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Molecular Weight Determination of Mesogenic Polyesters Using ^{1}H Nuclear Magnetic Resonance Spectroscopy

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A ^{1}H NMR method has been used for the molecular weight determination of mesogenic polydecamethylene-4,4'-fumaroyldioxy-dibenzoates (PDFOB). Experimentally observed and empirically calculated chemical shifts for all non exchangeable protons are in good agreement. The number-average molecular weight has been calculated from the ratio of integral intensities of resonances due to protons in the chain segments of the polymers to those from terminal protons. The correlation between molecular weight and intrinsic viscosity values is discussed. Results derived from NMR data are compared with those from other methods.

Keywords: proton spectroscopy, liquid crystal components.

INTRODUCTION

A fundamental property of all polymers is molecular weight. This property is of great importance since it is known in many instances

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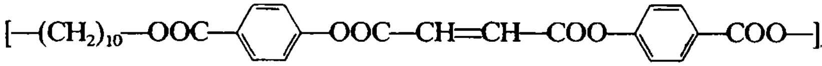
to affect various physical and mechanical properties of the polymers.

It has been shown[1-3] that a number-average molecular weight of a polymer can be obtained by high resolution NMR spectroscopy via a comparison of the integrated intensities of the signals from the end and internal group protons. The method is especially suited to cases in which the terminal group resonances are well resolved. A second requirement for precise results is high signal-to-noise ratios in the spectra.

Presently, we have used ^1H NMR to determine molecular weights of a series of poly-decamethylene-4,4′-fumaroyl-dioxy-dibenzoates (PDFOB)



These materials are of interest since they show liquid crystal properties with increasing values of *n*.

EXPERIMENTAL

a. Spectra

^1H spectra were obtained at 200 MHz with a Varian XL-200 NMR spectrometer. Samples were examined in 5 mm sample tubes as 3–4 weight % solutions in CD_2Cl_2, containing TMS as reference. Sweep width was 2000 Hz, with 32K data points and an acquisition time of 8.0 seconds. Pulse width was 45°, and typically 300 spectral accumulations were required for adequate signal to noise ratios. Temperature was 20.0°C.

Ratios of integrated intensities were calculated from peak areas determined by cutting and weighing procedures.

b. Materials

The synthesis of polymer samples was carried out according to[4] by polycondensation of 4,4′-fumaroyl-dioxy-dibenzoyl-dichloride (FOBCh) in diphenylether at 180°C with a flow of argon over the course of 2 hours. Putting non-equimolar amounts of monomers into polycondensation reactions allowed polymers with specific terminal groups to be obtained.

In this paper the results of study of nine PDFOB samples are presented. The samples can be divided into three series. Six polymers of the first series, samples **1–6**, were produced by polycondensation of FOBCh with an excess of 1,10-decane-diol. They have hydroxydecylene terminal groups. Two samples **7** and **8** of the second series

TABLE 1

Temperatures of phase transitions, T°C, and intrinsic viscosities, [η], of PDFOB samples

Sample	T_c, °C	η, dl/g
1	C 142°—144° I	0.25
2	C 145°—146° I	0.26
3	C 148°—149° I	0.29
4	C 154° I	0.43
5	C 160° I	0.51
6	C 164° LC 174° I	0.84
7	C 159° LC 184° I	0.42
8	C 164° LC 182° I	0.80
9	C 166° LC 175° I	1.03

were synthesized with an excess of FOBCh and so polymer molecules have 4-carboxy-phenyl end groups. The sample **9** has the terminal groups of both types. The presence of definite terminal groups helps in the study of polymer molecular weight by NMR.

Polymer intrinsic viscosities, [η], were measured with the aid of a Ubbelohde viscosimeter in $CHCl_3$ at 25°C. Phase transition temperatures, T_c^0, were measured by polarizing-optical microscopy using Boethius apparatus (Dresden, GDR). All the data on intrinsic viscosities and phase transition temperatures are collected in Table No. 1. The dependence of PDFOB intrinsic viscosity on the reagent ratio during synthesis is shown in Figure 1.

RESULTS AND DISCUSSION

a. PDFOB ¹H NMR spectrum analysis

Typical PDFOB high resolution spectra are shown in Figure 2. The difference between the spectra of Series I and the Series II samples is caused by the presence of different terminal groups in the polymer molecules. In the first group spectra the triplet from terminal α-methylene protons is observed near 3.58 ppm. Terminal OH proton resonances were not clearly distinguishable.

