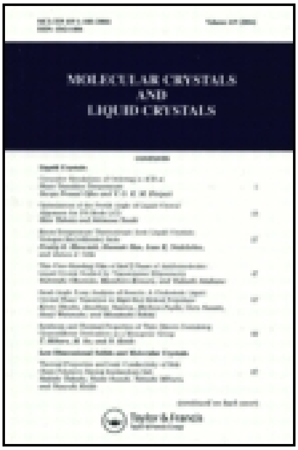

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Synthesis and Characterization of Novel Side-Chain Liquid Crystalline Polycarbonates, 3. Dynamic Mechanical Analysis of the Secondary Relaxation Processes

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SYNTHESIS AND CHARACTERIZATION OF NOVEL SIDE-CHAIN LIQUID CRYSTALLINE POLYCARBONATES, 3[a]. DYNAMIC MECHANICAL ANALYSIS OF THE SECONDARY RELAXATION PROCESSES.

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Abstract The dynamic mechanical properties of two homologous series of side-chain liquid crystalline polycarbonates were studied. One series with oxynitrostilbene mesogenic groups and alkyl spacers of different lengths and another series with phenyl benzoate mesogenic groups with alkoxy tails of different lengths. The influence of spacer length and tail length on the low temperature relaxation processes was investigated. For the polymer with an undecyl spacer also the influence of side group crystallinity on the secondary relaxations was analyzed. A γ-relaxation could be ascribed to motions of either the spacer or the alkoxy tail. Three different β-relaxations could be ascribed to the carbonate groups in the backbone and to the mesogenic groups in the frozen liquid crystalline state and in the crystalline state, respectively. The α-relaxation, corresponding to the glass transition, showed a strong shift to lower temperatures with increasing spacer length but was hardly influenced by the tail length.

INTRODUCTION

Side-chain liquid crystalline polymers (SC-LCPs) form a relatively new class of polymeric materials. By their unique combination of liquid crystalline and polymeric properties they are particularly interesting for sophisticated electro-optical applications[1]. They offer clear advantages over conventional liquid crystals in for example processability, dimensional stability and mechanical flexibility of devices. An almost unlimited flexibility of structural design has led to the synthesis of hundreds of different side-chain LCPs with different backbones, mesogenic groups, spacers and tails. In our previous publications we described the first synthesis of side-chain LCPs with a polycarbonate backbone[2,3].

Traditionally the characterization of SC-LCP properties has been focused on differential scanning calorimetry (DSC) for detection of the phase transitions and on

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[a] Part 2 of this series has previously been published as ref. 3.

polarized light optical microscopy (PLOM) and X-ray diffraction for identification of the liquid crystal phase structures. With applications in the field of optical data storage, piezo-electricity, holographic imaging and nonlinear optics coming closer to practical implementation, more fundamental knowledge was necessary about the dynamic behaviour and processability of SC-LCPs. Thus also other analytical techniques came into use: dielectric relaxation spectroscopy (DRS)[4,5] and nuclear magnetic resonance (NMR)[6,7], giving useful information about *e.g.* the side group dynamics for applications where switching of these groups plays a role, and rheology[*e.g.* 8-11], important for anticipating and possibly controlling the flow behaviour during LCP processing and preparation of devices.

Dynamic mechanical analysis (DMA), widely used in polymer research, has only scarcely been used in studying the properties of SC-LCPs. This is mainly due to the fact that the operating range of DMA is usually limited to the sub- and near-T_g (or T_m) range. Since the interesting phase transitions in SC-LCPs usually lie far above their T_g, DMA is not frequently used for studying the properties of side-chain LCPs, in contrast to rheological analysis which is carried out in the liquid crystalline and isotropic phase. However, several relaxation processes can take place between about -150°C and the glass transition or melting point. DMA therefore, especially in combination with dielectric relaxation spectroscopy, can significantly contribute to the understanding of the low-temperature dynamics of side-chain LCPs. Only recently two papers on mechanical spectroscopy of side-chain LCPs were published: on SC-LC polysiloxanes near the glass transition[12] and on SC-LC polyacrylates from low temperatures up to the clearing point[13]. Mulligan and coworkers[14,15] reported the dynamic mechanical thermal analysis of SC-LC polymethacrylates from below the T_g up to the clearing point[b)]. The dielectric and dynamic mechanical analysis of a side-chain LC polysiloxane by Simon and coworkers[16] was mainly focused on the near-T_g temperature range.

