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DYNAMICS OF LIQUID CRYSTALLINE SIDE-CHAIN POLY(VINYL ETHER)S

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ABSTRACT

Segmental mobility between 100 and 350 K is reported for a series of mesomorphic side-chain poly(vinyl ether)s with 4–11 methylene carbon atoms in the spacer and phenyl benzoate and stilbenyloxy groups used as mesogens. A glass–rubber transition (α) appears in the vicinity of 300 K. Three subglass processes, referred to as β , γ , and δ obey the

Arrhenius and Cole-Cole equations. The δ -process is present only in polymers with flexible and dielectrically active tail groups, e.g., in polymers with an ethoxy group, in which case the process can be assigned to torsion about the pendant phenyl-carbon-ether-oxygen bond. The activation energy ($35 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$) of the γ -process is insensitive to the morphology and is assigned to local motions within the spacer. The activation energy of the β -process varied considerably among the studied polymers (60 to $126 \text{ kJ}\cdot\text{mol}^{-1}$). The absence of the β -process in the stilbenyloxy polymer suggests that this process is due to reorientation of the carboxylic group in the phenyl benzoate moiety. The relaxation strength associated with the β -process passes through a maximum as the spacer length increases. In a polymer with a short spacer group, the participating carboxyl group is not able to reorient completely. In polymers with longer spacer groups, reorientation is more complete but the concentration of active mesogens is lower. Phenyl-benzoate polymers with 11 carbon atoms in the spacer, with different tacticities, exhibited the same dielectric relaxation behavior.

INTRODUCTION

Liquid crystalline poly(vinyl ether)s have been extensively studied at our departments. References 1–7 are a selection of recent papers on the subject. It is no exaggeration to state that the seeds of the original ideas on the photoreactions ultimately leading to the making of these poly(vinyl ether)s are due to Professor Bengt Rånby.

This paper reviews the work carried out on the dynamics of side-chain liquid crystalline poly(vinyl ether)s reported in two recent papers [1, 2]. In these studies the segmental mobility was assessed by dielectric spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The structures and names of the studied polymers are shown in Fig. 1. The number of carbon atoms in the spacer group was varied between 4 and 11 in the series of polymers with phenyl-benzoate mesogen (PX-PBVE-*m*). The tacticity of PEtO-PBVE-11 was systematically altered from 25% meso (so-called “syndiotactic”) to 75% meso (so-called “isotactic”). The terminal group, which in these studies was either an ethoxy- or a cyano-group, is decisive for both the dynamics and the structure formed. Finally, the effect of the mesogen, phenyl-benzoate (PX-PBVE-*m*) or stilbene (PVN-SVE-11), on the relaxation behavior is discussed.

The polymers used in these studies showed smectic mesomorphism, in most of the cases S_B [1]. However, the cyano-containing polymers exhibited S_C mesomorphism [1, 2]. Further details about the morphological structure of these polymers are reported elsewhere [3–5]. The dielectric work was essentially carried out at temperatures below the glass transition temperature. The paper gives 1) a brief presentation of dielectric relaxation behavior including the assignment of the relaxation processes to groups in the repeating unit, 2) a demonstration of the influence of the length of the spacer group on the segmental mobility, 3) information concerning the influence of tacticity on the segmental mobility, and 4) the relationship between the dielectric relaxation behavior and the degree of orientation.

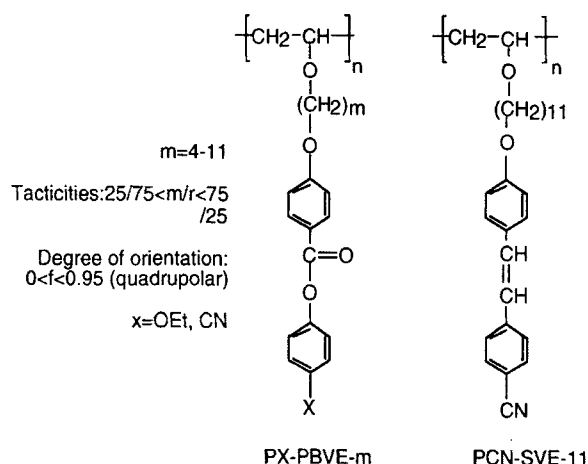


FIG. 1. Structures of the polymers considered.

