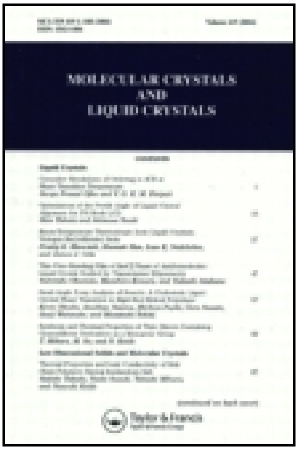

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Molecular Dynamics of Liquid Crystalline Side-Chain Oligoacrylates and Oligomethacrylates with 4-Cyanazobenzene Side Groups. Influence of External Fields on Dielectric Properties

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Molecular Dynamics of Liquid Crystalline Side-Chain Oligoacrylates and Oligomethacrylates with 4-Cyanazobenzene Side Groups. Influence of External Fields on Dielectric Properties

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Dielectric behavior of several smectic side-chain oligoacrylates and oligomethacrylates with 4-cyanazobenzene mesogenic side groups has been investigated. Below the glass transition temperature two relaxation regions of dipole relaxation (the γ_1 and the β processes) caused by local mobility were detected. The molecular mobility of the γ_1 process increases with spacer length but in the case of the β process the mobility is not changed. In the LC state, near T_g transition, two cooperative processes, α- and δ, related to the reorientation of transverse ($\mu_\perp$) or longitudinal ($\mu_\parallel$) components of the dipole moment of the mesogenic group, respectively, were observed. The orientation in external electric or mechanic fields leads to the establishment of planar or homeotropic orientation of mesogenic side groups.

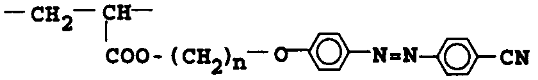
Keywords: dielectric relaxation; liquid crystalline side-chain polymers; orientation by electric or mechanic fields

INTRODUCTION

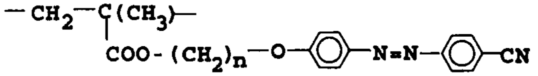
The dynamics of macromolecules in thermotropic side-chain polymers exhibit some specific features. They are due to the anisotropy of interactions which are especially marked under the effect of external orienting fields [1-4]. Dielectric relaxation method is very fruitful for molecular mobility investigation in thermotropic side-chain polymers. In these systems the molecular mobility of main chains and of mesogenic groups separated from the backbone by the flexible spacer is relatively independent, which favours the formation of the LC order. Five dielectric relaxation processes -δ, α, β, γ_1, and γ_2 - were actually found in a series of thermotropic side-chain polymers of different structure[1-7].

LC side-chain polymers and oligomers are easily oriented by external fields. In this case either planar or homeotropic orientation of mesogenic side groups is established [1-5]. After alignment in external oriented fields the intensity of the α and δ cooperative dielectric transitions is changed.

This work presents the dielectric investigation of a number of side-chain smectic oligoacrylates **(OA-n)** and oligomethacrylates **(OM-n)** with 4-cyanazobenzene mesogenic groups[8]:



OA-n with **n=3, 5, 7, 9 and 11**



OM-n with **n=3, 5, 7, 9 and 10**

LC side-chain polymers containing azo-groups in the side chains have attracted much attention since these systems might be used as optically non-linear media for reversible optical data storage[9].

The specific aims of this paper are: 1) the investigation of molecular mobility in **OM-n** and **OA-n**, and the identification of the observed dielectric transitions, 2) the establishment of relationships between molecular motion and spacer length, 3) to determine the influence of different types of external fields on the orientation of mesogenic side groups.

EXPERIMENTAL

The temperature dependences of tgδ were obtained with the aid of TR-9701 bridge in the temperature range from -170 to +170^{0}C and in the frequency range from 60 Hz to 1 MHz. The films 50 μm thick placed between brass electrodes were used as samples in dielectric measurements. Film orientation was carried out in an external electric field or by mechanical shear[1,2,5].

RESULTS AND DISCUSSION

OM-n and **OA-n** oligomers exhibited in the glassy state the β and the γ_1 dielectric processes. The temperature dependences of tgδ for **OM-7** in the glassy state are shown as a typical example of dielectric behavior (Fig.1). In accordance with the conclusions in works[3-5], the β process can be related to the rotational mobility of the mesogen about its long axis. The contribution to the β process is provided by the polar ether groups adjoining the mesogen. The source of the γ_1 process is the reorientation of methylene spacer[5,10,11]. During reorientation, the methylene spacer also includes the ester group at the basis of the side chain, and, therefore, this motion is dielectrically active.

