Side-Chain Liquid Crystalline Poly(*N*-maleimides). 5. Dielectric Relaxation Behavior of Liquid Crystalline Side-Chain and Amorphous Poly(*N*-maleimides). A Comparative Structural Study[†]

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ABSTRACT: A series of five nonaligned comblike poly(*N*-maleimides) have been studied by frequency (200 Hz–100 kHz) and temperature (from 123 to 423 K) dependent dielectric measurements. Three of them are smectic side-chain liquid crystal polymers (SCLCPs) and the other two are amorphous materials. These samples also allow us to study the possible influence of the smectic field. By a change of the chemical nature of the structure of mesogens, a self-consistent assignment of the different relaxational processes has been possible. Six main relaxation processes have been found and assigned: (i) Two relaxations, β_1 and β_2, are produced at temperatures below T_g, due to rotational motions and torsional oscillations of the mesogens, respectively. They can be attributed to the reorientation of the perpendicular component to the major axis of the permanent dipolar moment located at the center of the mesogenic groups. In polymer V, these two relaxations are reduced to one β_2. Here the second type of motion is no longer possible because of the absence of an oblong moiety with interphenylenic ester groups and because of the presence of a tetramethylbutane group as a substituent in the phenylene group. (ii) Two relaxations, γ_2 and γ_1, are located at the lower temperature and attributed to localized motions of *n*-alkoxy pendant groups linked to mesogens in para position and to the spacer with its interconnecting functional groups which link it to the main chain and the mesogen, respectively. (iii) Two relaxations, α and δ, respectively, are produced at temperatures above T_g which are assigned respectively to dipole reorientation of the main chain motions and to displacements of the mesogens which are able to reorientate the dipolar moment component parallel to the long axis of the mesogens. The absence of a δ-process in polymers I and II may be due to the absence of orientational rotation of the anisodiametrical mesogenic group; as a result, the orientation of the parallel component $\mu_\parallel$ of the dipole moment of the mesogen does not take place. It is possible that topological constraints imposed by a strong smectic field due to the existence of a long range order in the smectic layer of these two highly ordered polymers may be responsible for this behavior by hindering such a motion. The structure and phase transitions of the five polymers were studied by optical polarizing microscopy, small and wide-angle X-ray diffraction on aligned and unaligned samples, and differential scanning calorimetry.

Introduction

In spite of the ever increasing quantity of experimental data, the correlation between the motions of the main chain and the pendant mesogenic unit is not well understood.[1–3] In most cases it is not possible to find a consistent and satisfactory agreement between the different laboratories on the interpretation of results in the current literature. There are still many questions open to discussion. This may be due to the diversified chemical structure of SCLCPs which is very difficult to systematize.

In order to identify the origin of the relaxation mechanism, we have investigated different molecular structures of the mesogenic pendant group connected to the same type of main chain via the same intermediate group and spacer. This approach may help to make the assignment of the observed relaxation processes and motions to the different parts of molecules more accurate. This type of study has been carried out previously.[4,5] Kremer et al.[5] have studied a set of combined main-chain side-group liquid-crystalline polymers by broad-band dielectric spectroscopy to analyze their molecular dynamics. By variation of the chemical structure, a detailed assignment of the observed relaxational processes was possible.

In the paper presented here the dielectric properties of a series of poly(*N*-maleimide) polymers with the general chemical structures shown in Figure 1 will be described.

As can be seen from these chemical structures, the polymers under study differ only in the structure of the oblong part of the side chains (mesogens in three of the five macromolecules) and the pendant end groups. It is therefore possible to study the effect of each part of the side chain on the dielectric relaxations.

The selection of ten carbon atoms as spacer length may lead to a weaker coupling between the mesogenic groups and the main chain, thus allowing the mesogens to have some independent mobility.

Polymers with phenylbenzoate mesogenic groups and some other main chains more flexible than poly(*N*-maleimides) have been studied very recently.[6–27] Phenylbenzoates as mesogenic groups may impart some special characteristics to their side-chain liquid crystalline polymers. For instance, the primary significant characteristic of phenylbenzoate moieties may be their strong interactions governed by electronic and geometrical factors, allowing the mesogenic side groups to achieve more ordered packing with some peculariarities with respect to some other mesogens. Thus, ester groups may play the role of

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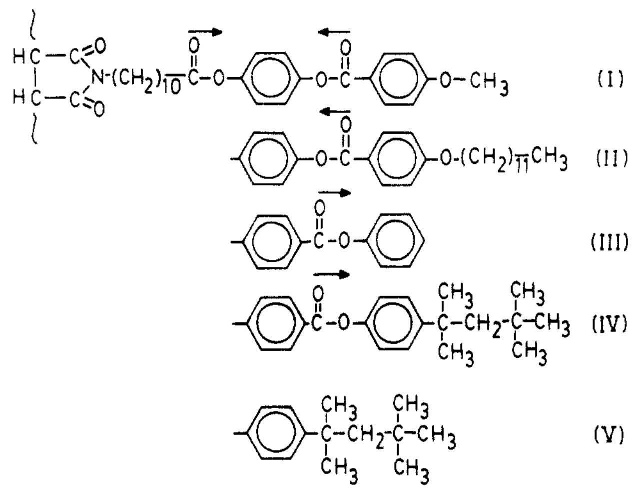

Figure 1. Schematic representation of the chemical formula for the structural units of the investigated series of poly(*N*-maleimides) (see text for notation).

hinges, which ensure the realization of the conformations, required for ordering in the liquid crystalline state through the anisodiametric groups of the side chains.[11,13] This may give rise to three microregions in the layered structure with different electronic densities (three component system).[23,26,27] Sometimes and for reasonably flexible main chains the phenylbenzoate group yields highly ordered smectic mesophases.[12,14] According to Freidzon et al.[12] the detection of T_g is very difficult because of their stiffness. However, we believe that this fact can be due to the existence of a strong smectic field created by these phenylbenzoate groups when some special spatial situations of them (conformations) are realized, as we will see later on in the case of some of our polymers. There exist some other types of characteristic behavior which make attractive the incorporation of the phenylbenzoate group into more stiff main chains.[6-27] All these factors may exert some peculiarities on the dynamic of these SCLCPs. However, they have not been studied by dielectric spectroscopy. The high tendency of the poly(*N*-maleimides) backbone toward side-chain order in conventional comblike polymers seems to be of prime importance.[28-31] Studies on molecular motions in non-liquid-crystalline comblike poly(*N*-maleimides) are very scarce. Apart from the reduced work developed on nuclear magnetic relaxations on some poly(*N*-*n*-alkylmaleimides),[32,33] also few studies have been reported on the dielectric relaxations of poly(*N*-alkyl- and *N*-arylmaleimides)[34] and some of their copolymers with styrene.[35] In general, three relaxations were observed and assigned to the glass to rubber transition, a local motion, and an in-phase deformation of the maleimide ring, respectively.

The introduction of a functional group such as –COO– at the interconnecting link between the spacer and the anisodiametrical substituent and the orientation of the second ester bridge between two *p*-phenylene rings with respect to the ester linking the mesogen and the spacer can be parallel or antiparallel. It may affect to a certain extent or significantly the packing properties in the solid state as well as their corresponding dielectric behavior. Therefore this may be of interest from the structural point of view.

Experimental Section

The monomers were synthesized according to procedures described elsewhere.[36] The polymers were obtained by radical polymerization in solution at 80 °C using benzene as solvent and AIBN as initiator. The polymers, depending on their solubilities, were precipitated with methanol, 2-propanol, or methyl isopropyl ketone and then precipitated 3 times from benzene solution.

Molecular weights of samples were determined by size exclusion chromatography (SEC) using Styragel columns with upper porosity ratings of 10^3, 3×10^3, 3×10^3, 4×10^4, 10^5, and 10^6 Å (Waters description) with THF as solvent. The calibration was done with polystyrene standards (Waters Associates and Pressure Chemical Co.). The measurements were performed at 23 °C with a Waters Associated Model 200 gel permeation chromatograph. Some other experimental details have been given elsewhere.[37] Molecular weight averages and some other characteristics are shown in Table I. This crude approach to obtain molecular weight distributions is done very often in the case of side-chain liquid crystalline polymers.[38-42] For these reasons the values gathered in Table I do not represent absolute values but estimated ones. They may be useful only in those cases in which data are discussed for comparative purposes. All the SEC chromatograms showed a unique peak in the high molecular weight region and were free of tails in the low molecular weight region, which is characteristic for the presence of oligomers and monomers.

The liquid crystalline behavior and the transition temperatures of the samples were determined by differential scanning calorimetry using a Perkin-Elmer DSC-4 with a TADS data station. DSC data were recorded during the heating scans at 20 °C and polarizing optical microscopy by using a Carl-Zeiss microscope equipped with a Mettler FP82HT and a Mettler F880 microprocessor, magnification ×250. The samples were prepared between untreated glass slides.