DIELECTRIC RELAXATION AND STRUCTURAL ASSIGNMENT OF RELAXATION PROCESSES

The dielectric relaxation of PEtO-PBVE-11 is shown in Figs. 2 and 3. This polymer exhibited four dielectric relaxation processes: α , the glass-rubber transition at 290–300 K; and three subglass processes referred to as β , γ , and δ . PCN-PBVE-11 exhibited only three dielectric processes, α , β , and γ [1]. The low temperature process, δ , was absent in PCN-PBVE-11, and this process could be assigned to

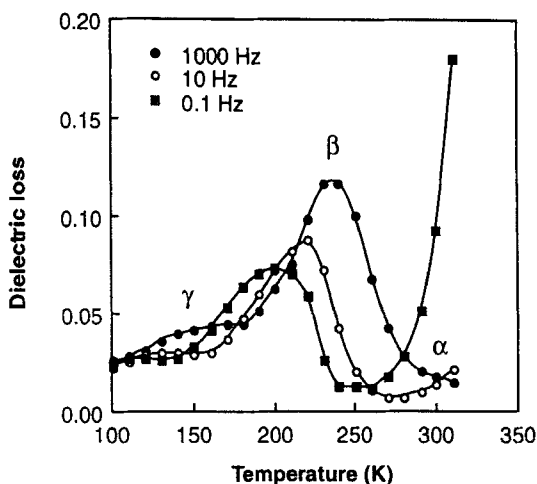


FIG. 2. Dielectric loss of oriented (mesogens are oriented in the plane perpendicular to the applied electric field) PEtO-PBVE-11; isochronal curves at the frequencies displayed in the graph as a function of temperature. Data of Ref. (A), with permission from Butterworth-Heinemann Ltd., UK.

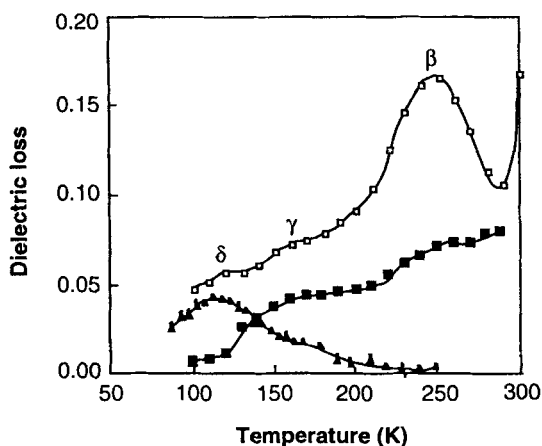


FIG. 3. Dielectric loss of unoriented PEtO-PBVE-11 (\square), PCN-PBVE-11 (\blacksquare), and poly(*p*-ethoxystyrene) (\blacktriangle) at 4500 Hz as a function of temperature showing the δ -process. Data of Ref. (A), with permission from Butterworth-Heinemann Ltd., UK.

torsion about the pendant phenyl-carbon-ether-oxygen bond in PEtO-PBVE-11 [1]. This conclusion was supported by the presence of a dielectric relaxation process for poly(*p*-ethoxy-styrene) in the same temperature/frequency range (Fig. 3). The subglass processes β and γ showed an Arrhenius temperature dependence, and they were also symmetrically broadened according to the Cole-Cole equation [1, 2]. The activation energy of the γ -process was insensitive to the length of the spacer group, the mesogen, the terminal group, and the morphology, with a value of 35 ± 5 $\text{kJ}\cdot\text{mol}^{-1}$ [1, 2]. The γ -process was assigned to local motions in the spacer group. The segmental mobility of the spacer group is also reflected in the change in *trans*-content from 70% at 203 K to 60% at 323 K [2]. The *trans*-content in all of the liquid crystalline poly(vinyl ether)s is approximately 10% greater than that given by a calculation of a polyethylene chain at the corresponding temperature using simple Boltzmann weighting, assuming the energy differences between *trans* and *gauche* to be 2.1 $\text{kJ}\cdot\text{mol}^{-1}$ and between *trans-trans* and *gauche-antigauche* to be 8.4 $\text{kJ}\cdot\text{mol}^{-1}$ [2].

The β -process was not present in the stilbene polymer which provides evidence indicating that this process is due to reorientation of the mesogenic carboxylic group in the phenyl-benzoate polymers (Fig. 4) [2]. The β -process showed a large variation in activation energy among the studied samples, from 60 to 128 $\text{kJ}\cdot\text{mol}^{-1}$ [1, 2].

