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Study of the Molecular Mass Dependence of the Twist Viscosity Coefficient of a Nematic Thermotropic Main-Chain Polymer

T. Klein,[†] Hong Xi Jun,[‡,§] P. Esnault,[†] A. Blumstein,[‡] and F. Volino[*,†,‖]

Centre d'Etudes Nucléaires de Grenoble, DRF/SPh/PCM 85X, 38041 Grenoble Cedex, France, and Polymer Science Program, Department of Chemistry University of Lowell, Lowell, Massachusetts 01854.. *Received October 31, 1988;*
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ABSTRACT: The twist viscosity γ_1 of a nematic main-chain polymer of the type $(RF)_{\bar{x}}$ [R = rigid mesogenic unit, F = flexible spacer $(CH_2)_n$] has been studied as a function of temperature T and molecular mass M. The particular polymer studied is poly[oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy-(1,12-dioxo-1,12-dodecanediyl)] (DDA9). Thirteen samples with well-characterized molecular mass distributions were prepared. For M ranging between 2250 and 8400 [$5 \leqslant \bar{x} \leqslant 19$], γ_1 can be represented to a good approximation by γ_1 (kP) $\simeq 6.35 \times 10^{-30} S^2 M^{\beta} \exp(E_2/RT)$, with $\beta = 6.0 \pm 0.3$ and $E_2 = 15.3 \pm 1.1$ kcal/mol. Comparison with previous results obtained with a similar polymer differing by the number of methylene groups (seven) in the spacer (AZA9) is made.

Introduction

In a previous paper,[1] we have reported measurements of the twist viscosity coefficient γ_1 of a nematic main-chain polymer, poly[oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy(1,9-dioxo-9-nonanediyl)] (AZA9) as a function of temperature T and molecular mass M. The data could be satisfactorily described in the whole nematic range by a law of the form

$$\gamma_1 \propto S^2 M^{\beta} \exp(E_2/RT) \qquad (1)$$

where S is the usual nematic order parameter and $E_2 \approx 17.8$ kcal/mol is an apparent activation energy, which was found independent of M. The study mentioned above was based on a limited number of samples. In some cases, the molecular mass distribution was not known. Consequently, the molecular mass dependence of γ_1 could not be described with precision. Nevertheless, from the limited data, it was obvious that the average value of β was near 5. Two regimes could, however, not be excluded: one for small M with $\beta > 5$ and the other for larger M with $\beta \lesssim 4$, the change in behavior occurring around a critical mass $M_c \sim 5000$ where both the nematic–isotropic transition temperature T_{NI} and the corresponding enthalpies and entropies of transition exhibit a change in behavior as a function of M.

In this paper, we describe a much more detailed study of a similar polymer poly[oxy(3-methyl-1,4-phenylene)-azoxy(2-methyl-1,4-phenylene)oxy(1,12-dioxo-1,12-dodecanediyl)] (DDA9), differing from the AZA9 polymer by the number (10 instead of 7) (and parity) of methylene groups in the spacer. Particular attention was paid to the characterization of samples in terms of molecular mass distribution and to the possible influence of an isotropic component (N + I biphase) that exists in all samples depending on temperature. A detailed study of this biphase and its influence on the nematic properties of such thermotropic polymers was reported elsewhere.[2-4]

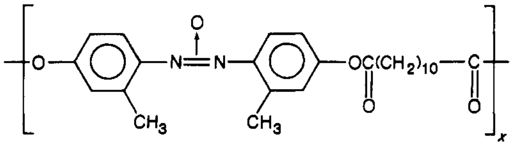

Table I
Physical Data for DDA9 Polymer Samples

sample	$\bar{x}$[a]	M_n(GPC)	M_n(visc)	T_{KN}[b]	T_{NI}[b]	T_{IN}[b]	T_{NK}[b]
2	25.0	11300	18100	123	166	155	74
3	18.6	8400	11000	123	163	152	86
4	17.5	7900	10000	121	161	152	86
5	15.3	6900	8500	121	159	149	88
6	14.1	6400	7550	120	159	149	87
8	12.1	5500	5200	118	157	147	80
10	10.4	4700	3700	116	151	142	81
11	8.9	4000	3050	114	147	139	76
12	6.7	3050	2800	107	140	132	64
13	5.6	2550	2000	98	129	123	55
14	5.0	2250	1500	89	121	116	51
5a	15.3	6900					
7a	8.4	3800					

[a] Degree of polymerization. [b] °C.