The structure of the mesophases was identified by X-ray diffraction. Three types of X-ray diffraction experiments were carried out. All the X-ray experiments were recorded at room temperature.

In the first series, X-ray diffractograms were recorded on a flat camera. They were obtained at low and wide angles (SAXS and WAXS), with a Rigaku RV 200 generator using Ni filtered Cu Kα radiation. Working conditions were 40 kV and 40 mA. A pinhole collimator was used. Well-oriented samples were produced when possible by drawing fibers out of the mesophase with a pair of tweezers.

A second series of X-ray patterns (SAXS) were obtained on the same X-ray generator, but in the angle recording mode. These diffractograms were measured in a range from 1 to 8 2θ deg. Working conditions were 40 kV and 40 mA. Measuring conditions for the maxima which appeared between 1 and 7 2θ deg were the following: divergency $^1/_6$°; reception 0.1 mm; dispersion $^1/_6$°; intensity 1×10^3; recorder speed, 5.

A third series of X-ray diffraction data (WAXS) were recorded on a Philips PW 1710-30 X-ray diffractometer using Ni-filtered Cu Kα radiation (40 kV and 40 mA) from 2 to 40 2θ deg.

In the second and third series of experiments, previous to the X-ray runs, the samples were cast on glass slides from polymer solution in $CHCl_3$, dried in vacuum at 70 °C and annealed at temperatures above their respective glass transition for periods of time from 2–3 h to 12 days and then slowly cooled to room temperature.

Results from the three series of X-ray experiments have been used all together in each one of the cases. They will comment on separately for each polymer.

Results from the three series of X-ray experiments are shown in Table II.

A certain number of characteristics relative to the thermal behavior of the polymers under study needed for the discussion and interpretation of the experimental results are given for each one of the polymers as follows.

Polymer I. Poly{*N*-[10-((4-((4′-methoxybenzoyl)oxy)phenoxy)carbonyl)-*n*-decyl]maleimide}. The glass transition temperature is T_g = 18 °C obtained at a rate of heating of 20 °C/min, and the smectic isotropic transition has the following thermal properties: T_{CI} = 143 °C and ΔH_{CI} = 2.2 kJ/mol, and ΔS_{CI} = 5.3 J/(mol K).

Upon cooling from the isotropic melt, the smectic phase begins at the clearing point in the form of a sanded texture which, after further cooling, forms larger domains with a small sized schlieren texture of four arms with singular points. This texture remains unaltered even after 3 days of thermal annealing or even when the samples are annealed on glass slides which have been treated

Table I
Preparation Conditions, Organic Elemental Analysis, Molecular Weight of the Structural Unit, Weight- and Number-Average Molecular Weights, $\bar{M}_w$ and $\bar{M}_n$, the Ratio of the Weight- to Number-Average Molecular Weights, $\bar{M}_w/\bar{M}_n$, and Number-Average Degree of Polymerization $\overline{DP}_n$ As Determined from $\bar{M}_n$

polymer sample	t (h)	AIBN (% molar)	yield (%)	organic elemental analysis	% C	% H	% N	MW (structural unit)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$\overline{DP}_n$
I	48	2.0	96	found	66.55	6.43	2.81	507.6	54.7	6.0	9.1	118
				calcd	68.62	6.55	2.76					
II	90	2.0	90	found	72.77	8.35	2.14	661.9	7.1	2.2	3.2	33
				calcd	72.59	8.38	2.12					
III	168	1.6	98	found	70.29	6.67	3.00	477.6	8.2	2.5	3.3	52
				calcd	70.42	6.54	2.93					
IV	144	2.0	99	found	74.08	8.17	2.50	588.8	59.8	9.0	6.7	152
				calcd	73.32	8.03	2.37					
V	144	3.0	99	found	74.08	9.06	2.50	469.7	2.7	1.9	2.3	40
				calcd	74.16	9.23	2.98					

Table II
Interplanar Distances of Five Poly(*N*-maleimides) Examined at Room Temperature

polymer sample	interplanar spacings (Å)						
	d_1 (±1)	d_2 (±1)	d_3 (±0.5)	d_4 (±0.5)	d_5 (±0.5)	d_0 (±0.05)	L
I	30.8	15.5	10.4			4.40	31–32
II	59.2	29.5	19.7	14.8	12.1	4.48	50
III		15.8	10.6			4.36	32
IV						difuse halo	
V						difuse halo	

Table III
Glass Transition Temperatures T_g, Clearing Temperatures T_{Cl}, and Activation Energies for Dielectric Relaxations in a Series of Five Poly(*N*-maleimides)

polymer sample	T_g (°C)	T_{Cl} (°C)	E_a (kJ/mol)				
			γ	β_1	β_2	α	δ
I	18	143		59	40	320	*a*
II	41	167	26	65	40		*a*
III		122[b]		43	24	290	160
IV	32	*c*			35	~300	120
V	43	*c*		*a*			130

[a] These relaxations have not been observed. [b] Transition estimated from polarizing optical microscopy. [c] They are amorphous materials.

chemically or by any particular physical treatment such as rubbing or by structural replica induced alignment with lecithin, compounds which have lipophilic end groups, or compounds having a polar group and clean glass surfaces.

Schlieren textures are characteristic of compounds with ordered structures in layers. The absence of two arm single points is also indicative of a smectic structure.

The diffraction pattern obtained from stretched fiber shows six equatorial arcs of diffraction in the direction perpendicular to the direction axis. They correspond to the first (30.8 Å), second (15.5 Å), and third (10.4 Å) orders of diffraction from the planes of a smectic structure with periodicity of ~31 Å.

A rough estimation of the possible mode of arrangement of the side mesogenic groups of this SCLCP using conventional molecular models and nominal values for the standard bond lengths and valence angles gives us a value of L = 31–32 Å which is almost identical with the observed layer spacing. It corresponds to the most extended conformation, i.e. with the spacer and the side chain in their most extended conformations. So a monolayer structure for this polymer at room temperature can be assumed, in which these side chain groups (spacer, mesogen, and pendant groups) are arranged antiparallel so that the methoxyl pendant group of one chain is surrounded by methylene groups from the flexible spacers of another chain. The results of small angle experiments confirm the assumption of the existence of this type of structure.

Two sharp meridional arcs are shown in the direction of the fiber axis. Sharp wide-angle maxima indicate a very ordered interlayer hexagonal packing of the mesogenic groups. Three diffraction arcs correspond to a spacing of d_0 = 4.40 Å. The average intermolecular distance in intralayer packing of mesogenic groups, calculated according to De Vries[43] as $D_0 = d_0 \times 1.117$ Å, is D_0 = 4.91 Å, which is typical of highly ordered smectic phases and correspond to dense hexagonal packing of benzene rings[44,45] in oblong molecules. The diffraction patterns obtained from the stretched fiber imply an orthogonal array between the backbone and side chains of macromolecules; i.e., the side chains are perpendicular to the smectic layers, these being parallel to the direction of stretching.

Polymer II. Poly{*N*-[10-((4-(((4′-(*n*-dodecyloxy)benzoyl)oxy)phenoxy)carbonyl)-*n*-decyl)]maleimide}. The glass transition temperature is T_g = 41 °C, and the smectic–isotropic transition has the following thermal properties: T_{Cl} = 167 °C and ΔH_{Cl} = 15.3 kJ/mol and ΔS_{Cl} = 34.7 J/(mol K).

Below the glass transition temperature this polymer gives diffraction patterns consisting of two very narrow meridional arcs of d_0 = 4.35 Å which are related to the lateral spacing between mesogenic side groups. Ten equatorial arcs are also present giving d spacings of first (59.2 Å), second (29.5 Å), third (19.7 Å), fourth (14.8 Å), and fifth (12.1 Å) orders of diffraction.

The diffraction patterns have also been interpreted as smectic layer spacings. The spacing d = 59.2 Å is slightly greater than the length of the structural unit of the polymer, calculated from standard bond lengths and angles (molecular models) with the assumption of an all-trans molecular conformation for the spacer and the *n*-alkoxy pendant group.

There are two sharp meridional arcs in the direction of the fiber axis. Sharp wide-angle maxima indicate a very ordered intralayer hexagonal packing of the mesogenic groups. These diffraction sharp arcs correspond to a spacing of d_0 = 4.48 Å. The average intermolecular distance in intramolecular packing of mesogenic groups, calculated according to De Vries[43] as $D_0 = d_0 \times 1.117$ Å, is 5.00 Å, which is typical for highly ordered smectic phases and corresponds to dense hexagonal packing of the benzene ring[41,42] in oblong molecules.

