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Registry No. (S)(EO) (block copolymer), 107311-90-0; cyclopentane, 287-92-3.

Deuterium Magnetic Resonance Study of Some Liquid-Crystalline Polysiloxanes

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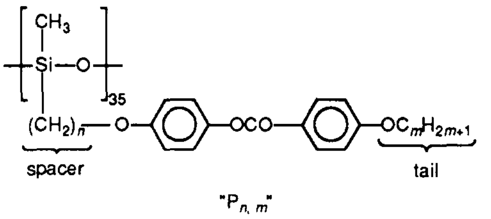
ABSTRACT: Deuterium nuclear magnetic resonance is used to study two side-chain poly(methylsiloxanes) and their corresponding low molecular weight mesogens. The compounds are selectively deuterated and are studied as a function of temperature over their mesomorphic regions. The measurement of the various quadrupolar splittings and, in some cases, of the dipolar interactions are analyzed in terms of orientational order, using a single-order parameter model. In addition, some information is given about the probability distribution of gauche conformers in the aliphatic chains of the various compounds.

1. Introduction

In previous papers[1-3] we have described the synthesis and mesogenic properties of a series of poly(methylsiloxanes) substituted by the following phenyl benzoates:



"$P_{n,m}$"

For an understanding of the relationships between structure and properties, investigations on chain conformation, molecular order, and dynamics of the mesogenic groups are necessary. Some results have been recently obtained by small-angle neutron scattering,[4] dielectric investigations,[5] and ^{13}C NMR measurements.[6] Deuterium magnetic resonance is also particularly useful and has been extensively used to study molecular structure and ordering of liquid-crystalline phases.[7-15]

In the present paper we report a ^2H NMR study of two polymers of the series $P_{4,1}$ ($n = 4$, $m = 1$) and $P_{4,8}$ ($n = 4$, $m = 8$) and of the two corresponding low molecular weight (LMW) mesogens group $M_{4,1}$ and $M_{4,8}$.

The mesogens are selectively deuterated in the spacer and in the tail. Quadrupolar and dipolar interactions are analyzed in terms of the model of Hsi et al.[7] The single-order parameter of the model and the probability of gauche conformers in the aliphatic chain are deduced. The results obtained with different labeling sites are compared, concerning both the LMW and the polymer mesogens.

2. Experimental Section

2.1. Materials. The synthesis of the deuterated mesogenic groups has been performed by using the same classical reactions described in a preceding paper.[1] The compounds are labeled

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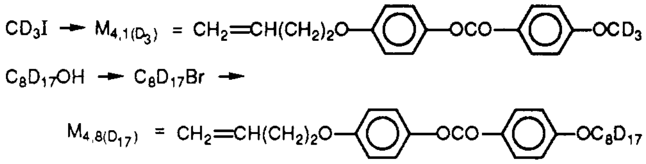
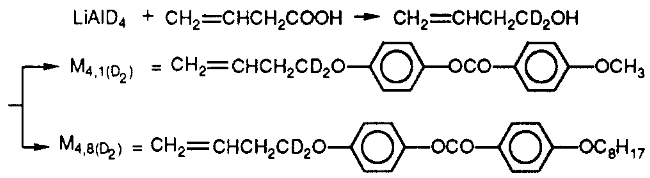
either in the tail or in the spacer.

The starting deuterated materials are CD_3I and $C_8D_{17}OH$ in the case of compounds that contain deuterium in the tail:

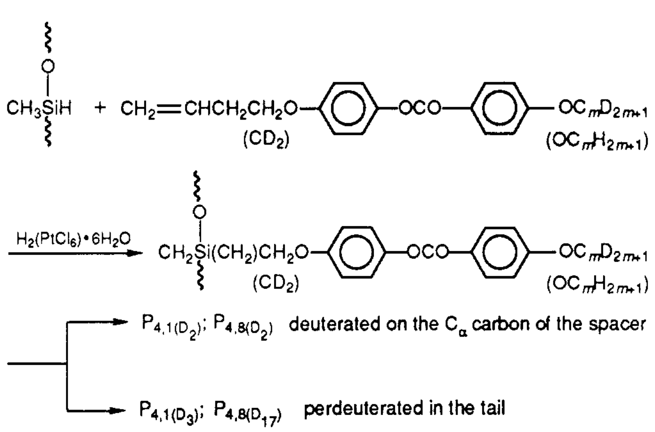


The deuteration of the C_α carbon of the spacer uses $LiAlD_4$ as a reducing agent of an acid:[16]



This reaction is performed in dry ether under refluxing conditions. The complex is then hydrolyzed, and the excess $LiAlD_4$ is destroyed by dropwise addition of water. After treatment with 10% H_2SO_4, the aqueous phase is continuously extracted with ether during 8 h. Deuterated butenol is obtained from ether by distillation.