In the second polymer series the signal of the carboxyl proton is observed at 7.25 ppm *i.e.* between the phenyl and vinyl proton lines. That this line belongs to the carboxyl proton is confirmed by the fact that when D_2O is added into the sample immediately before the

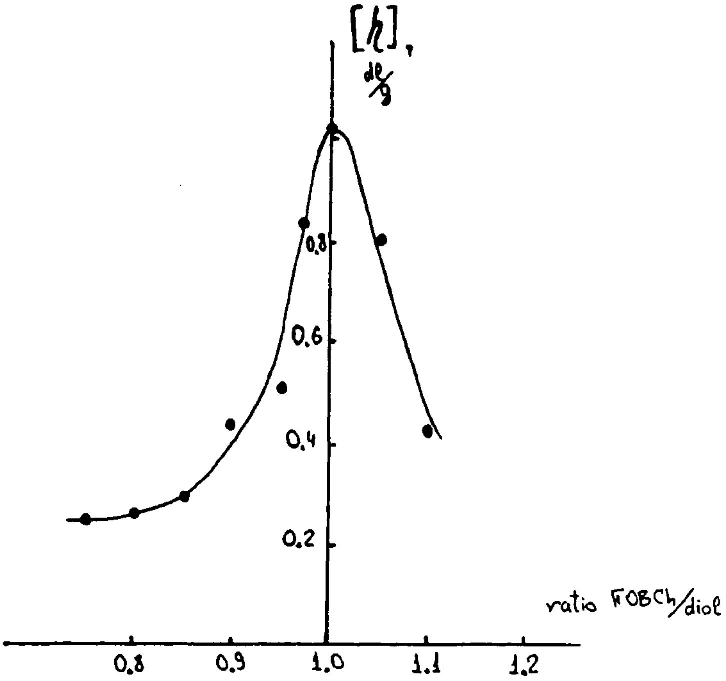


FIGURE 1 The dependence of PDFOB intrinsic viscosity on the reagent ratio.

experiment the line intensity markedly diminishes as a result of proton exchange. The spectrum of the sample **9** contains the signals of both α-methylene and carboxyl protons.

Analyses of the ^1H spectra were carried out by first order methods. The observed chemical shifts were compared to those calculated via application of known empirical rules for ^1H chemical shift data and results are collected in Table 2. For aromatic protons, the agreement between calculated[5] and observed results is within 0.1 ppm. In the case of the olefinic protons the application of the Tobey-Simon rules[6,7] yields calculated chemical shifts within 0.26 ppm of those observed.

In the case of methylene proton resonances, a recent report[8] has suggested modifications of the early rules of Shoolery[9] for the prediction of proton shifts. The modifications take into account "β" effects which were not included in the early work. For methylene protons of terminal CH_2OH groups, the original Shoolery rules lead to considerably better agreement between observed and calculated data. In contrast, for "internal" methylene protons the new parameters[8] give a slightly better fit between the experimental and calculated data.