An advantage of DMA for studying segmental mobility is that it measures the mobility of polar as well as non-polar groups or chain segments, whereas for instance dielectric spectroscopy requires the presence of polar moieties. Mulligan *et al.*[14], referring to measurements in the LC phase, mention the high sensitivity towards changes in the physical state of the polymer as another advantage, enabling the detection of phase transitions which are difficult to detect with other techniques, for example smectic-smectic transitions.

The present paper describes the dynamic mechanical analysis of two series of side-chain LC polycarbonates, displayed in Figure 1. In this paper in particular, as a part of our investigations on the dynamic behaviour of SC-LC polycarbonates by a parallel study of dynamic mechanical analysis, dielectric relaxation spectroscopy and

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[b)] Distinction between DMA and rheological analysis is not always clearly made, especially not in the case of rheological measurements in the dynamic mode. In the present work we use the terms DMA for sub- and near-T_g (or T_m) measurements, where material flow is impossible, and rheology for super-T_g (or T_m) measurements, where in principle flow is possible.

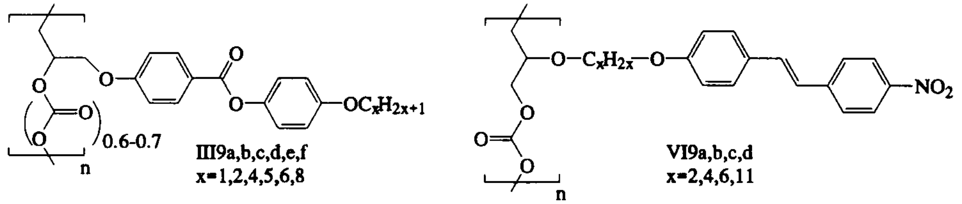

Figure 1. Structure of the two series of side-chain liquid crystalline polycarbonates studied in the present paper.

rheology[17], we will study the secondary or sub-T_g relaxations by DMA. By systematically changing the chemical structure (spacer length, tail length) and the physical state of the polymer (frozen LC/crystalline) we will try to identify all the different relaxation peaks and assign them to specific motions of the polymer backbone and side groups in the glassy state.

EXPERIMENTAL PART

The polycarbonates studied in this paper and displayed in Figure 1 were prepared by copolymerization of mesogenic epoxides with carbon dioxide (polymers **III9a-f**, with alkoxy tails of different lengths)[17,18] or by polycondensation of mesogenic diols with diphosgene (polymers **VI9a-d**, with alkyl spacers of different lengths)[3]. For details on synthesis, characterization and phase behaviour is referred to the original papers.

Samples, free of air inclusions and inhomogeneities were made from the powdered polymers by pressing tablets in a specially designed press, operating under vacuum at elevated temperatures well above the T_g of the polymers. The tablet was then melted in a rectangular mould above the clearing point (polymers **VI9a-d**, **III9a**) or well above the T_g (polymers **III9c,f**) and cooled to room temperature. The dimensions of the small rectangular bars of approx. 2x4x20 mm were carefully made uniform with a metal file.

The sub-T_g dynamic mechanical spectra were recorded on a Perkin Elmer DMA 7 Dynamic Mechanical Analyzer; the temperature scale was calibrated with mercury and indium. Small rectangular bars of the polymers were subjected to a sinusoidal deformation at constant frequency, using the three point bending method on a standard 15 mm bending platform. Measurements were carried out at a frequency of 1 Hz and a heating rate of 2 or 5°C/min. The amplitude of the sinusoidal deformation was kept constant (25μm) by adjusting the static and dynamic forces with changing temperature. The static force was set 10% higher then the dynamic force, in order to ensure good contact between sample and probe.

All measurements were done on unaligned samples. The LC polycarbonates have, as far as we know from microscopic observations, no tendency towards spontaneous homeotropic or planar alignment. Also the sample preparation methods did not induce such alignment.