The corresponding polymers are obtained by a hydrosilylation reaction as previously described:[1]



The transition temperatures of all the compounds are given in Table I.

2.2. NMR Measurements. The samples are placed in 3-mm-i.d. and 20-mm-long Pyrex tubes.

The deuterium frequency of the Fourier transform Brüker MSL 200 NMR spectrometer is 30.72 MHz.

The spectra are obtained by the spin–echo technique. Usually 100 and 400 scans, respectively, are necessary for LMW and polymer compounds. Heating is supplied by an air stream. A thermocouple is used to monitor and regulate the temperature, accuracy being about ±1 °C.

The spectra are recorded by first heating the sample to the isotropic state and then slowly cooling through the various mesophases.

3. Spectral Analysis

In order to analyze the NMR spectra, we had to use some approximations that significantly simplify the interpretation of the results: (i) All the mesophases are assumed to be uniaxial, and each mesogenic group is approximated by a cylinder whose symmetry axis is collinear with the L "major molecular axis". (ii) The deuterium quadrupole tensor is considered axially symmetric with the axis along the C–D bond vector.

In the limits of these approximations only a single orientational order parameter, S, is required to describe the molecular ordering. The deuterium quadrupole interaction, ν_i, and the dipolar coupling, D_{ij}, can be written in frequency units as[7]

$$\nu_i = \frac{3e^2qQ}{4h} S\, Y(\theta_i)$$

$$Y(\theta_i) = \frac{1}{2}(3\cos^2\theta_i - 1)$$

$$D_{ij} = -\frac{\gamma_i\gamma_j h}{2\pi^2(\mathbf{r}_{ij})^3} S\, Y(\theta_{ij})$$

$$Y(\theta_{ij}) = \frac{1}{2}(3\cos^2\theta_{ij} - 1)$$

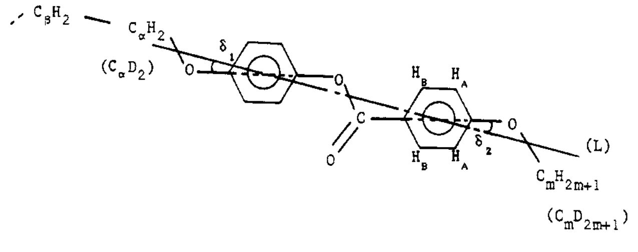
θ_i represents the angle between the C–D bond of the ith deuterium and the L axis. θ_{ij} is the angle between L and the vector $\mathbf{r}_{ij}$ connecting the nuclei i and j with the respective γ_i and γ_j gyromagnetic ratios.

Deuterium quadrupole interaction constants, e^2qQ/h, for deuterons bonded to aliphatic carbons average to about 168 kHz. So, in the mesophases, each type of deuterium exhibits a quadrupolar splitting, Δ_i, of magnitude:

$$\Delta_{i_{\mathrm{kHz}}} = 2\nu_i = (3/2)168S\, Y(\theta_i)$$

Our aim is the determination of S through the experimental determination of Δ_i and/or D_{ij}.

Assuming a rigid and coplanar structure for the phenyl benzoate moiety, the L axis, in this plane, is defined by the angles δ_1 and δ_2 between L and the 1–4 axis of the two phenyl rings:



We have considered the angles determined by X-ray crystallography on similar compounds:[17]

$$\delta_1 = 11° \pm 1° \qquad \delta_2 = 12°\ [illegible]\ 1°$$

These values are close to results obtained in other systems.[7,13]

The C–O–C angle evaluation (σ) is more critical and was found to range between 115° and 125°.[7,9,12,13,15]

We assumed that the tetrahedral angle, τ, is 109.47° in all configurations.

3.1. Partially Deuterated Spacers. The dipolar splitting, which is approximately 100 Hz, is unresolved due to the line width of the signals and the magnitude of the quadrupolar splitting (30–70 kHz) (Figure 1).