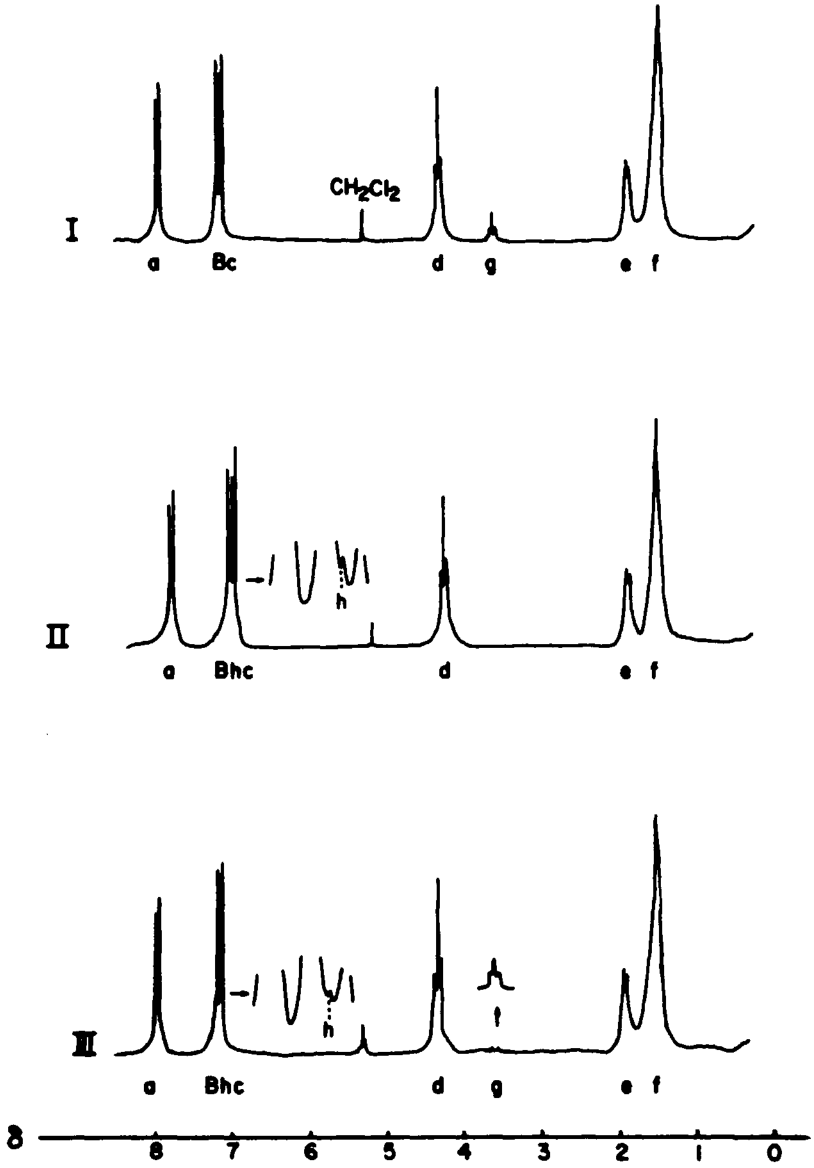
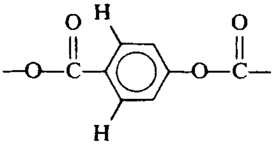
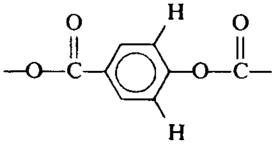
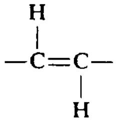
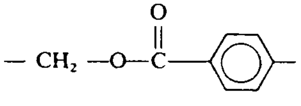
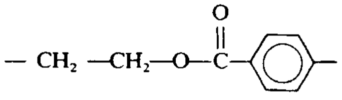
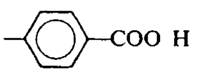


FIGURE 2 High resolution ^{1}H NMR spectra of PDFOB.
I—sample N 2; II—sample N 7; III—sample N 9.

TABLE 2

Calculated and Observed* ^1H Chemical Shifts of PDFOB

Line	Proton (s)	δ_H (obs'd)	δ_H (calc'd)	References
a)		8.10	8.01	5
b)		7.28	7.26	5
c)	 $-\overset{H}{C}=\underset{H}{C}-$	7.23	6.97	6,7
d)		4.31	4.11 4.03	8 9
e)		1.76	1.73	8
f)	$-CH_2-CH_2-OH$	1.35	1.43	8
g)	$-CH_2-OH$	3.58	3.46 3.27	9 8
h)		7.25	—	—

* –3–4% solutions (by wt.) in CD_2Cl_2

b. PDFOB number-averaged molecular weight determination

The comparison of the integral intensities of PDFOB spectrum components allows determination of the degree of polymerization, n, and, accordingly, the number-averaged molecular weight, M_n, for the samples under investigation. The value n is directly obtained from the

TABLE 3

Integral intensities of ¹H spectrum components, I, degree of polymerization, *n*, and molecular weight, M_n, of PDFOB samples. In parentheses quantity of protons producing the line is shown.

Sample	I (rel. units)					n	$M_n \cdot 10^{-3}$
	a, (4)	$b + c$, (6)	d, (4)	$e + f$, (16)	g (4)		
1	42.3	69.3	49.0	209	6.00	6.9	3.58
2	59.4	91.8	72.6	335	8.07	7.6	3.93
3	38.1	65.7	43.3	155	4.60	8.4	4.32
4	46.2	74.3	51.7	197	3.50	14	7.09
5	54.1	82.0	64.8	241	3.23	17	8.57
6	48.8	83.0	59.6	209	1.40	38	18.9
9	402	565	391	1523	1.22	(160)	(79)

intensity ratio of any spectrum line to the *g* or *h* terminal proton group line.

