Macromolecules 1993, 26, 1595–1602

Characterization and Analysis of the Phase Behavior of Poly(1,4-phenylene 2,5-di-*n*-alkoxyterephthalate)s

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Received April 22, 1992; Revised Manuscript Received August 6, 1992

ABSTRACT: The synthesis and characterization of two poly(1,4-phenylene 2,5-di-*n*-alkoxyterephthalate)s (n = 6 and 16) with defined end groups is described. These materials represent stiff-chain polyesters with flexible side chains which exhibit sufficient solubility in common organic solvents and a melting point far below thermal decomposition. Analysis of the intrinsic viscosities as a function of molecular weight shows that these polyesters are semiflexible with a Kuhn length of the order of 10^2 Å. The various solid and liquid crystalline phases have been investigated by thermal analysis and wide-angle X-ray scattering. Polyesters with short side chains (n = 6) exhibit a glass transition, a smectic-like, layered mesophase, and a nematic mesophase which transforms to an isotropic phase. The material with long (n = 16) side chains exhibits a side chain melting, a smectic-like mesophase, and a transition to the isotropic phase. The occurrence of a layered mesophase can be explained by a microphase separation of the main and side chains. It is shown that the transition temperatures of the liquid crystalline phases reach plateau values with increasing molecular weight as expected for the semiflexible main chain.

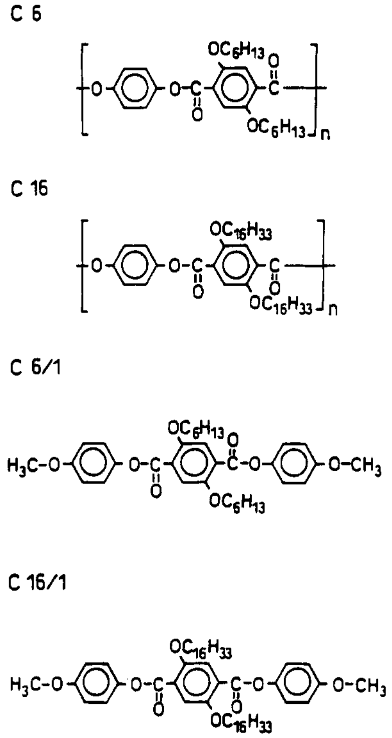
Introduction

Stiff-chain macromolecules substituted by flexible side chains present an interesting type of polymers since these materials very often exhibit sufficient solubility in common organic solvents and a melting point located far below the temperatures where thermal decomposition prevails.[1] This is in contrast to the situation encountered when studying the corresponding unsubstituted rigid rod polymers, which are mostly found to be insoluble. Also, melting points are located at very high temperatures if a melting transition is present at all.[2,3] The flexible side chains allow the transition points to be lowered in a systematic fashion and at the same time they increase the solubility. This observation is in accord with the notion that flexible side chains act much in the way of a "bound solvent" by increasing the entropy of dissolution and by screening the interaction between the rodlike main chains.[4,5]

Up to now a great variety of stiff-chain macromolecules with flexible side chains have been prepared and studied.[1,6] In many cases the sufficient solubility allowed an investigation of the solution properties. A point of particular interest is given by the various mesophases which can be observed in these systems due to the drastic lowering of the melting transition. Here it has been shown[7-9] that most of these systems form a novel, layered mesophase akin to the smectic type in low-molecular-weight systems. Such a layered mesophase was first observed[7] on the poly(1,4-phenylene 2,5-di-*n*-alkoxyterephthalate)s (Chart I).

The organization of these materials in the solid state as well as in the mesophase is governed by layered structures. Two modifications termed A and B differing in layer spacing were found.[8] Figure 1 displays the structural organization suggested for the poly(1,4-phenylene dialkoxyterephthalate)s.[8,10]

Chart I



The driving force for such an organization is the unfavorable interaction between the polar main chains and the apolar alkyl side chains. Hence, the formation of layered structures in the solid state and in the molten state can be compared best with the microphase separation in block copolymers. Therefore the stability of the layered structure at elevated temperature will dependent on the length of the side chains in comparison to the length of the main chains. The latter factor comes into play because the steric repulsion of the main chains is the primary cause for the formation of the liquid crystalline phase. Shortening of the side chain at constant length of the main chains will destabilize the smectic-like spatial organization and leads to the observation of an ordinary nematic phase. In consequence, for alkyl side chains comprising 5–6 carbon atoms a transition from the smectic-like to the nematic phase can be observed.[11]

In this paper we wish to report a comprehensive study of the poly(1,4-phenylene 2,5-di-*n*-alkoxyterephthalate)s

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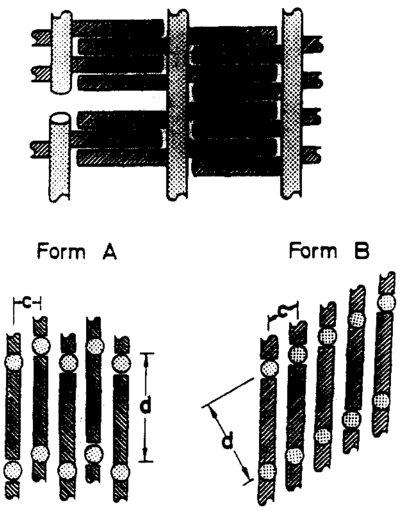


Figure 1. Scheme of the structural organization of the main and side chains in polyesters C*n* according to refs 8 and 10.