RESULTS AND DISCUSSION

Secondary relaxations of polycarbonates

Irrespective of their structures, the tan δ curves of all side-chain LC polycarbonates show a strong β-relaxation peak in the temperature range typically from -100°C to -50°C (see Figure 3 and Figure 4). This relaxation, rather strong for a secondary transition (tan $\delta_{max} \approx 0.1$), does not only occur in the LCPs but also in some of our model polymers, displayed in Figure 2. For these model polymers the relaxation strength is even higher: tan $\delta_{max} \approx 0.6$. Udipi and Gillham found the same β-relaxation even in poly(ethylene carbonate)[19]. Since in these cases the carbonate group is the only strong dipole it must be held responsible for this β-peak and it must be concluded that the β-relaxation is a backbone relaxation. It is either a relaxation merely of the carbonate group, possibly an oscillatory rotation around the chain axis, or, as suggested by Udipi and Gillham[19], an in-chain motion of short chain segments. This strong glassy state relaxation is characteristic for all types of polycarbonates[20,21]. In aromatic polycarbonates, such as the Bisphenol A polycarbonate, it generally appears between -100°C and -80°C at 1 Hz[21-23].

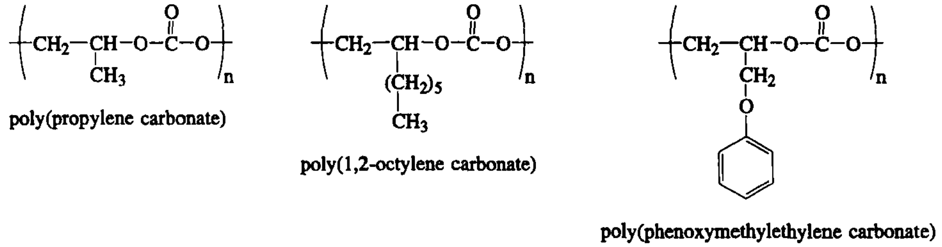

Figure 2. Model polymers used to study the basic dynamic mechanical and dielectric relaxations of polycarbonates with an aliphatic backbone and different side groups.

Spacer length dependence of the secondary relaxations

Figure 3 shows the storage modulus, E′, and the damping factor, tan δ, of polymers **VI9a-d**. The E′ curves show a strong drop at the glass transition temperature and conform the DSC measurements the T_g clearly decreases with increasing spacer length (from 53°C to 21°C). The only apparent exception is polymer **VI9d**, which has a crystalline phase and softens at its melting point.

With increasing spacer length also the absolute value of E′ decreases, even for polymer **VI9d** with a high degree of crystallinity. The fact that polymer **VI9d** does not have a higher modulus enhances the suggestion[3] that only the mesogenic groups crystallize and that the spacers and backbone remain amorphous. Two main factors are responsible for this decrease of E′. Firstly, the decreasing concentration of backbones, determining the elasticity modulus by the chemical bonds along the chain,

