temperature of {monomers, $ZnCl_2$} complexes. (a) {$(M_1)_2$, $ZnCl_2$}; (b) {$(M_2)_2$, $ZnCl_2$} S_1 and S_1' could be S_A phases (from their optical textures, fluidity), S_2 is tentatively identified as an S_E phase.

the complexes. In particular, for [$(M_2)_2$, $ZnCl_2$] one can conceive two possible lamellar arrangements, mono- or bi-layered as shown in Figure 4.

The systematic study of the stability of the mesophases *versus* temperature will be presented in detail in a forthcoming paper which will describe a variety of molecules with decoupled polar C≡N end groups. For the remainder of this work it is important to note that the temperatures at which nitriles begin to polymerize (200°C) are compatible with the existence of an oriented smectic phase.

3. ELABORATION OF THE POLYMERS

Throughout the following account, poly-M_1 and poly-M_2 will be called (respectively) P_1 and P_2.

3.1. General considerations

Following a technique described in the literature[1] the complexes are heated for four hours at a temperature in the range 200–230°C in the presence of a small amount (6% by weight) of HPO_3 (a proton donator acting as an activator). Note that drastic conditions avoiding any trace of moisture are necessary.

After polymerization, $ZnCl_2$ and HPO_3 are removed by repeated washing with water. This operation is carefully monitored by observing the X fluorescence of P, Zn, and Cl. The elimination of unreacted monomer M_1 from P_1 as initially produced, is achieved by washing in cold nitromethane. Upon evaporating the solution, M_1 can be identified from its texture and transition temperatures. The intensity of the C≡N line in the I.R. system strongly decreases during the washing process.

P_2 is extracted from the $M_2 - P_2$ mixture as obtained by fractional recrystallization in hot nitromethane. Its IR spectrum shows that the C≡N line disappears (Figure 5).

3.2. Miscellaneous properties of P_1 and P_2

P_1 and P_2 are yellow-brown solids; both have a well resolved IR spectrum (Figure 5) in which phenyl rings ($\lambda^{-1} = 3050\ cm^{-1}$) aliphatic chains ($\lambda^{-1} \approx 2900\ cm^{-1}$)

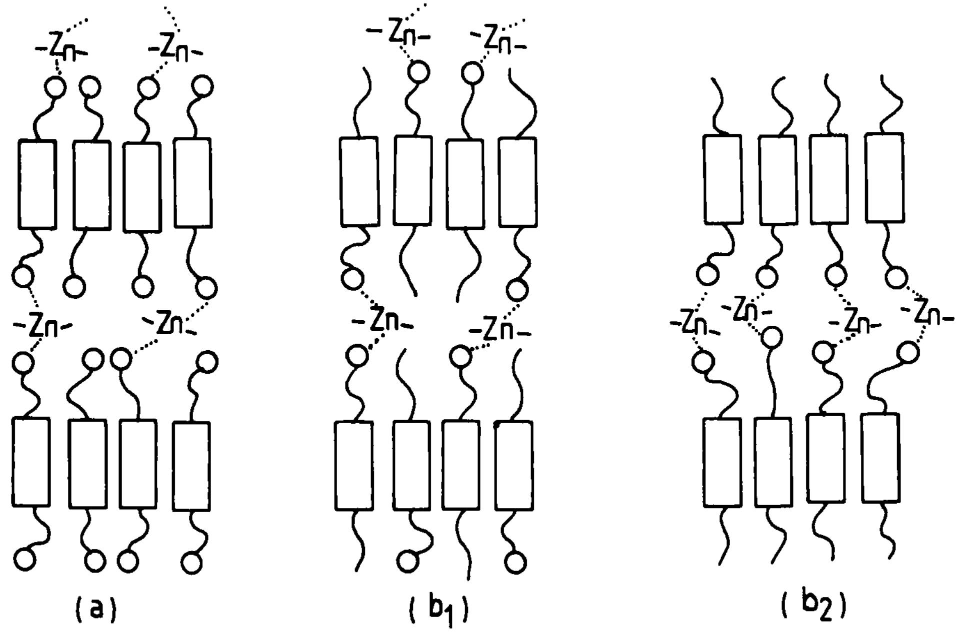

FIGURE 4 Schematic view of lamellar ordering in {M_1, M_2 − $ZnCl_2$} complexes. (a): {$(M_1)_2$ − $ZnCl_2$}; (b_1) and (b_2) are possible mono- or bilayered arrangements for {$(M_2)_2$ − $ZnCl_2$}.