In all analyses, we have assumed that the ether group remains coplanar with the phenyl ring. The orientation of the C_α–D bond depends only on the chain conformation. If p_α is the probability of a gauche conformation at carbon α (both g^+ and g^-), the quadrupolar splitting Δ_α of the $OC_\alpha D_2$ deuterons is described by the relation established by Hsi et al.[7] assuming a fast exchange between the trans and gauche conformers

$$\Delta_\alpha = (3/2)168S\left[\left(1 - \frac{1}{2}p_\alpha\right) Y(\theta_1) + \frac{1}{2}p_\alpha\, Y(\delta_1')\right] \quad \text{(I)}$$

θ_1 and δ_1' being the angles between the C–D bond and the L axis in the cases, respectively, of trans conforma-

Table I
Phase-Transition Temperatures (°C) for the Vinyl Derivatives and the Corresponding Polymers[a]

vinyl derivative				substituted polymer				
sample	$K \rightarrow S_A$ or I	$S_A \leftarrow N$	$N \leftarrow I$	sample	T_g	$S_B \leftarrow S_A$	$S_A \leftarrow N$	S_A or $N \leftarrow I$
$M_{4,1(D_3)}$	91.5		[51]	$P_{4,1(D_3)}$	7		74	104
$M_{4,1(D_2)}$	90		[51.5]	$P_{4,1(D_2)}$	9		74	102
$M_{4,8(D_{17})}$	55.9	56.1	71.1	$P_{4,8(D_{17})}$		56		132
$M_{4,8(D_2)}$	55.9	57.6	72.5	$P_{4,8(D_2)}$		57		133

[a] Brackets indicate monotropic transition.

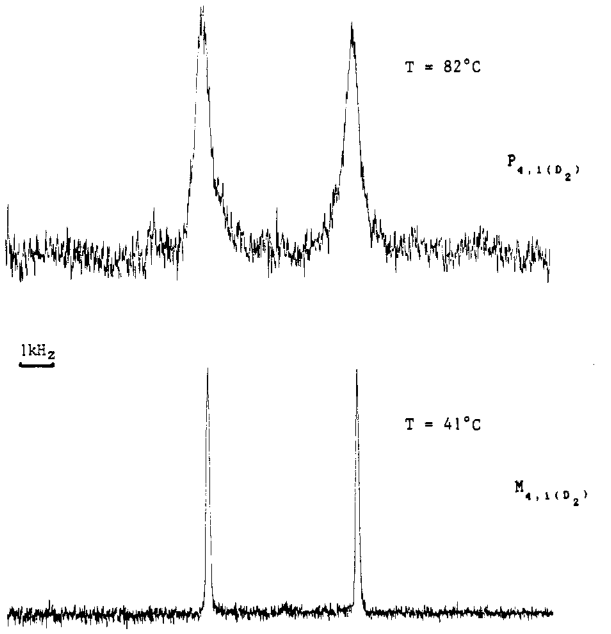


Figure 1. Deuterium magnetic resonance spectra of $P_{4,1(D_2)}$ polymer and $M_{4,1(D_2)}$ LMW deuterated in the methyleneoxy group.

tion and gauche conformation:

$$\cos \theta_1 = \cos (\tau/2 + \delta_1') \cos (\tau/2)$$

$$\delta_1' = \delta_1 + \sigma - \tau$$

The poor accuracy of the σ angle does not dramatically affect the $Y(\delta_1')$ and $Y(\theta_1)$ values. If $\delta_1 = 11°$ and $\sigma = 118.5°$,[9,12] $Y(\delta_1') = 0.825$ and $Y(\theta_1) = -0.465$.

3.2. Perdeuterated Tails. 3.2.1. Methoxy Tails. The three deuterons of the methyl group are equivalent due to fast rotation around their C_3 symmetrical axis.

Because of the relatively low value of the quadrupolar splitting, the dipolar ones, especially the proton–deuterium interactions become evident on the spectra (Figure 2).

Proton–Deuterium Dipolar Interaction. The spectral analysis shows that each line of the quadrupole doublet splits into a quintet. The relative intensities of these signals are in good agreement with the values 1-4-6-4-1 calculated by Hayamizu et al.[12] taking into account coupling between the methyl deuterons and both the H_A and H_B protons of the phenyl ring.