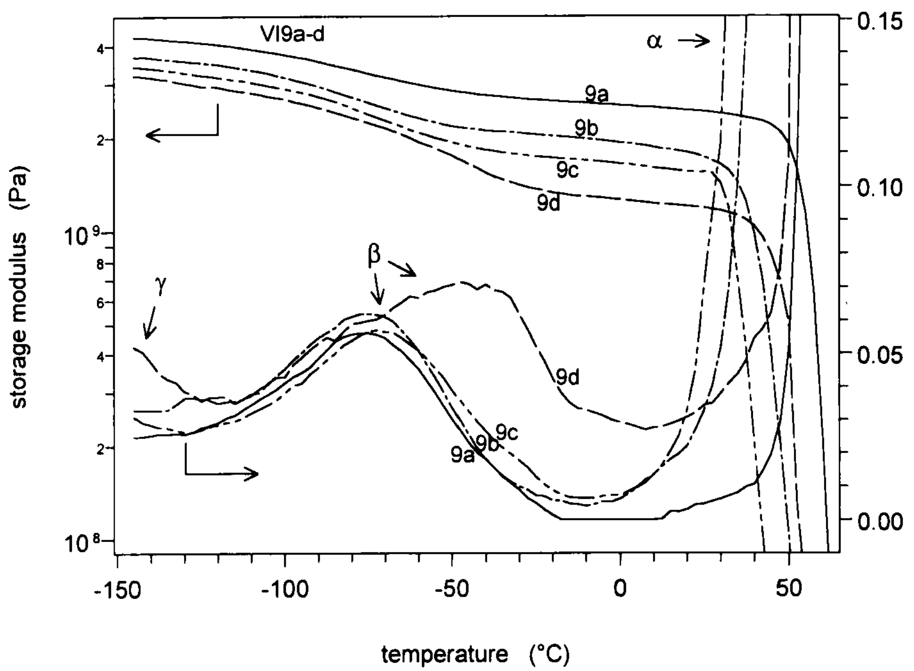

Figure 3. Storage modulus E′ and loss factor tan δ of polymers **VI9a-d** measured by DMA. Heating rate 5°C/min, frequency 1 Hz, three point bending method.

and secondly, the increasing concentration of spacers, decreasing the Van der Waals interactions and the stiffness by their lower polarity and higher flexibility.

More interesting is the β-relaxation. This relaxation, appearing as a small drop in E′ between -100°C and -50°C, can best be observed from the damping peak in Figure 3, which is more illustrative than E′ or E″. In all polymers, including the model polymers, the position, strength and shape of the β-peaks is more or less the same and tan δ shows a clear maximum around -75°C. The only clear exception is polymer **VI9d**, which has a very asymmetric peak, obviously because of the presence of at least two partly overlapping relaxations. Since **VI9d** is the only polymer in this series which is able to crystallize, it was believed that this double peak could be related to crystallinity. This will be further described in the next section.

Another feature is the γ-relaxation, arising at the lower temperature limit of the measurements of polymers **VI9c** and **VI9d** only. This relaxation is clearly related to a motion of the spacer: none of the model polycarbonates without mesogenic side groups and none of the LC polycarbonates with very short spacers show the same relaxation. The γ-relaxation of **VI9d** is more distinct than that of **VI9c**. It is known that a γ-relaxation often occurs in the same temperature range (around -120°C at a frequency of 1 Hz) for polymers with linear $-(CH_2)_n-$ sequences with $n \geq 3$ or 4 in the side chains or the main chain. It is ascribed to a crankshaft motion of the $-(CH_2)_n-$ sequence[24]. The present observation, that the γ-relaxation occurs mainly in those polymers with a long spacer, is in good agreement with this crankshaft model.

Dependence of the secondary relaxations on crystallinity

Figure 4 shows the DMA curves of polymer **VI9d** for different degrees of side-group crystallinity. From the figure it is evident that the deviant behaviour of **VI9d** in comparison with polymers **VI9a-c**, can be ascribed to side-group crystallinity. The quenched sample (a) shows a single relatively sharp β-relaxation at the same position as polymers **VI9a-c** and a weak γ-relaxation. With increasing crystallinity the β-peak becomes broader and in the first instance it seems to shift to higher temperatures. However, looking at the different curves it appears that the β-relaxation peak consists of three separate relaxations with maxima around -100°C, -75°C and -40°C. The peak around -100°C is not very obvious, but its presence follows from the tailing of the β-peak to low temperature. The peaks around -75°C and -40°C clearly follow from the peak maxima around these values. The total relaxation strength of the β-relaxations does not change significantly, so the observed behaviour must either be caused by a shift of one or more peaks to higher temperature or by the formation of a 'new' peak at the expense of an existing one at lower temperature.