For the β and the γ_1 processes the temperature dependences of relaxation time for **OM-n** are shown in Fig.2. The dependences of temperature position of $tg\delta_m$ (relaxation time) for the β and the γ_1 relaxations on spacer length for **OA-n** and **OM-n** are presented in Fig.3. It is shown that in the case of the β process the dependence $T = \varphi(n)$ for **OA-n** and **OM-n** is described by curve 1 in Fig 3. This implies that kinetic characteristics of the β process (τ and U) are virtually independent of spacer length. Moreover, the analysis of kinetic characteristics for a number of LC side-chain polymers

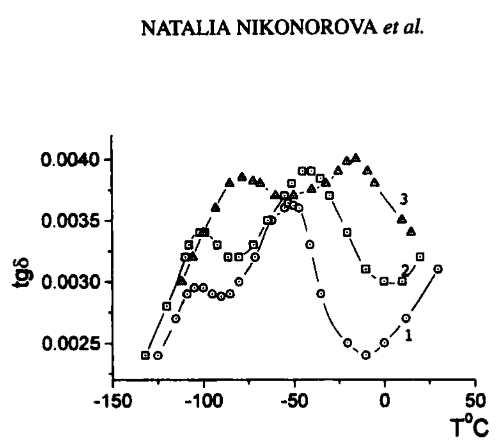


FIGURE 1 Temperature dependences of $tg\delta$ for **OM-7** at 0.1(1), 1(2), and 10(3) kHz

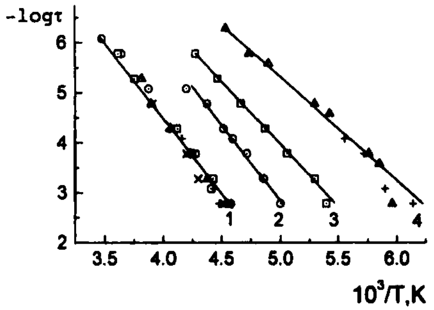


FIGURE 2 Temperature dependences of relaxation time for γ_l (1-4) and β processes (1) for **OM-3** (x), **OM-5**(o), **OM-7**(□), **OM-9**(Δ), and **OM-10**(+)

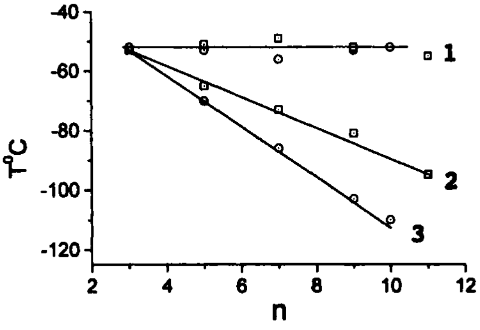


FIGURE 3. Temperature dependences of $tg\delta_m$ at 0.1kHz for **OA-n**(1,2) and **OM-n** (1,3) on spacer length for the β (1) and the γ_l processes (2,3)

with different structures[1,4,7,10,11] shows that for these systems the dependence of temperature position of tgδ_m on spacer length for the β process can also be expressed by curve 1 in Fig.3. This means that in the glassy state reorientation of mesogenic groups depends neither on the main chain structure nor on the spacer length and the mesogenic structure.

In contrast to the β relaxation, in the **OA-n** and **OM-n** series the molecular mobility of the γ_1 process depends on the methylene spacer length (Fig.3, curves 2 and 3). These curves show: 1) the increase in spacer length leads to the linear increase in the mobility of the methylene spacer, 2) relaxation times of the γ_1 process depend on main chain structure, and for **OA-n** relaxation times are higher than that for **OM-n**.

With decreasing spacer length the difference in the temperature position of tgδ_m between the β and the γ_1 processes decreases. For **n=3** only one relaxation, the γ_1 process, takes place. This implies that the two processes could be independent of each other at spacer length starting from n=5.

Near T_g two overlapping cooperative relaxation processes, α and δ, were observed in **OA-n** and **OM-n**. As a typical example, the temperature dependences of tgδ for **OA-7** and **OM-7** are shown in Fig.4. For **OA-n** and **OM-n** the α process is detected as a shoulder at the low temperature side of the well-defined δ peak. The temperature dependences of relaxation time for the α and the δ processes for **OA-7** and **OM-7** are shown in Fig.5. The relaxation times and T_g determined from dependences **$-\log\tau=\varphi(1/T)$** decrease with spacer length.