If we assume fast internal rotation of the methyl group and rapid rotation of the phenyl ring around the 1–4 axis,[15,18] an order of magnitude of the dipolar D_{D,H_j} ($H_j = H_A$ or H_B) interactions is given by considering an equivalent deuterium (D_{eq}) obtained by projection on the C_3 axis

$$D_{D,H_j} = -\frac{\gamma_H \gamma_D h}{2\pi^2 r_{D,H_j}^{\ 3}} Y(\theta_j)\, Y(\delta_2)\, S \qquad \text{(II)}$$

where r_{D,H_j} represents the internuclear distance between

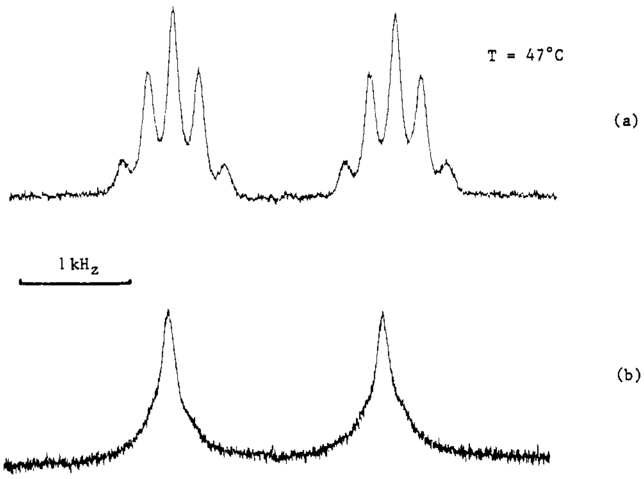


Figure 2. Deuterium magnetic resonance spectra of $M_{4,1(D_3)}$ LMW perdeuterated in the methoxy group: (a) without proton decoupling, (b) with proton decoupling.

D_{eq} and either H_A protons (r_{D,H_A}) or H_B protons (r_{D,H_B}). θ_j is the angle between the 1–4 ring axis and either the $D_{eq} - H_A(\theta_A)$ or the $D_{eq} - H_B(\theta_B)$ segment. Using the geometrical data,[9] C–C (phenyl) = 1.39 Å, C–O = 1.36 Å, C–D = 1 Å, D–C–D angle = 109.47°, C–O–C angle = 118.5°, the following values have been evaluated:[15]

$$r_{D,H_A} = 3.0\ \text{Å} \qquad \theta_A = 40° \qquad Y(\theta_A) = 0.38$$

$$r_{D,H_B} = 5.1\ \text{Å} \qquad \theta_B = 23° \qquad Y(\theta_B) = 0.77$$

$$\delta_2 = 12° \qquad Y(\delta_2) = 0.95 \qquad \frac{h\gamma_H\gamma_D}{2\pi^2} = 36.884\ \text{kHz·Å}^3$$

In the spectra (Figure 2), the spacing between the quintet peaks represents the sum[12] of the two dipolar interactions: $D_{D,H_A} + D_{D,H_B}$.

Quadrupolar Interaction. Considering fast reorientation of the methyl group about the C_3 axis, the quadrupolar splitting, Δ_{CD_3}, is then

$$\Delta_{CD_3} = (3/2)168Y(\tau)\ Y(\pi-\sigma-\delta_2)\ S \qquad \text{(III)}$$

with $Y(\tau) = -1/3$. The C_3 axis is inclined to L at nearly the magic angle; therefore, the determination of S from eq III is quite impossible. On the contrary, if S has been determined by ($D_{H_A} + D_{H_B}$) or Δ_α, the σ value can be deduced.

3.2.2. Octyloxy Tails. The identification of the different peaks is performed using Hsi et al.'s[7] interpretation (Figure 3). The decrease of Δ when m increases evidences the fact that the gauche conformation probabilities increase along the tail. If we consider a cylindrical shape for each mesogen,[7,9,10] the most probable structural defects are those that diverge the least from the axis of the molecule, i.e., "kink" defined by Hsi et al.,[7] so that a gauche segment ($g^{\pm}$) follows an opposite gauche segment ($g^{\mp}$): tt...tg$^{\pm}$tg$^{\mp}$tt... and tt...tg$^{\pm}$tttg$^{\mp}$tt...

CD_2 Groups. With these considerations, the quadrupolar splitting, Δ_m, of each CD_2 deuteron could be writ-

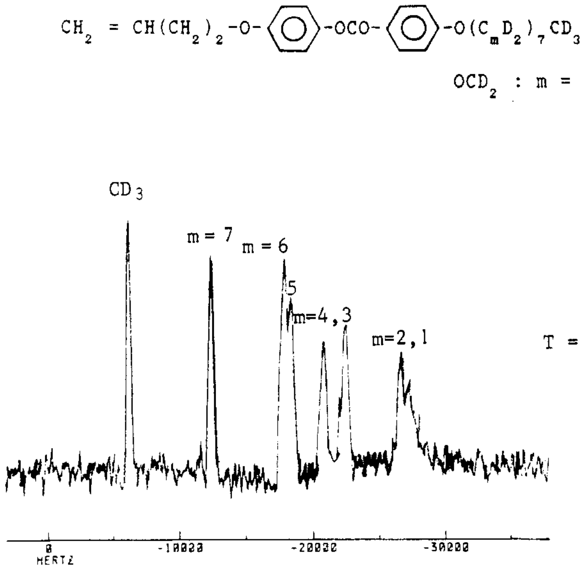


Figure 3. Deuterium magnetic resonance spectrum of $M_{4,8(D_{17})}$ LMW perdeuterated in the octyloxy chain. Only the high-field half of the spectrum is shown.