and COO groups (λ^{-1} = 1725 cm^{-1}) can be unambiguously identified. The relative intensities of COO and aliphatic chain absorption bands are quite comparable for monomers and polymers. When the polymerization is achieved, the $C\equiv N$ line, clearly visible in the monomer spectra (λ = 2245 cm^{-1}), almost disappears for P_2 and has an intensity strongly reduced for P_1.

Microanalysis data agree with the expected chemical composition for carbon and hydrogen but indicate a loss of nitrogen (P_1:C% calc 71.83, fnd 71.0; H% calc

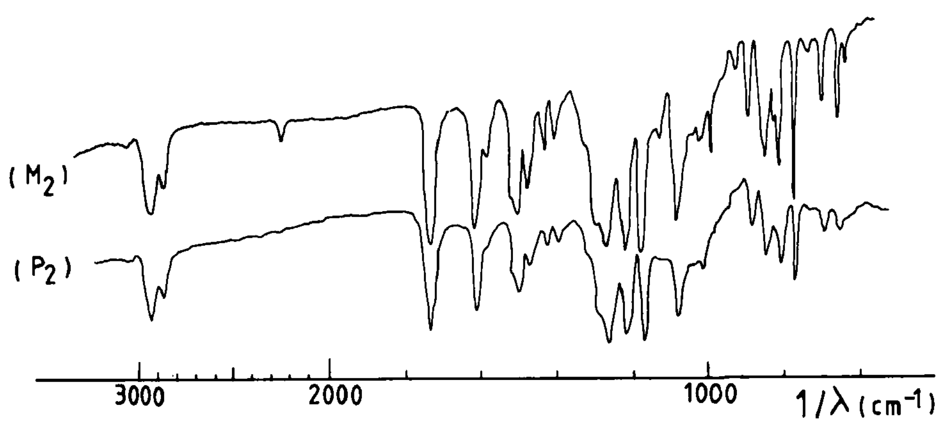

FIGURE 5 Infrared spectra of M_2 and P_2. Similar spectra are obtained from M_1 and P_1.

6.34, fnd 6.20; N% calc 4.93, fnd 3.80; P_2:C% calc 77.19, fnd 76.30; H% calc 7.60, fnd 7.50; N% calc 2.73, fnd 2.06).

Such a loss of nitrogen has been previously reported for polynitriles and has been attributed to cross linking of the polymer.[4] Interchain bondings can be formed by the elimination of ammonia between the terminal group of one chain (an imino group according to the polymerization mechanisms commonly accepted[1]), and mobile hydrogens of another. The latter can be either hydrogens of a terminal methyl of an R group in the case of a polymer from a mono-nitrile or hydrogens from a methylene in an α position in the case of a polymer from dinitrile. The observed loss of nitrogen for P_1 and P_2, however, does not exceed the values reported in the literature.[4]

P_1 and P_2 have both an electron spin resonance signal indicating less than one paramagnetic centre for 1000 monomer units, $\Delta B \sim 6$ Gauss, $g = 2.0027$). Such a feature is characteristic of conjugated polymers and has been observed in classical polynitriles.[7]

4. STRUCTURAL PROPERTIES OF P_1 and P_2

4.1. Specific properties of P_1

P_1 is infusible (at $T < 300°C$) and practically insoluble in the usual solvents. Since M_1 possesses two polymerizable C≡N groups, one can assume that the polymeric conjugated main chains are cross-linked through the side-chains. The IR spectrum of P_1 shows that the cross-linking is not complete however, since the CN line does not entirely disappear.

From optical polarizing microscopy a crystalline structure is assumed. Preliminary X-ray investigations confirm this. A schematic picture suggesting a possible lamellar arrangement for P_1 is proposed in Figure 6.