Polymers I and II are similar with respect to packing properties and they are clearly smectogenics. They differ only in the length of the *n*-alkoxy pendant group. This type of polymer, with the same structure but differing only in the length of the *n*-alkoxy pendant group, possesses a long-range orientational order in the smectic phases with a positional ordering in the layer. The layers have a somewhat greater thickness than of the molecular length[46] and are perpendicular to the preferred orientation.

Polymer III. Poly{*N*-[10-((4-((4′-phenoxycarbonyl)phenoxy)carbonyl)-*n*-decyl)]maleimide}. It has not been possible to estimate the glass transition temperature T_g. Sometimes the determination of T_g in SCLCPs with highly ordered smectic phases is very difficult specially in those cases in which the structure is quite stiff[12] and this may be the reasoning in the present case. This polymer is birefringent, although birefringency is very low. However, we have observed by optical microscopy two types of smectic mesophases, one at low temperature S_A and the other at high temperature S_B. Optical microscopy of the smectic phase S_A does not reveal any specific textures. It shows a rough texture. This conclusion has been reached from the characteristic textured formed by the polymer and confirmed by the X-ray study which has demonstrated the presence of an ordered layer structure. We have assigned them to a $S_A \rightarrow S_B$ transition with thermal properties of $T_{S_A\rightarrow S_B}$ = 110 °C, $\Delta H_{S_A\rightarrow S_B}$ = 4.91 kJ/mol, and $\Delta S_{S_A\rightarrow S_B}$ = 12.8 J/(mol K). Because of a very small effect between the S_B and isotropic phase, the transition could not be observed on the DSC trace. It was located at 122 °C by using a polarizing optical microscope.

We have been unable to obtain aligned specimens of this sample. We have obtained diagrams consisting of a broad diffuse outer peak in the range 4.4–5.0 Å which is related to the lateral spacing between mesogenic side groups and two peaks at low angles giving spacing of 15.8 and 10.6 Å. These two peaks seem to be the second and third orders of diffraction of a monolayer structure with spacing of d = 31.7 Å. This spacing agrees with that calculated from molecular models (32 Å).

The absence of the first maximum of diffraction, corresponding to this one layered packing, may be due to specific forms of electron density distribution,[23] which may lead to the extinction of the first-order reflection with d = 31.7 Å. At this point we should consider from the structural point of view the effect of the introduction of a second ester group on the mesophases and the relaxation process associated with the motions of the ester polar group adjoining the two p-phenylene rings. In nonpolymeric liquid crystals with ester linkages, the smectic nature of these small molecules is strongly dependent on the orientation of the ester linkage with respect to the alkoxy group.[47–49] Thus, for instance, molecules having the ester group in one sense, –COO–, are smectogenic, but the parent compounds with the ester group in the opposite sense, –OOC–, are nonmesogenic.[50,51] Generally, speaking, it can be said that the molecular arrangement in the smectic A phase is also affected by the orientation of the ester linkage.[52] In those cases in which the para-substituent is an n-alkoxy group, the smectic nature is also determined by the relative bulkiness of the n-alkoxy group.[53,54] The effect of linkages such as ester groups has been tentatively explained in terms of the electrostatic dipole–dipole and dipole–induced dipole interactions.[55] However, the smectic properties of nonpolymeric liquid crystals containing two ester groups are strongly affected not only by the electrostatic interactions but also by geometrical arrangements.[47]

Polymers I and II have the same mesogen group and different chain length of the n-alkoxy group. Both present a remarkable propensity toward smectic mesomorphism. They have two ester groups in the side chain with opposite orientations. The intermolecular attraction in the mesophase and its molecular order may compensate each other to yield highly ordered smectic mesophases. The effect has been observed by Schroeder[48] in the case of nonpolymeric liquid crystal such as p-phenylenebis(p-n-alkoxybenzoates) in which the mesogenic moiety is similar to that in our polymers I and II.

However polymer III presents some differences. It differs with respect to polymer I and II in the situation of the second ester group; i.e. they are situated in the same direction. And the n-alkoxy pendant group has been substituted by a hydrogen atom. Polymer II presents a less ordered smectic mesophase. The change of position of the ester link is accompanied not only by a change in the electrostatic pattern but also by the geometrical arrangement of the side chains. This conspicuous change in geometry must affect the smectic nature of the molecular packing of the side chain, as well as the intensity of the smectic field and its stability and the layered thickness. A very simple chemical modification such as the orientation of an ester group in a side chain of a SCLCP may have some type of influence on the dynamics of the chains as a whole.

Polymer IV. Poly{*N*-[10-((4-((4′-(1,1,3,3-tetramethylbutane)phenoxy)carbonyl)phenoxy)carbonyl)-*n*-decyl]maleimide}. The polymer shows only the glass transition T_g = 32 °C. This homopolymer as well as the next one shows no sign of ordered texture nor signs of birefringency when observed by polarizing optical microscopy. The X-ray diffraction diagrams only show a diffuse peak centered at 19 2θ deg (4.67 Å). Above T_g this polymer does not show any significant sign of thermal transition. For this reason it can be considered as an amorphous and noncrystallizing polymer. In this case the tetramethylbutane group acts as a truly antimesomorphic substituent by affecting the nature of the mesogenic character of the oblong moiety. The insertion of bulky alkyl pendant groups such as the tetramethylbutane hinders the formation of a SCLCP even in the cases in which it is attached to a highly ordered phase promoting oblong moiety such as 4-((4′-phenoxycarboxy)phenoxy)carbonyl. This is proof of the role played by the pendant n-alkyl groups in promoting and stabilizing mesophases.

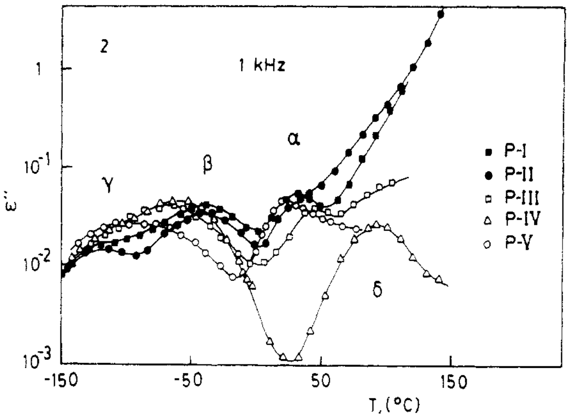

Figure 2. Temperature dependence of dielectric loss at 1 kHz for a series of five poly(N-maleimides). See Figure 1 for key to structural units.

Polymer V. Poly{*N*-[10-(4-(4′-(1,1,3,3-tetramethylbutane)phenoxy)carbonyl)-*n*-decyl)]maleimide}. The thermal properties are T_g = 43 °C. The X-ray patterns of this amorphous polymer V as well as the polymer IV are characterized by a diffuse X-ray scattering diagram in the region of small angles.

Dielectric Experiments. The samples used in the dielectric measurements were molded under light pressure at a temperature 10 to 20 °C higher than the clearing temperature for liquid crystals and then cooled slowly to room temperature. The runs on polymers with a liquid crystalline structure were carried out on nonoriented samples at temperatures lower than that of clearing. A General Radio 1020 A capacitance bridge was used in all the runs.

Results and Discussion

Figure 2 shows the temperature dependence of the imaginary component of the complex dielectric permitivity measured at 1 kHz in the five polymers studied in this work. Four relaxation zones can be distinguished, called hereafter δ, α, β, and γ in decreasing order of temperatures, as shown in Figure 2. This nomenclature has been chosen to be consistent with the literature on dielectric measurements on SCLCPs. A detailed description of the results obtained on each polymer is given as follows. Experimental results are given in Figure 3 (polymer I), Figure 4 (polymer II), Figure 5 (polymer III), Figure 6 (polymer IV), and Figure 7 (polymer V).

γ Relaxations. Two relaxation processes have been ascribed in the literature on SCLCPs to internal motions of the n-alkoxy groups attached to the mesogen as pendant groups[56–58] or to motions of the spacer.[57,58] We call them γ_2 and γ_1, respectively.

Polymer II is the only polymer in this series in which the ϵ'' vs T plot (see Figure 2) shows a maximum in the temperature interval of the γ (−122 °C at 1 kHz). The position of the maxima in the ϵ'' vs f isotherms (Figure 4a) gives a value of 26 kJ/mol for the apparent activation energy (see Figure 4d).