The β -process is tentatively assumed to be the result of a coordinated torsion about bonds 3 and 4, leading to mirror-imaging of the carboxyl group without any internal change in the surrounding groups (Fig. 5). The swept-out volume of the motion should also be relatively limited. The intramolecular energy barriers for rotations about bonds 3 and 4 were calculated for oligo-hydroxy benzoic acid [8], and it was concluded that, due to resonance stabilization, the carbonyl group should be planar with respect to the nearby phenyl group, i.e., bond 3 can take two stable angular values, 0 and 180° . These two energetically indifferent rotational isomers are separated by an energy barrier (*intramolecular*) amounting to about 20 $\text{kJ}\cdot\text{mol}^{-1}$.

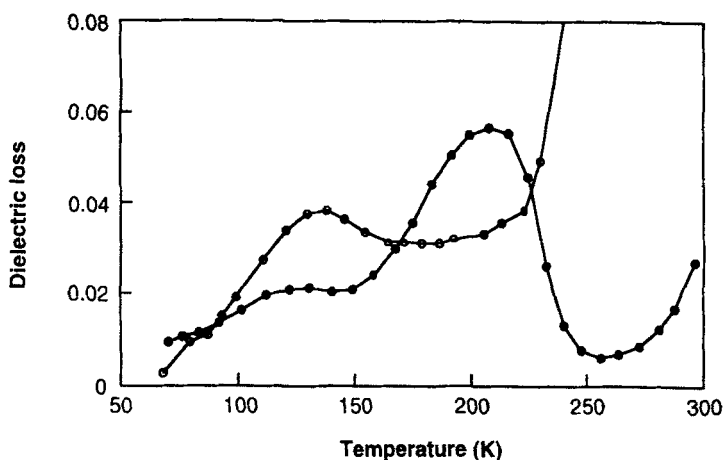


FIG. 4. Dielectric loss at 1 Hz of unoriented PCN-PBVE-11 (●) and unoriented PCN-SVE-11 (○) as a function of temperature. From Ref. 2, with permission from the American Chemical Society, USA.

mol^{-1} [9]. The energy barrier for torsion about bond 4 is, according to the semi-empirical AM1 calculations, less than $5 \text{ kJ} \cdot \text{mol}^{-1}$ [8], and four different stable conformers are present at torsion angles: -135° , -45° , $+45^\circ$, and $+135^\circ$. C-13 NMR indicates the onset of mobility of the phenyl groups in the mesogen between 228 and 253 K at the cross-polarization frequency 66 kHz [2], which is consonant with the dielectric data presented in Fig. 2.

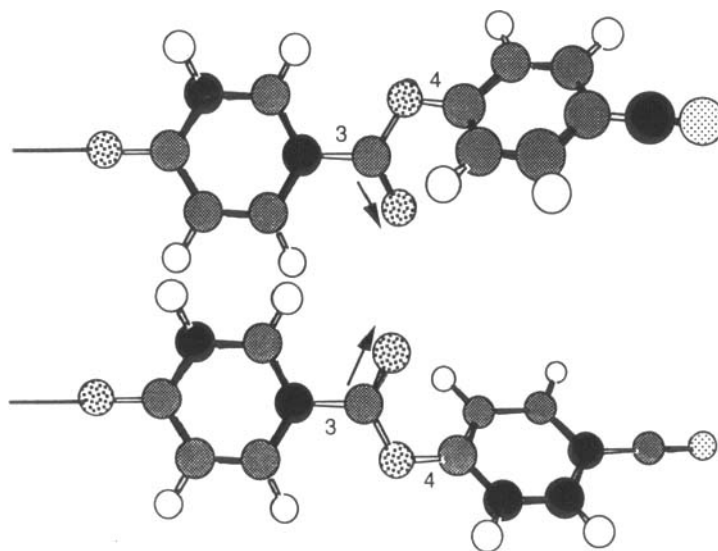


FIG. 5. Reorientation of the carboxylic group in the phenylbenzoate moiety. Drawn after Ref. 1, with permission from Butterworth-Heinemann Ltd., UK.

INFLUENCE OF SPACER LENGTH ON THE CHAIN DYNAMICS [2]

Figure 6 shows the effect of the length of the spacer group on the relaxation behavior. The trend is that the relaxation strength of the β -process goes through a maximum as the spacer length increases. This is probably due to the inability of the mesogen carboxyl group to reorient over complete three-dimensional space in polymers with shorter spacer groups. Reorientation is thus more complete in polymers with longer spacer groups. There is also a counteracting dilution effect originating from the nonpolar spacer group.