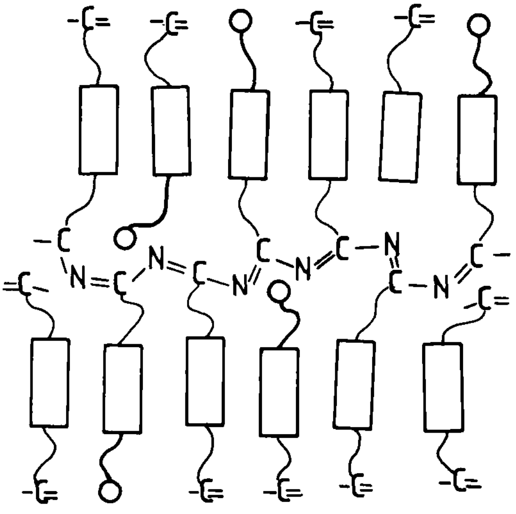

FIGURE 6 Schematic picture of dinitrile P_1. Circles indicate unreacted —C≡N groups.

$$C \xrightarrow{95} S_3 \xleftrightarrow{105} S_2 \xleftrightarrow{123} S_1 \xleftrightarrow{142} N \xleftrightarrow{232} I$$

FIGURE 7 Phase transition temperatures of P_2. From DSC measurements:
ΔH_{I-N} = 0,8 kJ/mole; ΔH_{N-S_1}: very low.
ΔH_{S_1-S2} = 1,8 kJ/mole; $\Delta H_{S_2-S_3}$ = 1,30 kJ/mole
$\Delta H_{C \rightarrow S_3}$ = 17 kJ/mole
The C → S_3 temperature corresponds to the beginning of melting (from DSC). The N.I. transition extends over a range of about 5°C.

4.2. Specific properties of P_2:mesomorphism

The polymerization of M_2, which has only one reactive C≡N, leads to a polymer, P_2 which is fusible and soluble. It can be recrystallized in hot nitromethane. P_2 exhibits a very interesting mesomorphic behavior (Figure 7).

Below the isotropic phase, P_2 possesses a nematic phase over a temperature range of about 100°C, followed by three smectic phases, S_1, S_2 and S_3. A very low enthalpy of transition is observed at the N ↔ S_1 transition indicating that this is virtually a second order transition. Thin preparations exhibit an homeotropic texture for all the phases. For thicker samples a slightly colored schlieren texture is observed in the S_1 phase.

The same kind of texture is encountered for the S_2 and S_3 phases together with rearrangements at the transitions. When observed between crossed polars, the sample becomes progressively darker from S_1 to S_2 and S_3 whilst the fluidity decreases. The measured enthalpies of the S_1 to S_2 and S_2 to S_3 transitions are consistent with a first order nature of these transitions (Figure 7).

The S_1 phase is miscible with the smectic A phase of M_2. More investigations are necessary to ascertain the nature of the S_2 and S_3 phases.

In contrast to what is generally observed for side-chain liquid crystalline polymers, P_2 crystallizes (Figure 7). There are two possible reasons for this. Firstly, the lower polymerization temperature (200 − 230°C instead of 300°C commonly used for polynitriles[1]) leads us to conclude that the main chain is not very long. Secondly the crystallization of P_2 is favored by several effects: the conjugated backbone is more rigid than is usual for conventional side-chain liquid crystalline polymers since it has a long rigid part joined to a rather short flexible spacer (C_6H_{12}) within the side chains. A schematic picture of such a polymer is represented in Figure 8.

5. ELECTRO-ACTIVE PROPERTIES OF P_1 and P_2

As obtained, P_1 and P_2 are good insulators ($\sigma < 10^{-11}\ \Omega^{-1}\ cm^{-1}$). A preliminary test of their electroactive potential has been performed on samples in the crystalline state. We have submitted them to the oxidizing action of iodine, to check whether they have ionization potentials low enough to form charge-transfer complexes.

Powders of P_1 and P_2 were exposed to iodine vapors with an inert gas; then pellets were pressed and the electrical conductivity measured *versus* frequency.