Materials and Methods

The synthesis of the DDA9 polymer is described elsewhere.[5] For the present study, a large amount of material was synthesized and fractionated. A large number of fractions were obtained from the same batch. The fractionation was performed by using a temperature gradient method.[6] The molecular masses were measured either by gel permeation chromatography (GPC)[7] or by viscometry[8] measurements. Some difference in the value of M is observed between the two methods. However, GPC is more reliable since it takes into account the actual mass distribution of each fraction. For this reason, the values of M deduced from GPC only have been used in this study. Figure 1 shows GPC curves $n(M_n)$ for some of the DDA9 samples used. The relation between the molecular mass M_n and the "elution distance" d_{el} quoted in Figure 1 was established by using DDA9 samples of known molecular masses. This relation is

$$\ln (M_n) = -0.07 d_{el} + 15.63 \qquad (2)$$

The value of the molecular mass M of each fraction was deduced from the relation

$$M = \bar{M}_n = \int n(M_n) M_n^{\alpha}\, dM_n \Big/ \int n(M_n) M_n^{\alpha-1}\, dM_n \qquad (3)$$

with $\alpha = 1$. Figure 1 shows that all curves are relatively narrow and have a regular bell shape, except fraction 10 and to a much lesser extent fractions 12 and 14, which exhibit a small hump or peak at large elution distance, revealing the existence of a small fraction of oligomers in these particular samples. This point will have some importance for the analysis (see below). The degree of polydispersity $\bar{M}_w/\bar{M}_n$ deduced from GPC curves is less than 1.1 for all samples ($\bar{M}_w$ is calculated from eq 3 with $\alpha = 2$). The various transition temperatures, solid to nematic T_{KN} and nematic to isotropic T_{NI} (on heating) or T_{NK} and T_{IN} (on cooling), were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-2C calorimeter, as described in ref 8. The physical data of all samples used in this study are collected in

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[*] To whom correspondence should be addressed.

[†] Centre d'Etudes Nucléaires de Grenoble.

[‡] University of Lowell.

[§] On leave from Institute of Organic Chemistry, Academia Sinica, Shanghai, Popular Republic of China.

[‖] Member of CNRS.

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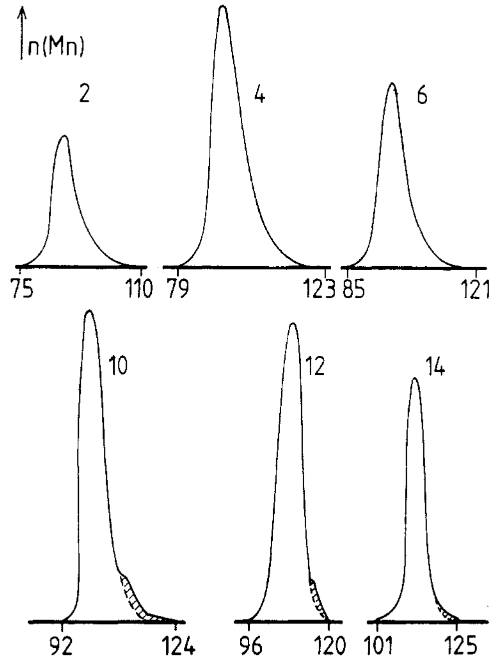

Figure 1. GPC curves of some of the DDA9 samples used (Table I). The horizontal scale is linear and represents the elution distance d_{el}, related to molecular mass M_n by eq 2.

Table I. All samples come from the same batch, except samples 5a and 7a.