In polymer I the γ relaxation appears as a very flat peak in the lowest temperature isotherms (Figure 3a). In

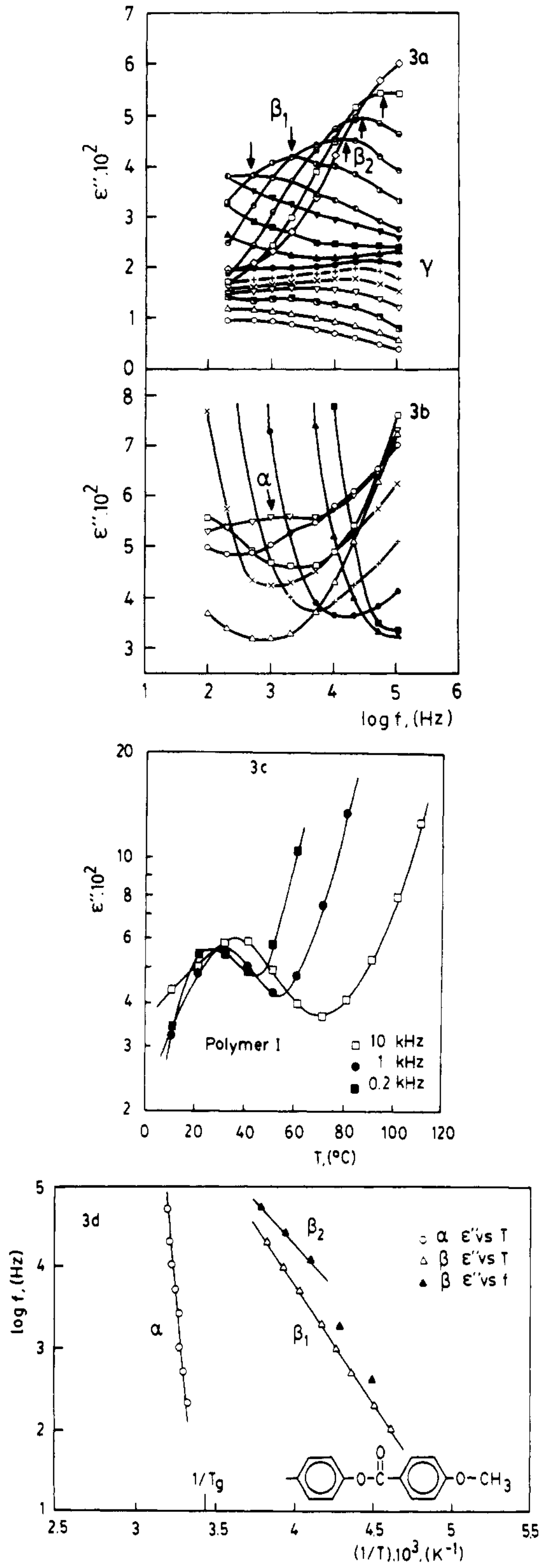

Figure 3. (a) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer I. Temperature range of β and γ relaxations: (○) −151.0 °C; (△) −140.7 °C; (◪) −129.8 °C; (▽) −119.2 °C; (×) −109.2 °C; (+) −99.0 °C; (●) −89.0 °C; (▲) −79.0 °C; (■) −69.2 °C; (▼) −57.7 °C; (◐) −49.6 °C; (◑) −38.7 °C; (◓) −28.4 °C; (◒) −18.5 °C; (□) −8.5 °C; (◇) 1.4 °C. (b) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer I. Temperature range of the α relaxation: (△) 11.0 °C; (□) 21.1 °C; (▽) 31.4 °C; (○) 41.3 °C; (×) 51.5 °C; (+) 61.4 °C; (●) 71.4 °C; (▲) 91.0 °C; (■) 101.3 °C. (c) Temperature dependence of the dielectric loss ϵ'' in the α-relaxation zone: (■) 0.2 kHz; (●) 1 kHz; (□) 10 kHz. (d) Relaxation frequencies of polymer I as a function of reciprocal temperature. In this figure the dielectric constant loss ϵ'' values for the β relaxation from isochronous curves maxima (○) and isothermal curves maxima (●) have been plotted.

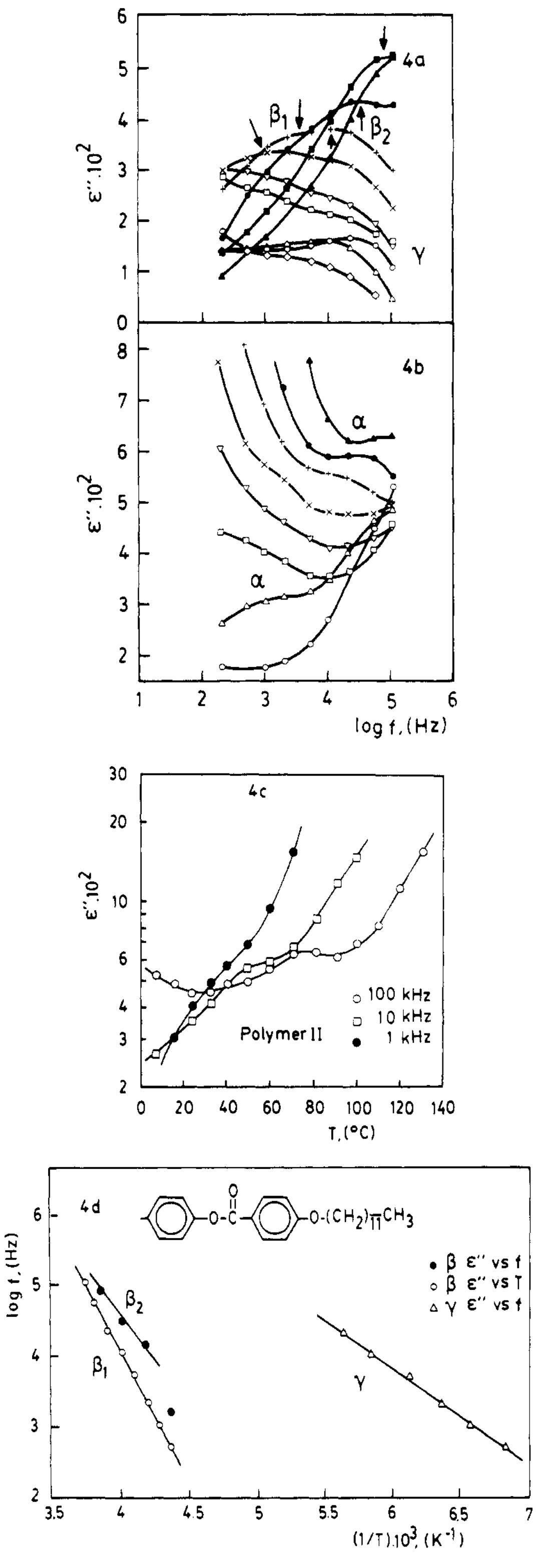

Figure 4. (a) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer II. Temperature range of β and γ relaxations: (◇) −132.7 °C; (△) −113.7 °C; (○) −92.5 °C; (□) −60.2 °C; (▽) −53.5 °C; (×) −44.0 °C; (+) −33.7 °C; (●) −23.6 °C; (■) −11.5 °C; (▲) −2.3 °C. In the γ-relaxation temperature range for clarity only some of the most significative isotherms have been represented. (b) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer II. Temperature range of the α relaxation: (○) 7.0 °C; (△) 10.7 °C; (□) 24.1 °C; (▽) 33.0 °C; (×) 40.0 °C; (+) 49.7 °C; (●) 59.4 °C; (▲) 70.2 °C. (c) Temperature dependence of the dielectric loss ϵ'' in the α-relaxation zone: (●) 1 kHz; (□) 10 kHz; (○) 100 kHz. (d) Relaxation frequencies of polymer II as a function of reciprocal temperature. In the figure the dielectric constant loss ϵ'' values for the α relaxation from isochronous curves maxima (○) and isothermal curve maxima (●) have been plotted.