The activation energy for the γ -process shows essentially no dependence on the size of the spacer group; it remains constant at $35 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$ (Fig. 7). There is a weak increasing trend in the activation energy for the β -process with increasing length of the spacer group (Fig. 7). However, the variation in activation energy among the different PEtO-PBVE-11 samples is considerable, and it is suggested that the morphology rather than the length of the spacer group is decisive.

INFLUENCE OF TACTICITY ON THE CHAIN DYNAMICS [2]

The configuration was only varied for PEtO-PBVE-11, and Fig. 8 shows that tacticity played only a minor role for the relaxation behavior of this particular polymer. The peak temperature positions, the activation energies, and the relaxation strengths were essentially the same for the three polymers. The unrealistically high unrelaxed dielectrical permittivity and dielectric loss for the isotactic polymer ($m/r = 75/25$) is considered to be associated with an experimental problem.

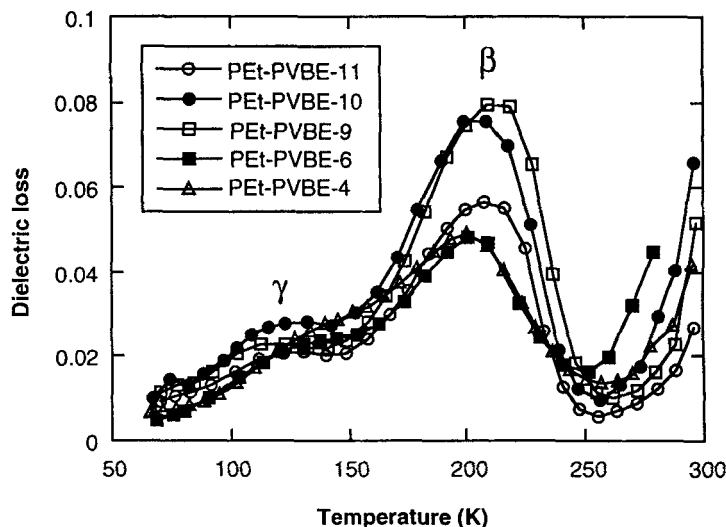


FIG. 6. Dielectric loss as a function of temperature for atactic, unoriented polymers with different spacer lengths. All data were obtained at 1 Hz. From Ref. 2, with permission from the American Chemical Society, USA.

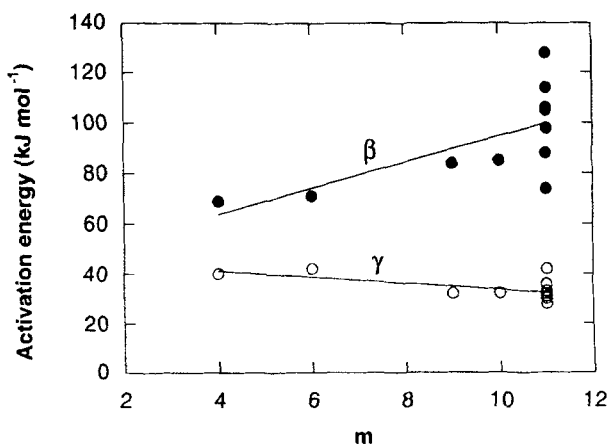


FIG. 7. Activation energy of β - and γ -processes as a function of the number (m) of carbon atoms in the spacer group.

The *trans*-content in the spacer group of PEtO-PBVE- m ($9 \leq m \leq 11$) at room temperature is approximately the same (73–78%), independent of the length of the spacer group.

THE INFLUENCE OF THE STATE OF ORIENTATION ON THE RELAXATION BEHAVIOR [1]

The state of orientation affected only the intensity of the relaxation processes, i.e., the relaxation strength. Neither the activation energy nor the temperature position of the loss peaks was affected by the state of orientation. The relaxation