Measurements of the twist viscosity coefficient γ_1 were performed by proton NMR using a Brüker CXP 90 pulse spectrometer working at 21.14 kG, by following the evolution of the line shape of a monodomain which has been rotated at a small angle to the static magnetic field of the spectrometer, at time 0. This angle was chosen equal to 27° in these experiments. The initially aligned samples were prepared by equilibrating at ~20 °C above T_{NI} during about 20 min and cooling in the nematic phase at the required temperature in the magnetic field of the spectrometer. This procedure allows the formation of nematic monodomains that are practically free from defects as revealed by the strongly orientation-dependent NMR line shapes.[16] The method and experimental details are described in ref 1 and 9. The analysis requires the value of the anisotropy of diamagnetic susceptibility per unit volume χ_a.[1] Magnetic measurements on one DDA9 sample (no. 14 in Table I) have been performed by using a SQUID magnetometer and the results are reported elsewhere.[10] If the influence of the second-order parameter $S_{xx} - S_{yy}$, whose increase with temperature is somewhat compensated by the decrease of the density, is neglected, it is found that χ_a for DDA9 polymers is approximately given by

$$\chi_a\ (\mathrm{cm^3/cm^3}) \approx 1.3 \times 10^{-7} S \qquad (4)$$

where $S = S_{zz}$ is the (usual) main order parameter which has been deduced from the main splitting of the ^{1}H NMR spectra as in ref 1. The corresponding coefficient in eq 4 for AZA9 polymers is $\approx 1.4 \times 10^{-7}$.[1,10]

Results and Analysis

The viscosity data were analyzed in terms of several models as in ref 1 with very similar results. Equation 1 was found to describe most of the data. Figure 2 shows the variation of γ_1/S^2 versus temperature in an Arrhenius plot, for 10 among the 13 samples considered. It is observed that parallel straight lines are obtained for all samples, showing that the (apparent) activation energy E_2 is independent of molecular mass, as for AZA9 polymers.[1] The present value of $E_2 \approx 15.3$ kcal/mol is comparable to the value ≈ 17.8 kcal/mol found for AZA9 polymers.[1]

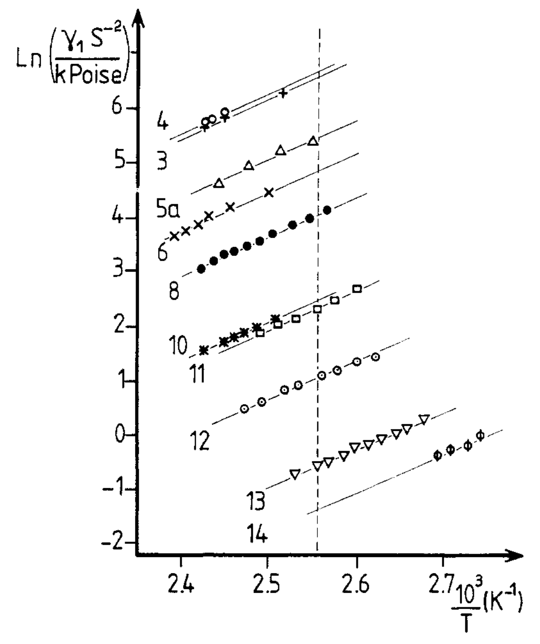

Figure 2. ln (γ_1/S^2) versus $10^3/T$ for 10 DDA9 samples (Table I). The slope of the parallel straight lines through the experimental points is $E_2 = 15.3$ kcal/mol ($E_2/R = 7700$ K). The vertical dashed line corresponds to 119 °C.

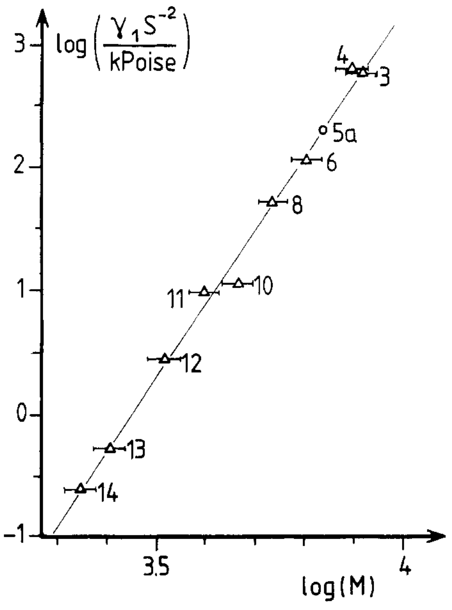

Figure 3. log (γ_1/S^2) versus log M at $T = 119$ °C deduced from Figure 2. The horizontal error bars on the values of M are deduced from the GPC curves. The slope of the straight line is 6.0.