ten[7] as a function of the p_m probability of a kink formation (the first gauche atom is C_m). The orientations of the C–D bond in the kinks are different depending on whether m is even or odd:

For deuterons bonded to odd m carbon (OCD_2 corresponds to $m = 1$)

$$\Delta_m = (3/2)168S\left[\left(1-\frac{1}{2}p_m-\frac{1}{2}p_{m-1}\right)Y(\theta_2)+\frac{1}{2}p_m\,Y(\delta_2')+\frac{1}{2}p_{m-1}\,Y(\pi-\sigma-\delta_2)\right] \quad \text{(IV)}$$

For deuterons bonded to even m carbon

$$\Delta_m = (3/2)168S\left[\left(1-\frac{1}{2}p_m-\frac{1}{2}p_{m-1}\right)Y(\theta_2)+\frac{1}{2}p_m\,Y(\pi-\sigma-\delta_2)+\frac{1}{2}p_{m-1}\,Y(\delta_2')\right] \quad \text{(V)}$$

with

$$\cos\theta_2 = \cos\left[(\tau/2)+\delta_2'\right]\cos(\tau/2)$$

$$\delta_2' = \delta_2+\sigma-\tau$$

If $\delta_2 = 12°$ and $\sigma = 118.5°$, $Y(\delta_2') = 0.82$, $Y(\theta_2) = -0.47$, and $Y(\pi-\sigma-\delta_2) = 0.135$.

OCD_2 Group. Assuming that the ether bond is coplanar with the benzoate ring, we take $p_0 = 0$:

$$\Delta_1 = (3/2)168S\left[\left(1-\frac{1}{2}p_1\right)Y(\theta_2)+\frac{1}{2}p_1\,Y(\delta_2')\right] \quad \text{(VI)}$$

Comparison with Δ_α allows us to estimate p_1 in relation to p_α.

CD_3 Group. Through the fast rotation around their C_3 axis, the quadrupolar interaction of the methyl deuterons becomes[7]

$$\Delta_8 = (3/2)168S\,Y(\tau)\,Y(\theta_{C_3})$$

In all-trans conformations the C_3 axis is almost parallel to L ($\theta_{C_3} = \delta_2'$). On the contrary, a gauche conformation of the C_7–C_8 bond induces $\theta_{C_3} = \theta_2$. So

$$\Delta_8 = -(1/2)168S[(1-p_7)\,Y(\delta_2')+p_7\,Y(\theta_2)] \quad \text{(VII)}$$

Δ_1 and Δ_8 only depends, respectively, on p_1 and p_7, so their comparison shows the evolution of p_m along the tail.

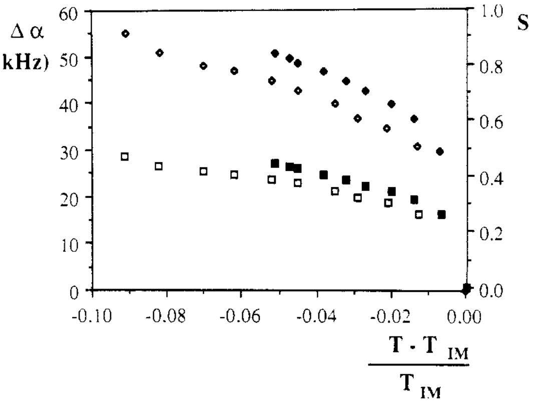


Figure 4. Quadrupolar splitting, Δ_α [(♦) $M_{4,1(D_2)}$; (◊) $P_{4,1(D_2)}$] and calculated values of the order parameter, S, using eq VIII [(■) $M_{4,1(D_2)}$; (□) $P_{4,1(D_2)}$] for deuterons in the spacer as a function of reduced temperature $(T - T_{IM})/T_{IM}$. T_{IM} is the clearing temperature.