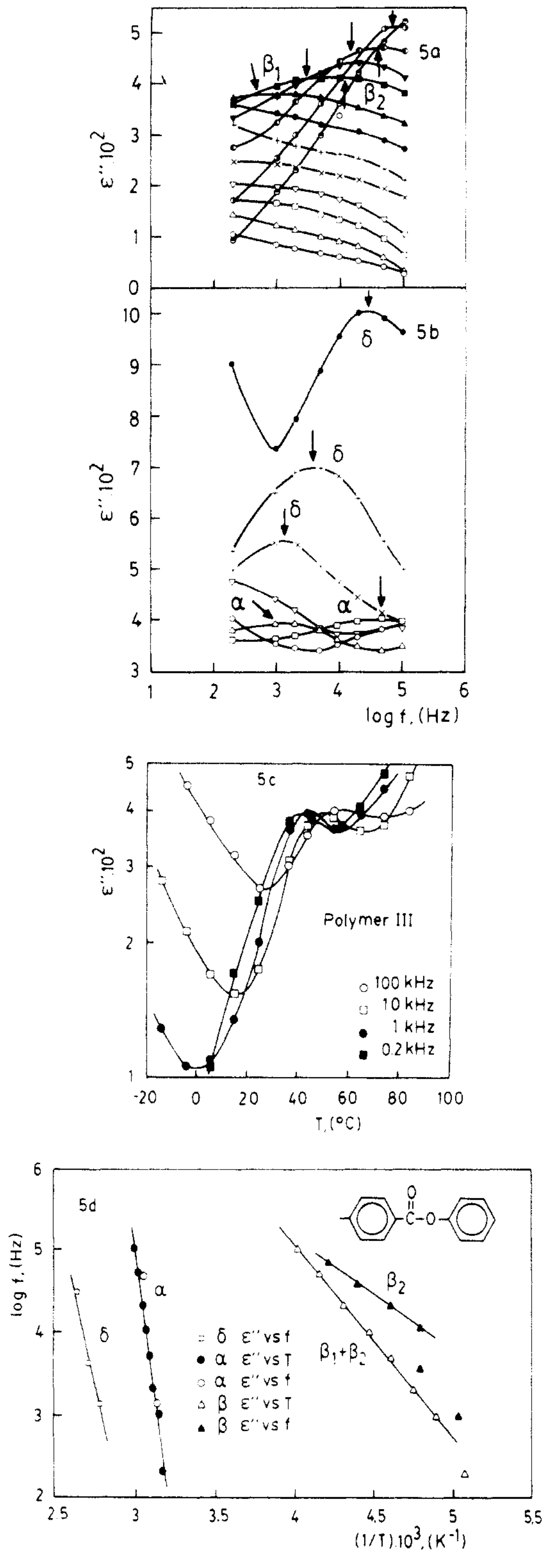

Figure 5. (a) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer III. Temperature range of β and γ relaxations: (○) −151.0 °C; (△) −139.0 °C; (□) −127.0 °C; (▽) −116.0 °C; (×) −106.2 °C; (+) −96.2 °C; (●) −85.0 °C; (▲) −75.3 °C; (■) −64.0 °C; (▼) −56.0 °C; (◐) −46.2 °C; (◑) −36.0 °C; (◒) −26.4 °C. (b) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer III. Temperature range of α and δ relaxations: (△) 44.0 °C; (□) 54.2 °C; (○) 64.7 °C; (▽) 74.5 °C; (×) 84.5 °C; (+) 94.3 °C; (●) 104.4 °C. (c) Temperature dependence of the dielectric loss ϵ'' in the α relaxation zone: (■) 0.2 kHz; (●) 1 kHz; (□) 10 kHz; (○) 100 kHz. (d) Relaxation frequencies of polymer II as a function of reciprocal temperature. In the figure the dielectric constant loss ϵ'' values for the α and β relaxations from isochronous curve maxima (●) and (△), respectively and isothermal curves maxima for the α, β, and γ relaxations, (○), (▲), and (□), respectively, have been plotted.

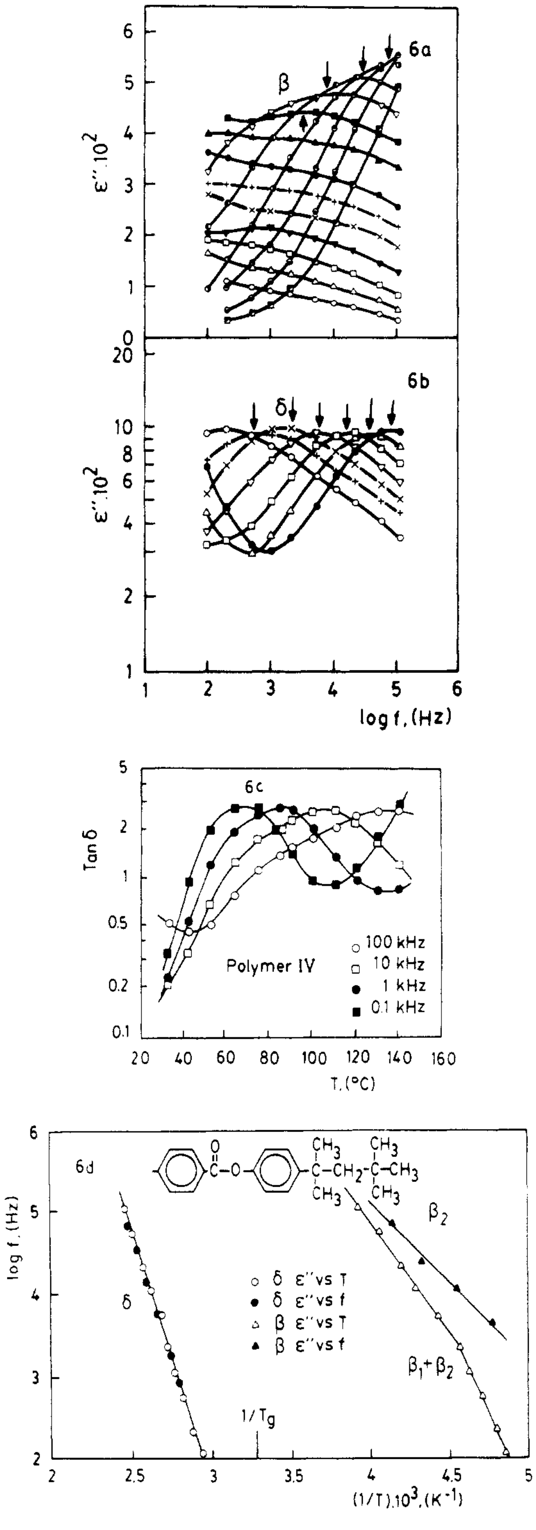

Figure 6. (a) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer IV. Temperature range of β and γ relaxations: (○) −146.3 °C; (△) −134.5 °C; (□) −124.0 °C; (▽) −113.5 °C; (×) −103.5 °C; (+) −93.3 °C; (●) −83.3 °C; (▲) −73.3 °C; (■) −63.0 °C; (▽) −52.7 °C; (◐) −41.8 °C; (◑) −31.3 °C; (◒) −21.6 °C; (⊖) −12.1 °C; (◧) −2.2 °C. (b) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer IV. Temperature range of α and δ relaxations: (○) 75.0 °C; (+) 84.4 °C; (×) 90.4 °C; (▽) 100.4 °C; (□) 110.3 °C; (△) 120.4 °C; (●) 130.3 °C. (c) Temperature dependence of the dielectric loss tangent (tan δ) in the α- and δ-relaxation zone: (■) 0.1 kHz; (●) 1 kHz; (□) 10 kHz; (○) 100 kHz. (d) Relaxation frequencies of polymer IV as a function of reciprocal temperature. In the figure the dielectric constant loss ϵ'' values for the β and δ relaxations from isochronous curves maxima (△) and (○), respectively, and isothermal curves maxima for the same relaxations, (▲) and (●), respectively, have been plotted.