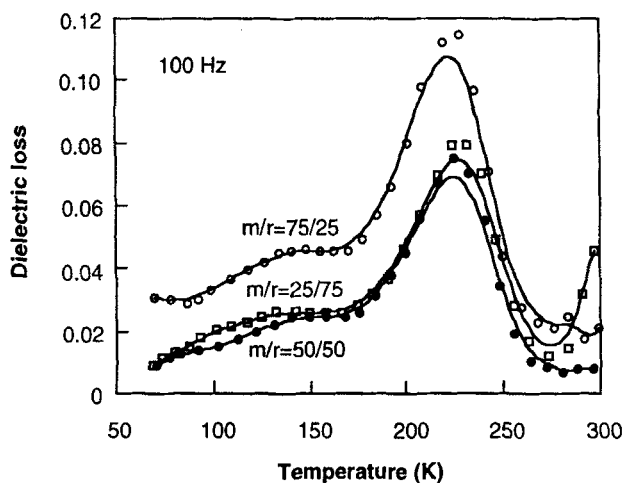


FIG. 8. Dielectric loss at 100 Hz as a function of temperature for PEtO-PBVE-11 with different tacticities. From Ref. 2, with permission from the American Chemical Society, USA.

TABLE 1. Strength of Relaxation Processes

Sample	Process	$\epsilon'_r - \epsilon'_u$ ^a
PEtO-PBVE-11 PLAN	β	1.40 ^b
PEtO-PBVE-11 ISO	β	0.90 ^b
PCN-PBVE-11 PLAN	β	0.32 ^b
PCN-PBVE-11 ISO	β	0.62 ^b
PEtO-PBVE-11 PLAN	γ	0.95 ^c
PEtO-PBVE-11 ISO	γ	0.58 ^c
PCN-PBVE-11 PLAN	γ	0.19 ^c
PCN-PBVE-11 ISO	γ	0.50 ^c

^aRelaxation strength, difference between “relaxed” and “unrelaxed” dielectric permittivity.

^bRelaxation strength at 200 K.

^cRelaxation strength at 100 K.

strength data shown in Table 1 were obtained by fitting the Havriliak-Negami equation to experimental data for PEtO-PBVE-11 and PCN-PBVE-11.

For PEtO-PBVE-11, the relaxation strengths for β and γ of the oriented sample were 1.55 to 1.80 times that of the isotropic sample. The mesogens in the oriented sample were aligned in the plane of the film (x), and the participating dipoles are expected to be randomly oriented in the yz -plane (Fig. 9). The number of participating dipoles in the β - and γ -processes should be 50% greater in a perfectly uniaxially oriented sample than in the isotropic analogue. We have currently no explanation of the anomalous behavior of PCN-PBVE-11 (Table 1).

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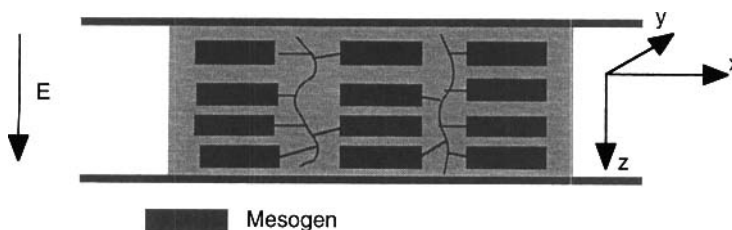


FIG. 9. Schematic representation of the organization of the mesogens in the oriented samples with the direction of the electric field (E).

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REFERENCES

- [1] U. W. Gedde, F. Liu, A. Hult, F. Sahlén, and R. H. Boyd, *Polymer*, **35**, 2056 (1994).
- [2] C. Hellermark, U. W. Gedde, A. Hult, C. Boeffel, R. H. Boyd, and F. Liu, *Macromolecules*, Submitted (1995).
- [3] F. Sahlén, A. Hult, U. W. Gedde, F. Ania, and J. Martinez-Salazar, *Polymer*, **35**, 4041 (1994).
- [4] C. Hellermark, U. W. Gedde, and A. Hult, *Ibid.*, Submitted (1995).
- [5] C. Hellermark, U. W. Gedde, A. Hult, C. Boeffel, and R. M. Richardson, *Macromolecules*, Submitted (1996).
- [6] H. Andersson, U. W. Gedde, and A. Hult, *Polymer*, **33**, 4014 (1992).
- [7] H. Andersson, U. W. Gedde, and A. Hult, *Mol. Cryst. Liq. Cryst.*, **243**, 313 (1994).
- [8] P. Lautenschläger, J. Brickmann, J. van Ruiten, and R. J. Meier, *Macromolecules*, **24**, 1284 (1991).
- [9] T. Scheafer, T. A. Wildman, and R. Sebastian, *J. Mol. Struct., Theochem.*, **89**, 93 (1982).