More interesting is the molecular mass dependence. The results in Figure 2 suggest that the quantity γ_1/S^2 should be plotted versus molecular mass at fixed absolute temperature as in ref 1. Figure 3 shows γ_1/S^2 versus M at $T = 119$ °C in a log-log plot. It is observed that almost all points fall, with very good accuracy, on a straight line whose slope is 6. A fit yields $\beta = 6.0 \pm 0.3$. The errors bars in the figure correspond to the width of the GPC curves. Two points exhibit appreciable deviation from this straight line, namely, those corresponding to samples 10 and 4 in Table I. These deviations can be explained as follows: as seen in Figure 1, sample 10 is the only one for which the GPC curve shows a sizable extra peak at a large elution distance, indicative of the presence of oligomers. These oligomers may play the role of a plasticizer. We have verified that addition of a small amount of low molecular mass compounds, such as a few percent (~5%) of p-azoxyanisole, induces a measurable decrease of γ_1 in DDA9 and AZA9 polymers. Thus, in the absence of these oligomers, the viscosity would have been (slightly) higher,

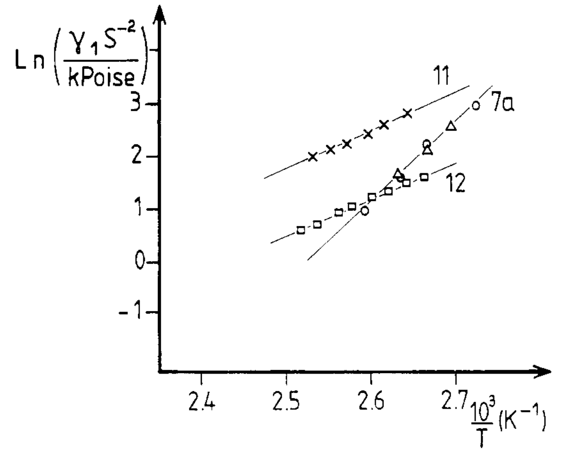

Figure 4. ln (γ_1/S^2) versus $10^3/T$ for sample 7a and for samples 11 and 12 for comparison. The slope for 7a is 29.5 kcal/mol whereas for 11 and 12 it is 15.3 kcal/mol (Figure 2).

bringing the point closer to the straight line.

A different explanation is invoked for sample 3. This sample is the only one which exhibits a N + I biphase throughout the entire mesomorphic interval (no pure N phase is observed before crystallisation). Since γ_1 is the twist viscosity of the N component of this biphase and since it is well established[2-4] that long macromolecules tend to accumulate in the nematic phase at the expense of the shorter accumulating in the isotropic component of the biphase, the (average) molecular mass of the nematic component is larger than the value deduced from the GPC curve. This again would bring the experimental point closer to the straight line.

We note that only 10 among the 13 samples considered in Table I have been analyzed. Sample 2 was too viscous and measurements of γ_1 for this sample would have required prohibitive time lengths for usual laboratory experiments (as expected from the M^6 law!). Sample 5, for reasons that are not clear at present, could never be aligned to obtain good monodomains. Finally, sample 7a gave results at variance with the other samples. Figure 4 shows γ_1/S^2 versus $10^3/T$ for sample 7a and for samples 11 and 12 for comparison, whose masses are larger and smaller than that of 7a. It is observed that although the dependence is linear, the slope is very different, corresponding to an apparent activation energy of ~29.5 kcal/mol, compared to 15.3 kcal/mol for all the other samples. This behavior is perfectly reproducible. Experiments performed with the same sample tube of 7a at several months intervals have yielded the same results within experimental accuracy. The origin of this behavior may be due to frequent manipulations of this sample at elevated temperatures and a corresponding increase in polydispersity.