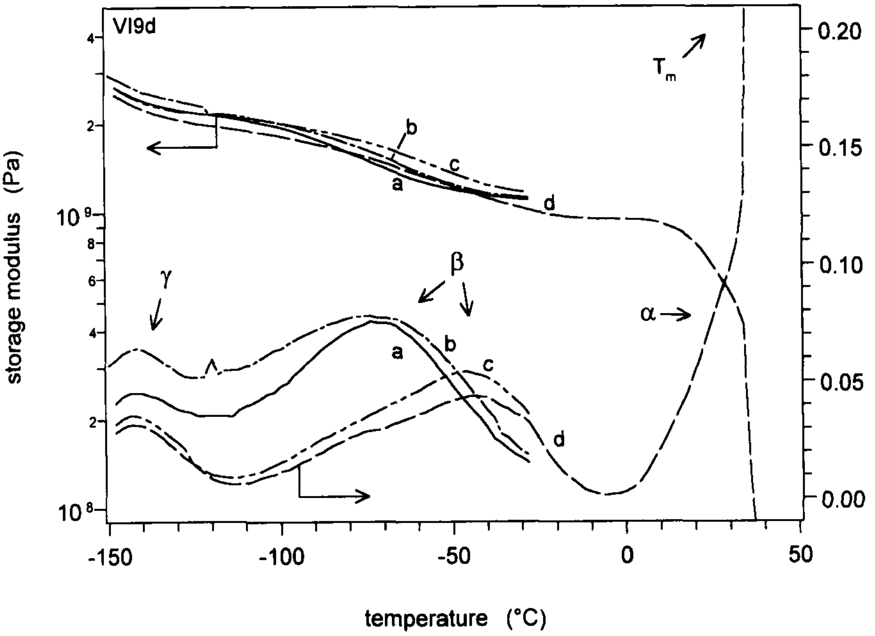

Figure 4. DMA curves of polymer **VI9d** after quenching (a) and crystallization for (cumulative) 1h at 30°C (b), 1h at 40°C (c) and 64h at 50°C (d). Three point bending, 1 Hz, 5°C/min.

In order to understand the origin of this apparent shift in β-relaxations one should realize that from the DSC and X-ray measurements it is known that the mesogenic groups crystallize, while there are no indications of backbone and spacer crystallization[3]. Given the complete phase separation in mesogen layers and backbone and spacer layers, it is not likely that side group crystallization has such a strong effect on the dynamics of the carbonate groups that their signal would shift significantly or that it would split into an 'amorphous' and a 'crystalline' fraction. It is more likely that the carbonate β-relaxation in the main chain (further called β_M-relaxation) of the non-crystallized sample and also of polymers **VI9b-c** overlaps with a certain mesogenic side group relaxation (further called β_S-relaxation). Of the latter relaxation it could indeed be expected that it is strongly affected by the state of order of the mesogens. On crystallization the β_S-relaxation of the frozen liquid crystalline side groups then slowly disappears in favour of a newly formed relaxation of the crystallized side groups, called β_{SC}. Crystallinity limits the translational and rotational mobility of the mesogenic groups and this must certainly be reflected in the relaxation time and strength of the mesogenic group relaxations.

Summarizing the above, we can conclude that the peak around -100°C is the β_M-relaxation of the carbonate group. Indeed, this position of the carbonate relaxation corresponds well with the one found for the model polycarbonates without mesogenic groups. The two relaxations β_S and β_{SC}, which on crystallization seemingly shifted to higher temperatures, correspond to motions of the mesogenic group. Dielectric analysis of the semi-crystalline sample over a wider frequency and temperature range has been used to study more precisely the relation between crystallinity and the sub-T_g relaxations. This will be described in a separate paper[25]. Comparative DMA studies on an amorphous and crystalline side-chain LC polymethacrylate have been reported by Laus *et al.*[13]. Unfortunately, they were only interested in the glass transition and melting process and they did not study the influence of crystallinity on the secondary relaxations.