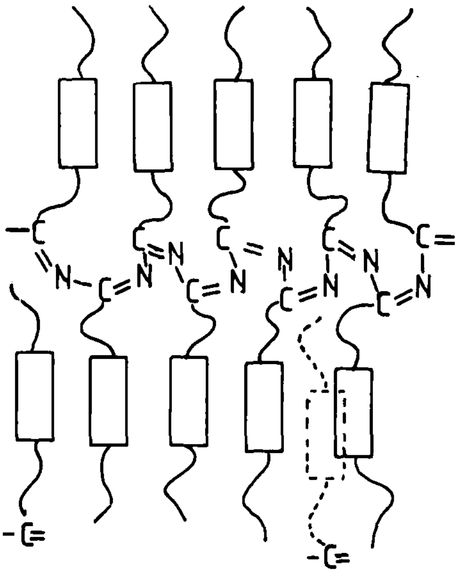

FIGURE 8 Schematic picture of mononitrile polymer P_2.

The results are given Figure 9. Up to 10^4 Hz the conductivity is independent of frequency. Its absolute value is not very high but it agrees well with the theoretical values predicting an electroactive behavior.

Furthermore, the variations of conductivity after doping can be correlated with ESR observations. When exposed to iodine, the polymers P_1 and P_2 give an ESR signal, the g factor of which shifts toward larger values. This is exactly the same effect as that observed for some other nitrogen-containing electroactive polymers.[18,19] This fact reinforces our belief that a charge transfer does occur betwen I_2 and P_1 or P_2.

CONCLUSION

We have shown that nitriles can generate highly ordered electroactive polymers in which conducting chains can be located in planes separated by spacers of controllable length. A dinitrile gives a cross-linked, almost insoluble and infusible polymer with a crystalline structure. A mononitrile, with a large enough decoupling of the C≡N from the rigid core, gives a mesomorphic polymer. The latter also shows the electroactive properties inherent in the main chain. It does not seem unreasonable to predict that it is possible to bring into the world of electroactive polymers the improvements of liquid crystalline polymers: easy processibility, the possibility of orientation into monodomains and anisotropy effects.

The selection of starting nitriles, with more flexible spacers could lead to a glass transition where the ordered state would be stable at room temperature. One

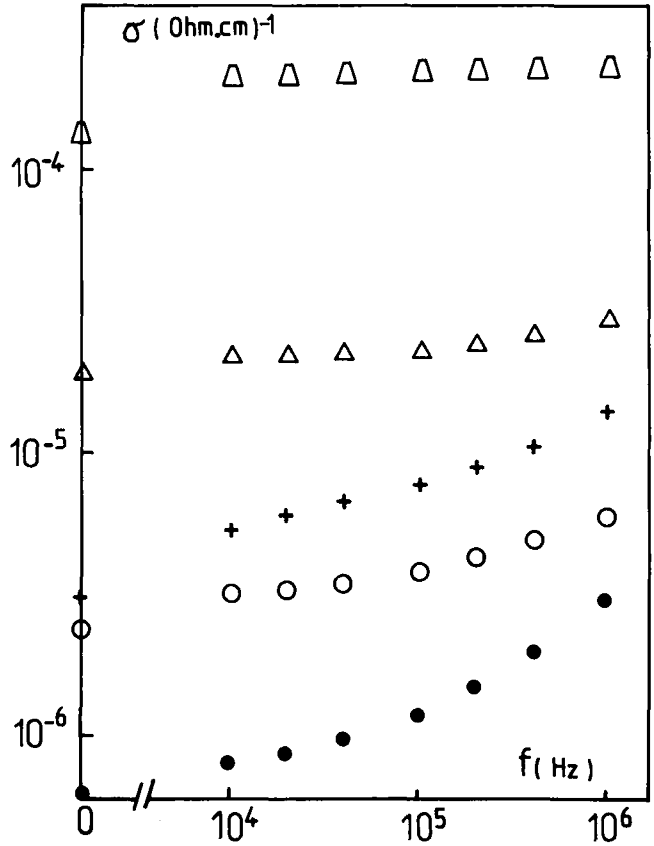

FIGURE 9 Electrical conductivity of polynitriles upon doping under partial iodine pressure in their solid state.
Δ: polybenzonitrile (P = 60 Torr, *t* = 5 hours)
○: P_1 (5 Torr, 15 hours); Δ: P_1 (5 Torr, 100 hours)
●: P_2 (5 Torr, 15 hours); + : P_2 (5 Torr, 100 hours)

important task (both theoretically and for practical applications) would be to correlate the electronic conduction properties with the microscopic and/or macroscopic order of the system. Such work is in progress in our laboratory.

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