In accordance with interpretation suggested previously for these processes, the α relaxation can be related to the segmental motion of main chains and to the rotation of mesogenic groups about the long mesogen axis, and the δ relaxation reflects the rotation of mesogenic groups about the short axis[1-5,7] . These relaxation transitions take place after the beginning of segmental mobility but the δ process is observed at higher temperatures than the α process because the rotation of mesogenic groups about the short axis requires greater free volume.

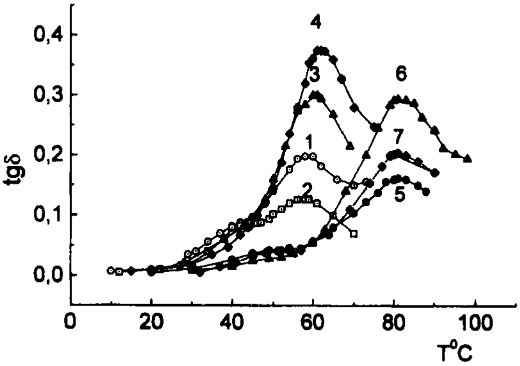


FIGURE 4. Temperature dependences of tgδ for OA-7 (1-4) and OM-7 (5-7) at 0.1kHz for the initial samples(1,5), and for samples oriented by direct (2) or alternating (4,7) electric field, or by mechanical shear (3,6)

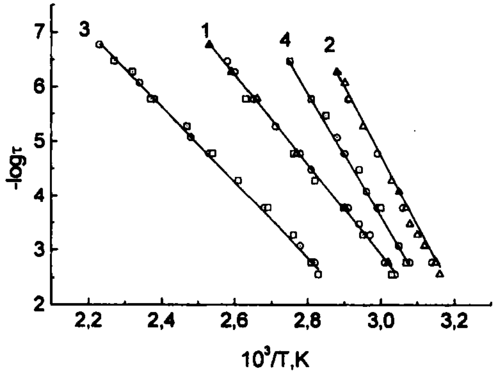


FIGURE 5. Temperature dependences of relaxation time in the range of the α (2,4) and δ (1,3) processes for OA-7 (1,2) and OM-7 (3,4)

After **OA-n** and **OM-n** are aligned in external fields, the orientation of mesogenic side groups takes place. As a result of orientation the intensities of the α and δ dielectric processes are changed. The relation between the transverse ($\mu_\perp$) and longitudinal ($\mu_\parallel$) components of the dipole moment of cyanazobenzene mesogenic groups in **OA-n** and **OM-n** is $\mu_\perp < \mu_\parallel$. It means that in the case of homeotropic orientation the intensity of the α process decreases and that of the δ process increases, and in the case of planar orientation the inverse situation is observed[5]. The comparison of intensities of the α and δ processes in Fig.4 for initial and oriented samples makes it possible to conclude that for **OA-7** and **OM-7** after orientation by mechanic shear and by alternating electric field homeotropic orientation takes place, and after orientation by direct electric field planar alignment of mesogenic groups is established. After orientation relaxation times of the α and the δ processes are not changed. It means that molecular mobility of both these processes is not also changed.

Establishment of planar or homeotropic orientation is also determined by spacer length. Hence, in contrast to **OA-7** and **OM-7,** in **OA-3** the alignment by mechanical shear or by direct electric field leads to the planar or homeotropic orientation, respectively.

The transition from oriented state to initial one is shown on Fig.6 where each point corresponds to the temperature position of $tg\delta_m$ at a certain frequency. The disappearance of mesogenic groups orientation begins at temperatures 10 - 15^{0}C below T_{cl} and the complete disappearance of orientation is observed at T_{cl} . This result can be considered as a criterion of application of oriented films of **OA-n** and **OM-n** for information storage.

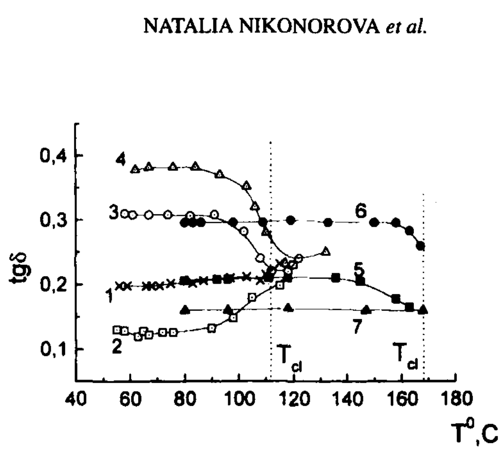


FIGURE 6. Temperature dependences of tgδ_m for **OA-7** (1-4) and **OM-7** (5-7) for initial (1,5), for homeotropic (3-6) and for planar orientation (2)

Acknowledgement

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