Simultaneous with the apparent shift in the β-relaxations the γ-relaxation changes as a result of crystallization. If just the peak height[17] of the tan δ curves is taken as a measure of the relaxation strength (or simply relaxation), then the γ-relaxation first increases and then decreases with increasing crystallinity. There is no shift in the peak position. Such behaviour could be explained by the liberation of some extra free volume for the spacers in the early stage of the crystallization or by the increase of the number of crankshafts[17]. If, more correctly (due to the partial overlap of the γ-peak and β-peak), we consider the difference between the γ-peak height and the minimum between the γ- and β-peak as a measure of the γ-relaxation, then the γ-relaxation only increases with crystallinity. This seems remarkable because intuitively one would expect an overall decrease in mobility and thus a decrease of the γ-relaxation when more mesogens are fixed in a crystal lattice. The explanation lies in the fact that within the sample there is a phase separation between stiff regions (crystallized mesogens), somewhat less stiff regions (frozen liquid crystalline mesogens) and soft regions (spacers and backbone). In a randomly oriented sample with a multidomain structure the softest regions, on average, undergo the largest deformations. *I.e.* effectively the amplitude of the deformation is higher for the softest regions. Higher deformations always result in a larger difference between maxima and minima in the tan δ curves. The principle behind all this is that relaxation is the direct respons of the sample to the applied deformation. Therefore, with increasing crystallinity and stiffness of the mesogen layers, the deformation of the spacers becomes larger and thus the γ-relaxation increases. This is possible because the crankshaft motion itself requires only a small free volume for the mobile CH_2-groups, while the groups on both sides of the crankshaft, *i.e.* the mesogens and the backbone, may be frozen[24]. This is indeed the case below -100°C.

A similar but much weaker effect was measured by dielectric spectroscopy[25]. This remarkable behaviour of the γ-relaxation confirms that only the mesogenic groups crystallize and not the backbone and the spacers. In that case the spacers would be more regular and the number of crankshafts would decrease significantly, causing a *de*crease of the γ-relaxation with increasing crystallinity.

Tail length dependence of the dynamic mechanical spectra

The influence of the tail on the dynamic mechanical properties is similar to that of the spacer. Figure 5 shows the DMA curves of polymers **III9a,c,f**. It can be seen that with increasing tail length in the first place the low temperature modulus decreases. There is a rather obvious similarity with the density of the polymers (determined by measuring the size and weight of the DMA bars), 1.29 g/cm^3, 1.15 g/cm^3 and 1.14 g/cm^3 respectively at room temperature. Both in the modulus and in the density the largest jump is found between polymers **III9a** and **III9c**. Apparently the packing of a monolayer structure (**III9a**) is considerably more compact than that of the double layer structure (**III9c** and **III9f**), giving rise to a higher density (or

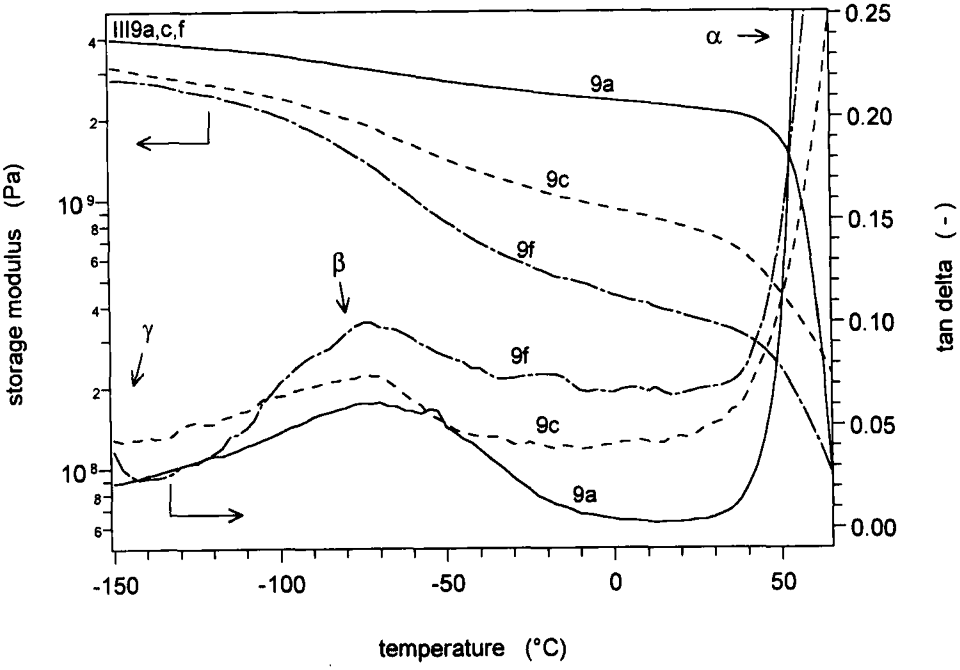

Figure 5. Influence of tail length on the Sub-T_g dynamic mechanical behaviour: storage modulus (left) and damping factor (right) of polymers **III9a,c,f**. Three point bending, 5°C/min, 1 Hz.