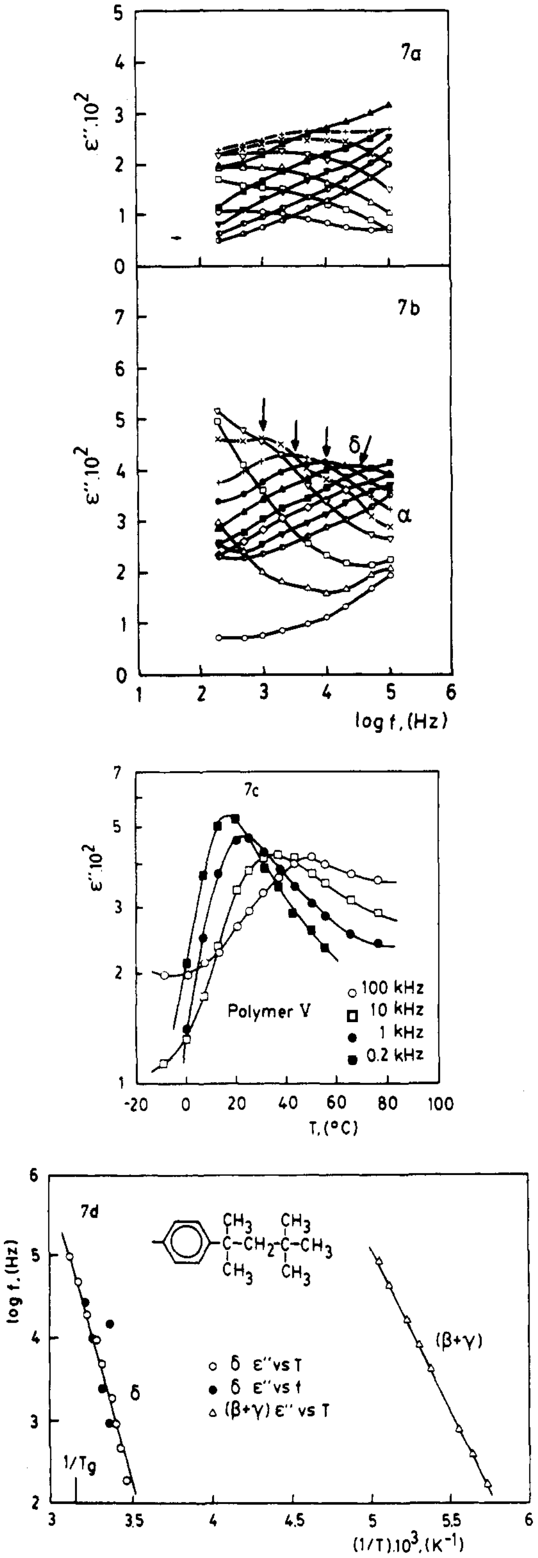

Figure 7. (a) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer V. Temperature range of β and γ relaxations: (○) -151.0 °C; (□) -137.5 °C; (△) -127.5 °C; (▽) -117.5 °C; (×) -107.5 °C; (+) -98.1 °C; (▲) -77.9 °C; (■) -46.5 °C; (▼) -38.6 °C; (◐) -28.1 °C; (◑) -18.6 °C. (b) Frequency dependence of the dielectric loss ϵ'' at various temperatures for polymer V. Temperature range of α and δ relaxations: (○) -9.7 °C; (△) 4.0 °C; (□) 12.9 °C; (▽) 20.2 °C; (×) 24.8 °C; (+) 30.9 °C; (●) 36.9 °C; (▲) 43.0 °C; (■) 50.1 °C; (◇) 55.5 °C; (▼) 65.5 °C; (◐) 76.1 °C. (c) Temperature dependence of the dielectric loss ϵ'' in the α- and δ-relaxation zone: (■) 0.2 kHz; (●) 1 kHz; (□) 10 kHz; (○) 100 kHz. (d) Relaxation frequencies of polymer V as a function of reciprocal temperature. In the figure the dielectric constant loss ϵ'' values for the δ and ($\beta + \gamma$) relaxation from the isochronous curves maxima (○) and (×), respectively, and a relaxation appearing in the α and δ range from isothermal curves maxima (●), have been plotted.

polymers III and IV the shape of the ϵ'' vs T curve at temperatures below the β maximum indicates the presence of the γ relaxation hidden by the low temperature side of the β relaxation due to the greater proximity between both relaxations. It is very difficult to determine accurately the position of the maxima and, consequently, no value of the apparent activation energy can be given for these relaxations. It was very difficult to separate the β and γ processes, although it is very clear from the trend that more than one process may be present.

In polymer V the ϵ'' plot (Figure 7a) does not allow a separation of the γ and the β relaxation zones. In the ϵ'' vs T plot a maximum appears below -100 °C, in the range of temperatures of the γ relaxation of polymers I and II, and a shoulder around -80 to 50 °C in the zone of the β relaxation of polymers III and IV.

The structure of the spacer in this series of poly(N-maleimides) differs from those of SCLCP previously studied with dielectric spectroscopy because of the chemical structure of the linking group >N– in the 2,5-dioxopyrrolidone-3,4-diyl residue of the backbone as well as the ester group –CO–O–, which links the spacer to the mesogen. In the majority of the SCLCPs studied by dielectric spectroscopy, the spacer and mesogen are linked together by an ether group –O– which is very flexible, more so than an ester group. In addition the ester group does not introduce any longitudinal distorsion in space.

In the series of polymers in this work the γ_2 relaxation is not possible in polymers I and III as they do not have any pendant group. They contain, like all the polymers of this series, a n-alkyl sequence of ten carbon atoms with two polar groups at both ends as spacer. The motion of this molecular structure leads to the appearance of this γ-relaxation process. This enables us to assign the process unambiguously to motions of the methylenic sequence which links the mesogen to the main chain.

Polymers IV and V containing a tetramethylbutane group as pendant group in the oblong part do not exhibit any special feature of relaxation behavior caused by the presence of the alkyl substituent. This side-chain substituent is nonpolar; hence motions due to it cannot be a source of dielectric losses. The shoulder appearing in the low temperature side of the β relaxation in Figure 2 in polymers I, III, IV, and V, can be assigned to motions in the spacer, i.e. to the γ process. Only in polymer II does there appear to be a γ peak as a maximum. This can be assigned to the overlapping of both γ_1 and γ_2 processes in this polymer.

β Relaxations. The β relaxation zone consists of two overlapping peaks called β_1 and β_2 in increasing order of frequencies at a given temperature. In polymer I, this is quite apparent in the -38.7 and -28.4 °C isotherms and also in the fact that the position of the maxima of the isotherms -8.5 °C, -18.5 °C, and -28.4 °C fit to different lines in the Arrhenius diagram than those corresponding to -38.7 °C and -49.6 °C (Figure 3d). In the former, the β_2 component is more prominent but at the lowest temperatures the predominant component is the β_1 as in the isochronous ϵ'' vs T curves. The 1 Hz ϵ'' vs T is included in Figure 2, the curves corresponding to other frequencies are not included but the position of the maxima is shown in Figure 3c. The slope of the log f vs $1/T$ diagram determined from the position of the maxima of these curves is closer to the one corresponding to the β_1 component. The apparent activation energies for the β_1 and β_2 relaxations are 59 and 40 kJ/mol, respectively (see Figure 3d).

In polymer II two components β_1 and β_2 can be ϵ'' resolved in the plot of ϵ'' vs f (Figure 4a) and also in the

Arrhenius diagram (Figure 4d), with apparent activation energies of 65 and 40 kJ/mol, respectively, the former calculated from the ϵ'' vs T maxima because only one isotherm shows the β_1 maximum (see Figure 4c).

The β relaxation of polymer III is located at lower temperatures than in the two previous polymers (Figure 2). The three polymers, I, II, and III, with two polar ester groups present in the side chain, differ in the relative position of their two ester groups. The small shift to lower temperatures in polymer III as compared with polymers I and II is thus caused not only by the position of the ester group but also by the more simple structure of the entire mesogenic group in part due to the absence of an *n*-alkoxy pendant group. The two components β_1 and β_2 are clear in the Arrhenius diagram (Figure 5d) but they overlap more in the ϵ'' vs f curves of Figure 5a. The apparent activation energies for the β_1 and β_2 relaxations are 43 and 24 kJ/mol, respectively. For polymer IV the shape of the ϵ'' vs f isotherms at −52.7 and −41.8 °C (Figure 6a) seems to indicate the presence of the two components of the β relaxation, but they are very overlapped. In fact, the log f vs $1/T$ curve (Figure 6d) determined from the maxima of the isochronous plot is slightly curved and these maxima cannot be ascribed to either of the two components β_1 or β_2. The apparent activation energy of the β_2 component calculated from the maxima of the ϵ'' vs f curves is 35 kJ/mol.

The intensity of the β relaxation zone in polymer V is smaller than in the rest of the polymers studied in this work. The results obtained do not allow a separation of the γ and the β relaxations.

The oblong part of the side chain of four of the five polymers of the series studied in this work can be considered, when dealing with dielectric tests, as a rigid rodlike unit with a permanent dipolar moment with a component $\mu_\|$ in the direction of the long axis and another component $\mu_\perp$ perpendicular to it. The rigid rodlike character lies in the impossibility of orienting the $\mu_\|$ component by means of rotations around the carbon–carbon single bonds inside the unit. The $\mu_\perp$ component nevertheless may change its orientation not only by the rotation of the whole unit as a rigid solid but also by torsional oscillations around certain bonds, such as those in which phenylene residues are linked directly by ester groups. They are a class of polymers having unusual configurational characteristics[59–61] as well as torsional potentials.[62,63]

The molecular mobility in mesogens with a single ester group as interconnecting functional group is determined by the torsional oscillation motion. The introduction of a second ester group as linking bridge between the mesogen and the spacer yields to a spacer rotational motion which leads to the appearance of a second relaxation process. These two processes are observed in the same temperature range.

At temperatures above the interval in which the γ_2 relaxation takes place, one has to accept that certain types of motions such as the Reneker effect,[64] the Pechhold "kink block" movement,[65] the crankshaft motion of Schatzki[66] and Boyer,[67] or the "flip-flop" motion of Boyd and Breitling[68] between the bonds among the methylenic units and interconnecting groups of the spacer can take place easily. This makes possible certain shifts and rotations of the rodlike units requiring only the rearrangement of the spacer. This is probably the case for the motions needed to orientate the $\mu_\perp$ component of the permanent dipolar moment, but the rotation needed to change the orientation of the $\mu_\|$ component is a large scale motion which probably requires certain flexibility of the main chain as well. From this point of view, we can formulate the hypothesis that in the temperature interval between the γ relaxation and the glass transition, the oblong moieties acquire, in the β relaxation, enough mobility to be able to orient the $\mu_\perp$ component in the direction of the applied field. A number of experimental works on SCLCPs or in polymers with mesogens, both in the side and in the main chain, support this idea.[5,56,57,69–71]

A comparative study of the β relaxation of the five polymers in this work may help to define the characteristics of this relaxation process. The value of the component $\mu_\|$ in polymers I and II should be larger than in polymers III and IV because of the presence of the *n*-alkoxy group at the end of the rodlike unit. The $\mu_\perp$ component should, nevertheless, be similar in the four polymers. Our experimental results show that the height of the β peak is very similar in the four polymers (Figure 1). This supports the hypothesis that the $\mu_\|$ component is not oriented in the motion responsible for the β relaxation. However, polymer V has only one carboxylic group in the oblong moiety and thus the $\mu_\perp$ component of the dipolar moment is smaller than in the rest of the polymers in this series. The height of the β relaxation in this polymer is much lower, confirming our hypothesis.