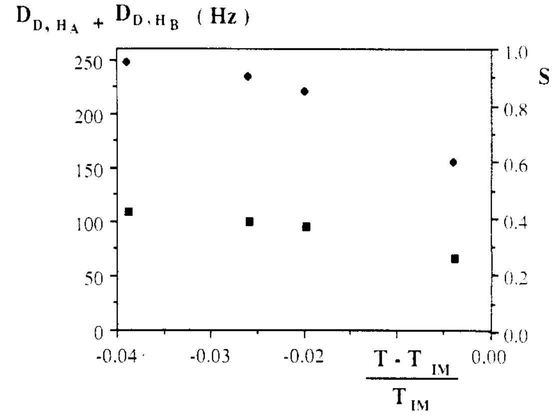


Figure 5. Dipolar interaction ($D_{D,H_A} + D_{D,H_B}$) (♦) and molecular order parameter, S (■), given by eq II for deuterons in the methoxy group of $M_{4,1(D_3)}$ as a function of reduced temperature $(T - T_{IM})/T_{IM}$.

4. Results and Discussion

The different deuterations allow the determination of the orientational order parameter for each sample with a fairly good accuracy.

4.1. Methoxy Mesogens: $M_{4,1}$, $P_{4,1}$. 4.1.1. Deuterons in the Spacer. The quadrupolar splittings, Δ_α, are plotted in Figure 4 as a function of reduced temperature. The values are quite similar for LMW and polymer.

Earlier work with similar compounds[6,7,9] has demonstrated that the kink probability, p_α, is close to zero, i.e., p_α values ranging between 0 and 0.1.[7] Equation I then simplifies to

$$\Delta_\alpha = (3/2)168S\,Y(\theta_1) \quad \text{(VIII)}$$

Calculated values of S from this equation, taking $Y(\theta_1) = -0.465$, are also reported on Figure 4.

4.1.2. Perdeuterated Methoxy Tails. The experimental dipolar interaction ($D_{D,H_A} + D_{D,H_B}$) and the molecular order parameter S calculated from eq II are given in Figure 5 for the low molecular weight mesogen $M_{4,1(D_3)}$:

$$D_{D,H_A} = 0.493S \qquad D_{D,H_B} = 0.198S$$

$$D_{D,H_A} + D_{D,H_B} = 0.69S$$

The lack of resolution in the case of the corresponding polymer $P_{4,1(D_3)}$ does not allow the accurate determination of the dipolar interaction.

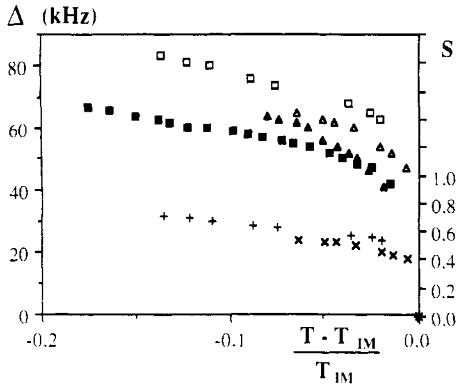


Figure 6. Quadrupolar splitting (Δ) for methyleneoxy deuterons either in spacer [(▲) $M_{4,8(D_2)}$; (■) $P_{4,8(D_2)}$] or in the tail [(△) $M_{4,8(D_{17})}$; (□) $P_{4,8(D_{17})}$] as a function of reduced temperature $(T - T_{IM})/T_{IM}$ and corresponding order parameter, S, given by VI assuming $p_1 = 0$ [(+) $P_{4,8}$; (×) $M_{4,8}$].

The S evaluations from the quadrupole interactions (Figure 4) or the dipolar ones (Figure 5) are in agreement, i.e., S around 0.38 at $(T - T_{IM})/T_{IM} = 5\%$ for the low molecular mesogen. Using these values the σ bond angle is calculated from eq III:

$$\Delta_{CD_3} = -84 Y(\pi - \sigma - \delta_2)\ S$$

σ is found to be about 110°.

4.2. Octyloxy Mesogens: $M_{4,8}$, $P_{4,8}$. OCD_2 Group. The quadrupolar splitting both for the deuterons in the spacer (Δ_α) and for the deuterons in the tail (Δ_1) are reported on Figure 6. The ratio between Δ_α (eq I) and Δ_1 (eq VI) allows the determination of the p_1 kink probability as a function of p_α:

(1) For $M_{4,8}$, Δ_α is close to Δ_1. Thus, the δ_1 and δ_2 angles being quite similar, the kink probabilities are the same for the two groups. Assuming $p_\alpha = p_1 = 0$, the molecular order parameter can be obtained (Figure 6) for each temperature.