lower free volume) and higher moduli. In analogy to what is described for the influence of the spacer, also in the case of an increasing tail length the decreasing concentration of polymer chains and the increasing apolar fraction are responsible for the decrease of the modulus. It is remarkable that also the relative and absolute drop in modulus at the β-relaxation are larger as the tail length increases. This should not be expected if the β-relaxation is only ascribed to the carbonate groups, since their concentration *de*creases with *in*creasing tail length. In analogy to the results above, it is therefore likely that the β-peak also contains a mesogenic relaxation. Considering the S_{A1} structure of polymer **III9a**, with full overlap of the interdigitated side groups, and the S_{Ad} structure of **III9c** and **III9f**, with only overlapping tails, it seems obvious that the tails indeed influence the relaxation of the mesogenic groups.

An increase of the tan δ curves of polymers **III9c** and **III9f** at temperatures below -140°C, indicates that there must also be a γ-relaxation, originating from motions of the aliphatic tails. Also in dielectric relaxation spectroscopy of side-chain LCPs such a γ-relaxation is often ascribed to a reorientation of the alkoxy end group of the mesogens[4]. A difference between spacer and tail is that the latter does not have a strong and unambiguous influence on the T_g, for polymers **III9a-f** all lying between 67°C and 97°C.

CONCLUSIONS

It was demonstrated that dynamic mechanical analysis can very well be used to study the low-temperature relaxation processes in side-chain liquid crystalline polycarbonates. By systematic variation of the polymer structure or its physical state a fundamental understanding of the motions in the LCPs in their glassy or crystalline

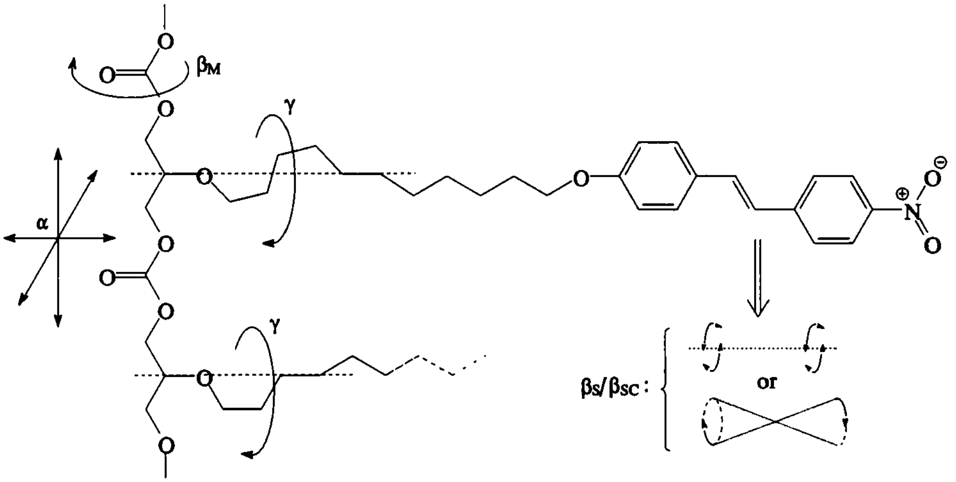

Figure 6. Assignment of the low temperature relaxations of the side-chain LC polycarbonates, illustrated by polymer **VI9d** with oxynitrostilbene mesogenic groups and an undecyl spacer.

state could be realized. The α-relaxation, corresponding to the glass transition, was easily detected by the strong drop in the storage modulus. In total four different secondary relaxations could be detected below the α-transition: the γ-relaxation of the spacers or tails, the β_M-relaxation of the carbonate group in the main chain, the β_S-relaxation of the mesogenic side groups in the frozen liquid crystalline state and, in the case of a semi-crystalline polymer, the β_{SC}-relaxation of the crystallized mesogens. An overview of the low-temperature relaxations and their suggested mechanisms is given in Figure 6. A more thorough description of the relaxation mechanisms will be given in a separate paper, including also the dielectric analysis[25].

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