This discussion shows the importance of the physicochemical aspect in this kind of study: a large number of sharp fractions with well-characterized molecular mass distribution are mandatory to obtain reliable experimental results from which a law can be deduced. Using the data shown in Figures 3 and 4, we have shown that for DDA9 polymers, γ_1 may be described by eq 1. The data are sufficiently accurate so that a value of the proportionality constant can be deduced. This value for DDA9 polymers is $K \approx 6.35 \times 10^{-30}$ $kP/(g/mol)^6$.

Discussion

The first point to be discussed is whether an equation such as eq 1 is unique for describing the data. The reader is referred to ref 1 for a detailed discussion. Two points can be stressed here. A power law for the molecular mass dependence is predicted by all theories[1] so that the form M^β is probably the only reasonable one. The difficulty in the interpretation is due to the value of β. A value as large as 6 is predicted so far only for nematic solutions of rigid rods[11] at constant volume fraction. Our system is thermotropic and the isolated polymers can be considered at most as semirigid, in which case the value of the exponent is predicted to be much smaller (≤3).[12] A theoretical explanation for our result is still to be found. The second point concerns the temperature dependence. It was stressed above that E_2 is only an apparent activation energy, corresponding to a pure Arrhenius law. However, a Vogel type law of the form

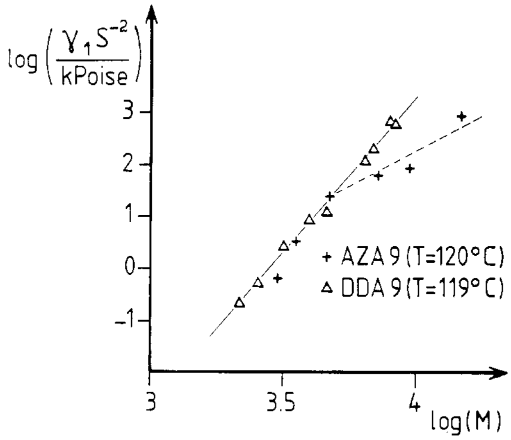

Figure 5. Comparison of γ_1/S^2 versus M for DDA9 polymers (this work) and AZA9 polymers (from ref 1). We note that whereas for log $(M) \leq 3.7$ $(M \leq 5000)$, the data for both polymers is consistent with the same M^6 law, for $M > 5000$ the slope is definitely smaller for AZA9 polymer. The slope of the dashed straight line is 3.4.

$$\gamma_1 \propto \exp[E'_2/(T - T_0)] \qquad (5)$$

where T_0 would be the "freezing temperature of the director", which is found in usual nematics,[1,13,14] is probably more reasonable. In our case, due to the high temperatures at which the nematic phase exists and to the relatively narrow nematic range, it is not possible to discriminate between the Arrhenius limit ($T_0 = 0$) and a situation with $T_0 \neq 0$. In fact, fits of eq 5 to the data of Figure 2 of comparable qualities are obtained for any value of T_0 ranging between 0 and ~160 K. The value of E'_2 is, however, a strong function of the value chosen for T_0 and decreases as T_0 increases, as for AZA9 polymers.[1] Study of γ_1 for a similar polymer with a very low value of T_{NK} would be of high interest in this respect. Indeed, for temperature points closer to T_0, the fit of eq 5 to the data is necessarily (much) more sensitive to the actual value of T_0.