The experimental data of the literature on SCLCPs with mesogens similar to that of our series but linked to the spacer by means of an ether group do not show the presence of the two subrelaxations β_1 and β_2 but a single β relaxation process with an apparent activation energy of 50–58 kJ/mol,[56,57,71] a value close to the one found for the rotation of the phenyl group of the mesogen as determined using NMR techniques.[69,72,73] The possibility of internal reorientations through the links between the ester groups and the phenylene, together with rotational diffusion of the mesogens as a whole may lead to a multiple relaxation process in our polymers. The β_2 process with lower relaxation times must correspond to a reorientation of the ester group which joints the mesogen to the spacer which is not present in the polymers studied in the above mentioned references.

The dipole–dipole correlation within the smectic layers of the liquid crystal polymers is greater than that for amorphous polymers. The increase in intensity of the relaxation with temperature has been attributed to the antiparallel orientation of the dipoles in liquid crystals of low molecular weight[74] and also in the relaxation which here we have called δ (attributed to the orientation of the $\mu_\|$ component) in liquid crystal polymers with side chains.[74–78] The effect on the β relaxation is analogous as shown in Figure 8, where the dielectric increment of the relaxation process $\Delta\epsilon = (\epsilon_0 - \epsilon_\alpha)$ has been plotted versus T. This magnitude is connected with the intensity and the interaction of the molecular dipole moment, the relaxation frequency, and the activation energy for the relaxation process.[79] The intensity of the β relaxation in polymers IV and V, both amorphous materials, is practically constant with temperature and considerably lower in the latter due to the lesser dipolar moment $\mu_\perp$. However, in polymers I and II, with a highly ordered smectic phase, the relaxation increases considerably with the temperature. In polymer III the behavior is similar to that of the previous polymers, although the intensity of the relaxation is less dependent on temperature at low temperatures in agreement with a lesser ordered smectic phase. As the γ_2 relaxation cannot be clearly separated from the β_2, the intensity of the joint relaxation (γ_2 + β_2) has been represented for all the polymers, calculated from the Cole–

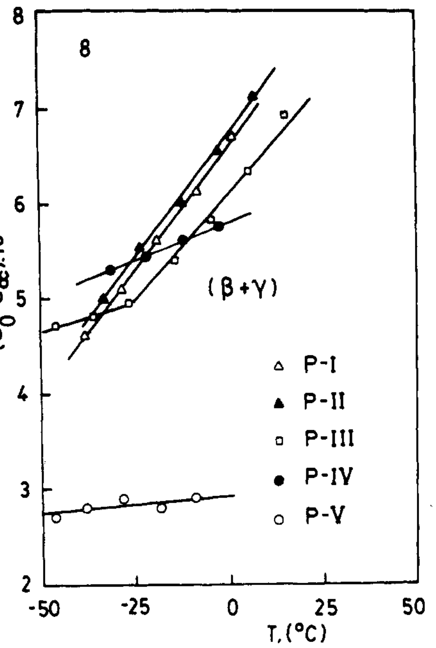

Figure 8. Temperature dependence of relaxation strength ($\epsilon_0 - \epsilon_\infty$), also known as the dielectric increment of the relaxation process. Here, ϵ_0 means the static dielectric constant and ϵ_∞ is the dielectric constant at frequencies above the relaxation, i.e. at low and high frequency limits, respectively. The intensity for the ($\beta + \gamma$) relaxation has been estimated from the Cole–Cole plots at different temperatures for the five poly(*N*-maleimides). The value used for ϵ_0 clearly corresponds in all cases to the β relaxation. However to calculate ϵ_∞, it has not been possible, in several polymers to separate the γ relaxation. For this reason, the values quoted in the figure represent greatly the overlapping of both relaxations. It is worthwhile to make mention, that the intensity of the γ relaxation is always lower than that of the β relaxation. (See Figure 1 for key to structural units.)

Cole arcs. It must be noted that in polymer II, where both relaxations can be separated, the intensity of the γ_1 relaxation is of the order of 20% of the β_2. The overlap of the γ_2 relaxation, therefore, should not alter the above reasoning.

The β relaxation appears at higher temperatures and with greater apparent activation energy in polymers I and II than in the other polymers. This may be attributed to the existence of the smectic field which imposes an additional barrier to the rotational movements of the mesogens.

α and δ Relaxations. At temperatures higher than the calorimetric T_g, two dielectric relaxations α and δ occur in SCLCP, which according to many authors may be attributed to motions of the main chains and to motions of the mesogenic groups in the side chain. When the spacer is short enough, these two types of motions are coupled together giving rise to a single relaxation process.

In polymer I, the α relaxation appears as a clear maximum in the ϵ'' vs T (Figure 3c). Only one isotherm ϵ'' vs f, the one at 31.9 °C, shows (Figure 3b) the α peak because the peak shifts rapidly in the frequency axis as the temperature rises. It corresponds to a very steep slope in the Arrhenius diagram. This a plot is represented in Figure 3d using the position of the α maxima of the isochronous curves. No significant curvature of this line is detectd in the experimental range of frequencies, as is to be expected from Williams–Landel–Ferry behavior, nevertheless the slope of this line would give an apparent activation energy of 320 kJ/mol, which is too high for a secondary relaxation. This means that the process is cooperative, since the activation energy is rather high. At temperatures above the α relaxation, a continuous increase of the ϵ'' value is observed without any sign of the δ relaxation below the smectic isotropic transition.

In polymer II, the α relaxation appears but only just as a shoulder in parts b and c of Figure 4 and the δ relaxation has not been detected.

In polymer III, the α relaxation appears in the ϵ'' vs T curves (Figure 5c) as a maximum which shifts slightly when the frequency changes, as corresponds to a relaxation process with a very high apparent activation energy, 290 kJ/mol (Figure 5d); consequently the peak can only be detected in two isotherms: 44.0 and 52.0 °C (Figure 5b). The frequency of the maxima in these two isotherms agrees well with that of the isochronous curves (Figure 5d).

At higher temperatures, the δ relaxation can be observed in ϵ'' vs f diagrams. Its activation energy is 160 kJ/mol. The height of the maximum increases rapidly with temperature, probably this relaxation overlaps with the component of ϵ'' due to dc conductivity. The values of ϵ'' in this range of temperatures are lower than in polymers I and II.

In the range of temperatures between 30 and 130 °C the α and δ relaxations appear (Figure 6b). Figure 6c shows for polymer IV the isochronous tan δ vs T plot (this representation has been chosen because it is clearer than the ϵ'' plot) in the same range of temperatures. At 0.1 kHz only one peak appears but two overlapped relaxation processes can be observed as the temperature increases; they have been ascribed to the α and the δ relaxations. The first of them appears as a shoulder of the δ relaxation and shifts from around 60 °C at 0.1 kHz to around 80 °C at 100 kHz. This allows the activation energy of the α relaxation to be estimated as roughly 300 kJ/mol, a value in the same order of magnitude as that of polymers I and II. The δ relaxation predominates over the α and its position in the ϵ'' vs f curves gives a value of 120 kJ/mol for its apparent activation energy. The intensity of the β relaxation in polymer V is smaller than in the rest of the polymers studied in this work. In the temperature interval between −10 and 80 °C, only one peak appears in polymer V in the ϵ'' vs T curves (Figure 7c). The peak broadens as the frequency increases. A behavior quite similar to the one shown in Figure 6c for polymer IV. The position of the maxima (Figure 7d) agrees quite well with that of the maxima in ϵ'' vs f curves, its activation energy is 130 kJ/mol. This peak is ascribed to the δ relaxation; the α one could only be detected as a shoulder in the 24.8 °C isotherm (Figure 7b).

The glass transition is a kinetic process characteristic of the glassy state, i.e. of the existence of states outside thermodynamic equilibrium at low temperatures. It is more a characteristic of the cooperative movement of the molecular groups of the amorphous material than of the structure of the polymer chain as is obvious from the existence of glass transitions in nonpolymeric materials. In SCLCPs, the glass transition should probably be seen as a phenomenon which affects the materials as a whole, i.e. mesogens and main chains. However, this question at present may be open to discussion.