For the first series of the samples **1**–**6** in which the proton signal of α-methylene terminal groups is well resolved the *n* value is reliably measured with good accuracy. In increasing order its values are 6.9; 7.6, 8.4, 14, 17 and 38 for the studied PDFOB polymers (Table 3).

The verification of Mark-Kuhn formula $[\eta] = k.\ M_n^\alpha$, for this series shows that all the points fall on a straight line in the logarithmic scale

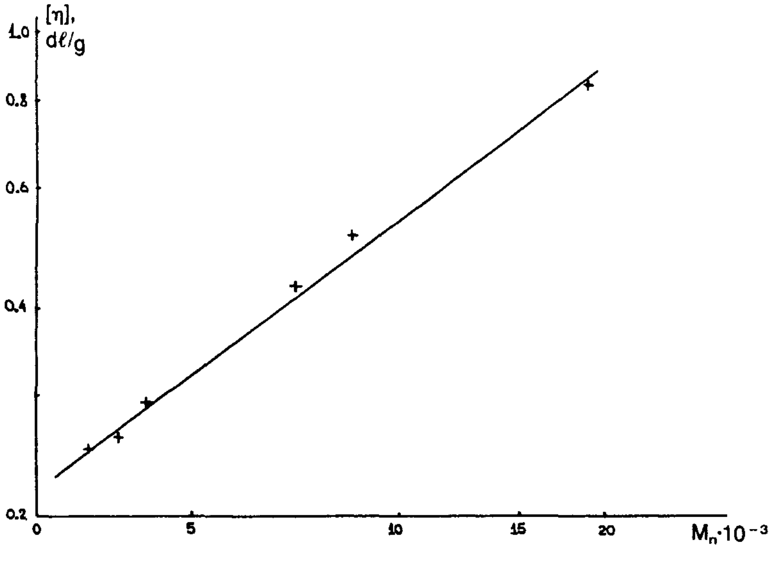


FIGURE 3 The dependence of intrinsic viscosity on number-averaged molecular weight.

(Figure 3). The index $\alpha = 0.74$, which characterizes the line inclination, is in good agreement with the results of Tsvetkov and others[10] for structurally similar polydecamethyleneterephthaloyl-bis-4-oxybenzoates.

The low intensity line *h* in spectra of samples **7** and **8** is observed against the background of strong lines *b* and *c*. Unfortunately, this fact leads to low precision in the line intensity measurements. Accordingly it is impossible to obtain the polymerization degree for PDFOB samples **7** and **8**.

Proton resonances from terminal groups of both types are observed in sample **9**. However, the line intensities are extremely low. For this sample 6,000 accumulations were required to obtain a good quality spectrum. Here again the *h* line intensity cannot be estimated reliably. Thus, the degree of polymerization is calculated only from intensity ratio of α-methylene proton line to other spectrum lines, the terminal groups of different types being assumed of equal probability.

The obtained value of *n* differs markedly from the data for the samples from **1** to **6**. The correspondent point, $M_n = 79 \cdot 10^3$, does not take place on Mark-Kuhn straight line. The difference can be explained by a number of factors. One factor responsible for it may be the removal of some residual hydroxyl groups, which constitute less than 1 percent of the initial proton quantity. This removal may result from a chemical side reaction, such as dehydration. The dehydration is not very significant with the greater amounts of OH-groups in samples **1–6**, but it could become statistically significant with very small amounts of OH protons present in sample **9**.

CONCLUSIONS

(a) The analysis of the ratio of integral intensities of the ^{1}H spectral lines provides the possibility for determination of number-averaged molecular weight in mesogenic PDFOB samples. If proton resonances of the terminal groups are well resolved, NMR spectroscopy provides reliable results in the polymer molecular weight range below $5 \cdot 10^4$.

(b) Empirical ^{1}H chemical shift correlations can be reliably applied to these polymeric materials. For internal methylene resonances, the recent modifications[8] to Shoolery's rules[9] give slightly better fits between calculated and observed parameters than do the original rules. Such is not the case, however, for methylene protons bonded to a carbon bearing a terminal OH function.

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