Of interest also is the comparison of results for the DDA9 reported here with those obtained for AZA9 polymers.[1] The temperature dependence of γ_1/S^2 is the same, with comparable values of the activation energies, suggesting that the relaxation mechanism at the molecular level involves mainly the repeating unit, which is similar in both polymers. The molecular mass dependence is, however, different. As seen in Figure 5, whereas for $M < 5000$, the data for AZA9 are consistent with a power law with $\beta \approx 6.0$, for $M > 5000$ the exponent is definitely smaller. In contrast, for DDA9 polymers, $\beta = 6$ is valid until at least $M \sim 8400$. Since the square of the ratio of order parameters of DDA9 and AZA9 polymers is at most equal to 2, Figure 5 shows that for $M < 5000$ both polymers have comparable values of the twist viscosity, but for $M > 5000$ this viscosity is much smaller for AZA9 than for

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DDA9. The physical reasons why these polymers behave differently at large masses may be related to the molecular arrangement of the macromolecules in the nematic phase. AZA9 polymer is less ordered than DDA9 polymer for comparable masses (odd–even effect is *S*[6,10]) and is a usual nematic, whereas DDA9 is a cybotatic nematic.[6] It is possible that for DDA9, this extra order would shift the change in molecular mass behavior to values of *M* higher than 8500, but this question remains open.

Finally, it must be noted that the twist viscosity coefficient γ_1 studied in this paper is of different nature than the oscillatory shear viscosity η^* previously measured[14] in the same polymers. This latter coefficient is smaller by several orders of magnitude than the corresponding γ_1. In fact, as suggested by rheooptical experiments on a similar polymer,[15] the values of η^* measured in the experimental conditions of ref 14 (high angular frequency velocities) are probably close to those of the second Miesowicz shear viscosity coefficient η_b (nematic director along with line of constant velocity). This coefficient is predicted to be much less sensitive to chain length than γ_1.[12] This may explain why the values of η^* are comparable for both polymers (within a factor smaller than 2 related to differences in nematic ordering), even for masses as large as 15 000.[14]

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Registry No. DDA9 (SRU), 79079-27-9; DDA9 (copolymer), 120667-65-4.

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Biaxiality of Molecular Ordering in Some Main-Chain Nematic Polymers: A Combined NMR and Magnetic Susceptibility Study

P. Esnault, D. Galland, and F. Volino*,†

Centre d'Etudes Nucléaires de Grenoble, DRF/SPh/PCM 85X, 38041 Grenoble Cedex, France

R. B. Blumstein

Department of Chemistry, University of Lowell, Lowell, Massachusetts 01854.

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ABSTRACT: The biaxiality of molecular orientational order of main-chain thermotropic nematic polymers ME9-Sn, poly[oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy(α,ω-dixo-α,ω-alkanediyl)], has been studied by combined proton NMR, deuterium NMR, and magnetic measurements. The main result is that the well-established increase of order (S_{zz}) with chain length is essentially caused by an increase of the biaxiality $S_{xx} - S_{yy}$ via a decrease of S_{yy}, with S_{xx} remaining constant. In other words, the increase of order is due to a progressive reduction of the orientational fluctuations of the aromatic core in one plane only; fluctuations in the perpendicular plane are not affected. An odd–even effect with the number *n* of methylene groups in the spacer, in phase with that of S_{zz}, is found for $S_{xx} - S_{yy}$. This behavior is directly linked to the particular structure of the repeating unit, in which the plane of the mesogenic core makes a large dihedral angle with the plane of the linkage ester group.

Introduction

An important aspect in the study of (uniaxial) nematic phases is the description of the molecular orientational order. For rigid, noncylindrical, elongated molecules, this order is characterized by two parameters. The first-order parameter S_{zz} (uniaxial term) pictures the average orientation of the main principal axis 0*z* of the ordering matrix (0*z* is the "long molecular axis") with respect to the mean director and the second-order parameter $\delta = S_{xx} - S_{yy}$ (biaxial term) reflects the difference in ordering of the two minor principal (short) axes 0*x* and 0*y*. The quantity $\eta_s = \delta/S_{zz}$ is the anisotropy parameter of the molecular orientational order and is directly related to the difference between the amplitudes of librations around the 0*x* and 0*y* axes.

The earlier mean-field theories[1,2] predict that for the uniaxial phase, both S_{zz} and δ depend on molecular shape but that $\delta = 0$ for molecules with cylindrical symmetry.

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* To whom correspondence should be addressed.

† Member of CNRS.

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