Indeed in the literature there are similar values of T_g for SCLCPs with the same spacer and analogous mesogens and ether linking bridge but with main chains of very different rigidity, acrylate, methacrylate, and siloxane,[3,57,80] which shows the influence of the mesogen and the structure of the liquid crystalline phase on the glass transition process. The spacer length may have a decisive influence.

It is important to mention that the apparent activation energy of the δ relaxation is lower than that of α, in spite of the fact it occurs at a higher temperature. This means that both relaxations tend to overlap as frequency diminishes. A similar result has been found in other SCLCPs[56,57,71,81] in which the α and δ relaxations show a temperature dependence of the frequency of the maxima following the Williams–Landel–Ferry equation[56,81] or the Arrhenius one.[71] In other references the merging of the α and δ relaxations at low frequencies is not clear.[56,80] In TSDC a unique relaxation peak is found at a temperature close to T_g, perhaps attributable to movements of the mesogens coupled to those of the main chain.[1-3] It could therefore be considered that the glass transition of the material is a process which involves to a greater or lesser extent all the material. It separates ranges of temperature in which the mobility of both the mesogens and the main chain is low or high, respectively. At temperatures higher than T_g, the movements of both groups are possible and are decoupled to a great extent in the polymers in this work due to the length of the spacer, giving rise to differentiated relaxations. In polymers with shorter spacers, a single relaxation is observed with or without WLF behavior and the movements of the main chain take the mesogens with them and vice versa. In our polymers the T_gs measured by DSC are lower than expected for poly(*N*-maleimides) with side-chain crystalline or amorphous structures. In fact they are not far from the values found in SCLCPs with smaller rigidity in the main chain. It seems that the glass transition temperature depends on the chemical structure of the spacer and oblong moiety even more than on the one of the main chain. Polymers I, II, and III with liquid crystalline structure present a glass transition temperature close to the amorphous polymers IV and V.

The dielectric relaxation α is found in the range of temperatures at which glass transition occurs. In the polymers where it has been possible to separate clearly this relaxation, there is no appreciable curvature in the Arrhenius diagram, possibly due to the narrow band of frequencies available. However the high apparent activation energy deduced from it makes it possible to associate this relaxation with cooperative movements of the main chains in the polymer. It would not be possible to justify values of the apparent activation energy of the order of 300 kJ/mol in rotational movements of the mesogens. Indeed, the δ relaxation, generally attributed, as we shall see below, to movements of the mesogen (even with displacements in its centre of gravity) presents much lower values of apparent activation energy.

In polymers with a siloxane main chain, Attard and Williams[80] found two relaxations, δ and α, in the range of temperatures immediately above T_g, with a similar slope in the diagram log f vs $1/T$ and with a clear dependence of its intensity on the alignment of the mesogens. This together with the low polarity of the main chain of the polymer led them to attribute both relaxations to different movements of the mesogens.[80,82] This would not seem to be the case for the polymers in this work.

The mechanism which leads to the orientation of the $\mu_\parallel$ component of the dipolar moment of the mesogen in liquid crystals of low molecular weight seems to consist of the rotation of the group around its short axis without displacement in the center of gravity. The δ relaxation in SCLCPs is attributed to the orientation of the $\mu_\parallel$ component of the permanent dipolar moment by movement of the mesogen. The fact that this is joined to the spacer chain causes a displacement of the center of gravity of the mesogen to happen at the same time. A rotation of 180° in $\mu_\parallel$ could occur when the spacer is shorter and the polymer is in the nematic phase,[57] but probably the movements are more restricted in the smectic phase. Vallerien et al.[56] have found that for some of their polymers the δ process has a small relaxational strength. A decrease of the height in this dielectric absorption can be explained by an enhanced dipole–dipole interaction according to the calculation made by de Jeu et al.[76,83] The same effect has been found by Kresse et al.[84] in the case of nonpolymeric liquid crystals which present highly ordered smectic mesophases.

The width of the δ peak in polymers III, IV, and V is greater than the one found in other SCLCPs in which the δ relaxation width can be characterized by means of a Cole–Cole parameter ranging between 0 and 0.3.[57,75,85-87] It is not surprising to find a broader relaxation peak in an amorphous polymer as polyver IV or V than in a nematic SCLCP. The intensity of the relaxation is nearly independent of temperature in polymers IV and V but increases rapidly in polymer III, a fact that can be attributed to the dipole–dipole correlation within the smectic layers as explained above for the β relaxation.

However Parneix et al.[88] have given a quite different explanation. They argue that the δ relaxation is much smaller in amplitude for a polymer with an alkoxy terminal group than, for instance, one with a strong polar cyano terminal group due to the small value of the longitudinal components ($\mu_\parallel$) of the dipole moment. This explanation can be ruled out, since in the present series, polymer III, with no polar terminal group displays this relaxation process.

Our interpretation on these last two processes is only partially in agreement with similar observations made by Attard et al.[80-82,89-92] on some other SCLCPs on one hand and in complete agreement with Kresse et al.[84] and Jeu et al.[76,83] on the other.

In our liquid crystal polymers the δ relaxation only appears in polymer III. In addition to the influence of the smectic field on the appearance of this transition in polymers I and II, the presence of the *n*-alkoxy chain on the pendant group of the mesogen also increases the dc conductivity of the material and consequently ϵ'' increases rapidly at high temperatures, hiding a possible dipolar relaxation process which may occur within this range of temperature.

In the two amorphous polymers, IV and V, the δ relaxation has a greater intensity than the α-relaxation and an apparent activation energy similar to those found in SCLCPs in isotropic phase,[74,85-87,93] while in polymer III, it is slightly greater due to the structure of the smectic phase and also similar to those found for SCLCPs with long lengths of spacer in nematic or smectic phases.[71,82,85-87,93]

Concluding Remarks

The relaxational movements observed by dielectric spectroscopy of a series of five poly(*N*-maleimides) are schematically indicated for polymers II and III in Figure 9. We have named the relaxation processes following the nomenclature of Zentel et al.[57,94]

At temperatures high enough, above the calorimetric glass transition, the motions of the main chain in the five polymers studied and the motions of the side chain are able to reorient the parallel component of the permanent dipolar moment of the oblong part of the side chain. Thus in polymers III, IV, and V they are allowed. As the temperature decreases, it is possible to detect at high frequencies that the side chains lose their mobility (what produces the δ relaxation in polymers III, IV, and V). So the motions of main chain and side chains are partially

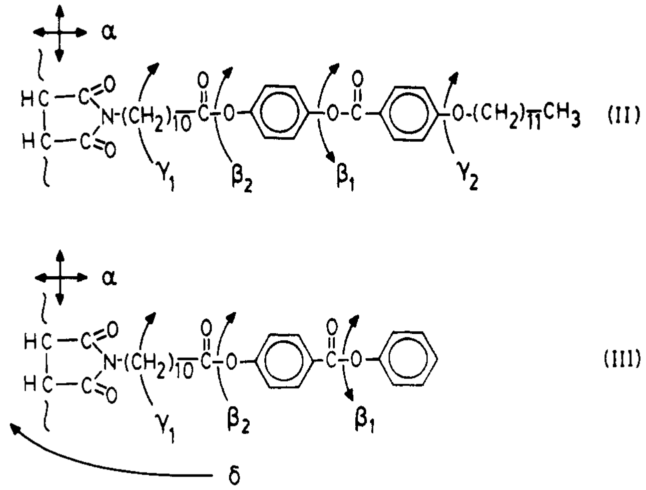

Figure 9. Scheme of the liquid crystalline side groups for polymers II and III and the relaxation motions which were observed for these two polymers in the measurements. They are indicated by arrows.

decoupled due to the length of the spacer. The temperature of the δ and α maxima tends to approach as the frequency decreases, merging both relaxations at a temperature close to the calorimetric T_g.

At temperatures below the calorimetric glass transition, rotational motions of the mesogens (or the oblong part of the side chain in amorphous polymers) and motions of the methylene groups in the spacer and pendant groups of the side chain are still allowed. As the temperature decreases, these groups lose their mobility producing the relaxations β_1 and β_2 (oblong moiety) and γ_1 and γ_2 (methylene groups).

Finally, we should like to make mention that our present results are in agreement with those found and assigned by Kremer et al.[5] in a series of combined main-chain side-group liquid-crystalline polymers on unaligned samples.

There is a series of factors such as mesomorphicity, correlated motions of dipoles from neighboring side chains in antiparallel or parallel configurations, etc., which may affect the appearance or disappearance of certain relaxations as well as their intensity, situation, and activation energies.

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References and Notes

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Registry No. I (homopolymer), 144668-94-0; II (homopolymer), 144668-96-2; III (homopolymer), 144668-98-4; IV (homopolymer), 144668-99-5; V (homopolymer), 144669-01-2.