(2) For $P_{4,8}$, Δ_1 is greater than Δ_α, which implies $p_\alpha > p_1$. If we still consider that the kink probability is almost zero for the first carbon of the tail ($p_1 = 0$), the p_α probability is found to be about 0.15 at $(T - T_{IM})/T_{IM} = 5\%$ and the molecular order parameter can be calculated (Figure 6). The S values for $M_{4,8}$ and $P_{4,8}$ are significantly greater than those obtained for the methoxy compounds, which confirms results obtained by ^{13}C magnetic resonance.[6]

CD_3 Group. From the quadrupolar splitting and the values of the order parameter (Figure 6), one can estimate the p_7 kink probability by the eq VII. This probability is found to be about 0.36 for $(T - T_{IM})/TI_M = 5\%$, for both the LMW sample and the polymer. Temperature has a little influence on this value (Figure 7b).

CD_2 Groups. For the LMW mesogen, $M_{4,8}$, the resolution of the spectrum allows the accurate determination of each methylene quadrupole splitting (Figure 7a). When eq IV and V are used, it is thus possible to calculate the kink probabilities along the octyloxy chain (Figure 7b). The results confirm a weak influence of the temperature and an almost linear increase in p_m except for the end methylene.[7] The extremity of the chain presents significantly more kinked conformers.

5. Conclusion

Different selective deuterations of the same compound lead to several ways of determining the order parameter. Their comparison allows, in the limits of simplified assumptions about the molecular structure and symmetry, a relatively good evaluation of S. This order parameter is found to be of the same order of magnitude for a polymer and the corresponding low molecular weight mesogen. Moreover, it depends significantly on the length of the alkoxy tail. In addition, this study provides evidence for the presence of gauche conformations in the octyloxy chains and in the spacer of the corresponding polymer.

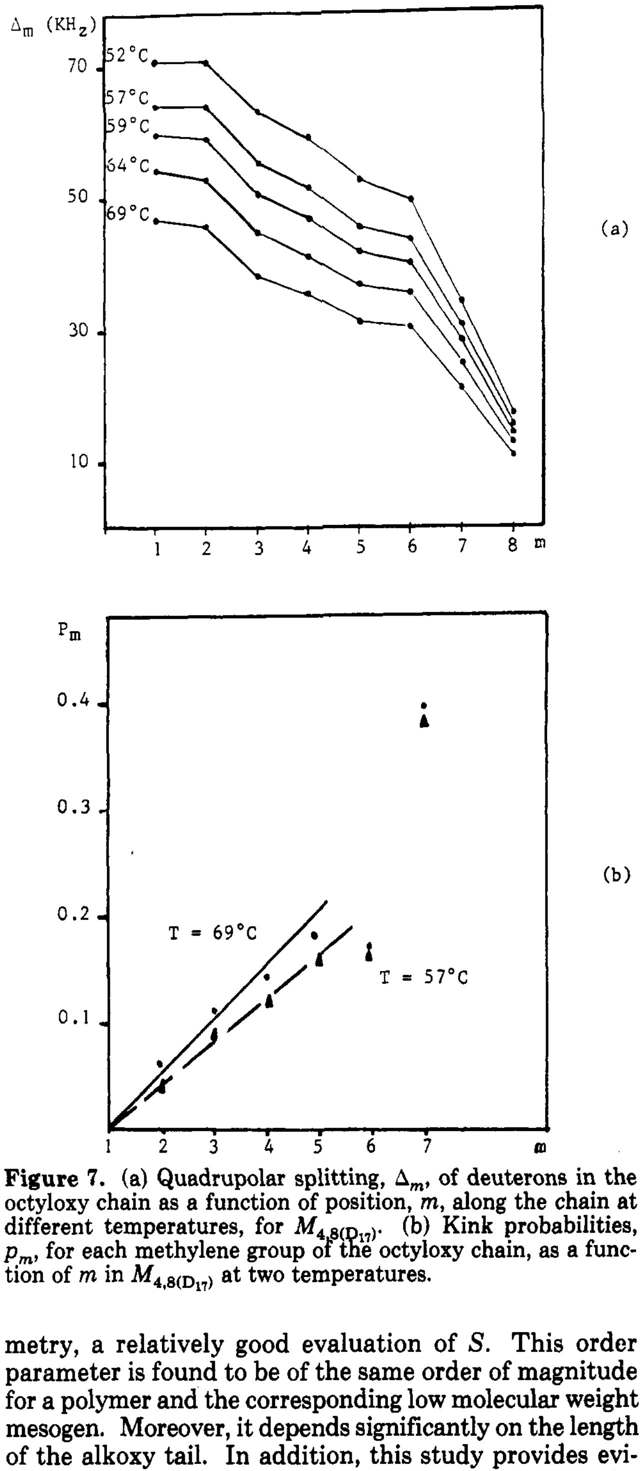


Figure 7. (a) Quadrupolar splitting, Δ_m, of deuterons in the octyloxy chain as a function of position, m, along the chain at different temperatures, for $M_{4,8(D_{17})}$. (b) Kink probabilities, p_m, for each methylene group of the octyloxy chain, as a function of m in $M_{4,8(D_{17})}$ at two temperatures.

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Chemical and Electrochemical Copolymerization of Aniline with Alkyl Ring-Substituted Anilines

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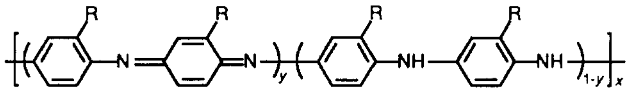
ABSTRACT: Poly(aniline-*co*-*o*-toluidine) and poly(aniline-*co*-*m*-toluidine) have been synthesized by both chemical and electrochemical copolymerizations of aniline with *o*-toluidine and with *m*-toluidine, respectively. The compositions of the copolymers were determined by ^{1}H NMR spectroscopy and could be altered by variation of the comonomer feed ratios. Thus, conductivity of copolymers can be controlled in a broad range, (e.g. when doped with 1 M HCl), from ca. 10 S/cm for homopolymer of aniline to ca. 0.1 S/cm for those of toluidines. The relationship between copolymer composition and comonomer feed ratio shows that the toluidines are more reactive than aniline in the copolymerization. The results are consistent with the proposed mechanism for the polymerization of aniline and its derivatives.

Introduction

Recent advances in the field of electrically conducting polymers have led to a variety of materials with great potentials for commercial applications. Among them, polyaniline is one of most interesting materials because of its moderately high conductivity (ca. 10 S/cm) upon doping with nonoxidizing Brønsted acids,[1,2] its well-behaved electrochemistry,[3-5] its possible processability,[6] and its good environmental stability.[2,7] Recently there have been several reports on the syntheses and properties of alkyl[8,9] or alkoxyl[10] ring-substituted polyanilines. These polyaniline derivatives have improved solubilities and different electronic and electrochemical properties in comparison with polyaniline. For example, poly(*o*-ethoxyaniline) was reported to be water soluble;[10] and both poly(*o*-toluidine) and poly(*m*-toluidine) showed interesting electrochemical properties which could be attributed to a reduction in π-conjugation of the polymers caused by steric effects of the substituent groups.[9] It is generally believed that polyaniline and related derivatives could be schematically represented by the following formula



where R is H for polyaniline, CH_3 for both poly(*o*-toluidine) and poly(*m*-toluidine), or CH_3O for polyanisidine, etc.; the value of y represents the oxidation state of the polymers.[11]

We have been interested in the kinetics and mechanism of the polymerization of aniline[12-14] in an effort to develop a new method to prepare the polymer with well-defined structure and improved electronic properties. Both chemical and electrochemical polymerization of aniline have been proposed to involve an incorporation of neutral aniline monomer into the growing polymer chain end via an electrophilic substitution reaction. The rate-determining step in the polymerization is the formation of dimeric species i.e., *p*-aminodiphenylamine, benzidine, and *N*,*N*-diphenylhydrazine. Kinetic studies of the electrochemical polymerization indicate that the rate of growth of the polymer chain is approximately 10^4 times higher than that of initiation.[13] This has been further confirmed by observation of a significant increase in the rate of polymerization when a small amount of the dimeric species was added as initiators.[14] It is well-known that studies of copolymerization could lead to the knowledge of the reactivities of monomers and their relationship with the chemical structure of the monomers and, therefore, to a better understanding of the mechanism of polymerization. Copolymerization also greatly increases the ability of the polymer scientists to tailor-make a material with specifically desired properties. As a typical example of application of copolymerizations in the field of conductive polymers, small quantities of *N*-(3-bromophenyl)pyrrole have been demonstrated to have a dramatic effect on the conductivity of the poly[pyrrole-*co*-*N*-(3-bromophenyl)pyrrole] with 10% incorporation resulting in a change in conductivity by 6 orders of magnitude.[15]

In the present paper, we report both chemical and electrochemical copolymerization of aniline with *o*-toluidine and with *m*-toluidine, respectively. The copolymers were characterized by IR and ^{1}H NMR spectroscopy, cyclic voltammetry (CV), and gel-permeation chromatography (GPC). The copolymer compositions were determined

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