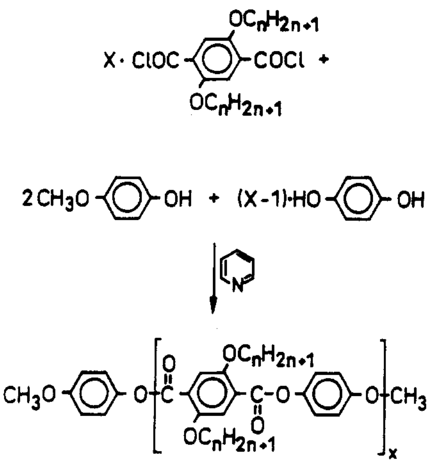
having hexyloxy side chains, termed C6, and hexadecyloxy side chains, termed C16. Since previous studies[12] have revealed that open hydroxy and carboxy end groups may influence the solution properties, a precalculated amount of 4-methoxyphenol was used to avoid end groups and to adjust the degree of polymerization to a given value. The polyesters are termed according to the theoretical number-average degree of polymerization (DP); e.g., C6/30 is a material with hexyloxy side chains polymerized in the presence of 4-methoxyphenol to obtain a DP of 30. For investigations in the oligomeric range, two model compounds, C6/1 and C16/1, were prepared by condensation of the respective acid dichlorides and methoxyphenol. By comparison of data obtained for different lengths of the main and side chains, the factors governing the stability of the mesophases can be discussed in detail.

Experimental Section

Materials and Methods. Toluene (analytical grade, Riedel de Haen) and pyridine (analytical grade, Fluka) were purified and dried by distillation over metallic sodium. 4-Methoxyphenol and hydroquinone (both analytical grade, Fluka) were sublimated prior to use. Thionyl chloride (analytical grade, Riedel de Haen) was purified by distillation. All other solvents and reagents were analytical grade and used as received. The 2,5-di-*n*-alkoxyterephthalic acid dichlorides were prepared as described previously.[7] The compound with the short side chains ($n = 6$) was purified by sublimation; the corresponding acid dichloride bearing the long side chains ($n = 16$) was recrystallized repeatedly from toluene and dried carefully in vacuo.

^{1}H- and ^{13}C-NMR spectra were recorded at room temperature in deuteriochloroform using a Bruker AC 400 spectrometer. Tetramethylsilane (TMS) served as an internal standard. Osmometric measurements were performed using the Knauer Membranosmometer 01.00 at 50 °C in *o*-dichlorobenzene. The membrane was made from regenerated cellulose. Vapor pressure osmometry was recorded on a Hitachi-Perkin-Elmer HPE-115 using chloroform at 25 °C. The densities of the solutions were determined using the DMA-60 apparatus supplied by A. Paar (Graz, Austria). Thermal analysis was performed using a Mettler TC 11 apparatus at a heating rate of 10 or 20 K/min. Wide-angle X-ray analysis (WAXS) was monitored with Cu Kα radiation in reflection using a Siemens D-5000 diffractometer equipped with a hot stage. Polarizing microscopy was done with a Zeiss Universalmikroskop equipped with a Mettler FP 82 hot stage. Gel permeation chromatography (GPC) was run using two columns (PSS Gel SDV 10^3 Å, 5 μm, and SDV 10^5 Å, 5 μm; Polymer-Standard Service, Mainz, FRG). Chloroform stabilized with 60 ppm amylene was used as eluent throughout all measurements. Viscosity measurements were performed using Ubbelohde viscosimeters with different widths of the capillaries.

Scheme I



Polycondensation. All polymer syntheses were done in *o*-dichlorobenzene with prescribed amounts of 4-methoxyphenol according to Scheme I. Hence, at full conversion all polyester molecules bear two 4-methoxyphenol end groups, the amount of which can be determined by ^{1}H-NMR spectroscopy. Thus for the synthesis of a polyester with degree of polymerization x, 0.02 mol of acid dichloride, $(1 - 1/x) \times 0.02$ mol of hydroquinone, and $2/x \times 0.02$ mol of 4-methoxyphenol were suspended in 100 cm^3 of *o*-dichlorobenzene with full exclusion of moisture. After dissolution of all reactants at ~120 °C, 22 mL (0.27 mol) of pyridine was slowly added with vigorous stirring at a temperature of approximately 100 °C under an atmosphere of dry nitrogen. After each addition of pyridine a transient red color appeared which probably originates from a charge-transfer complex of the base with the acid dichloride. The solution became more and more viscous and exhibited a slight yellowish color after full conversion. After the solution was stirred for an additional 3 h, it was poured into a fivefold volume of methanol. The precipitated polymer was filtered off and dried in vacuo. For purification the polyester was dissolved in chloroform and precipitated in methanol. After careful drying in vacuo, the purity of the material was checked by ^{1}H-NMR spectroscopy.

C6 polymer: ^{1}H-NMR (400 MHz, CDCl$_3$) δ 0.91 (m, 6 H, CH_3), 1.46, 1.52 (m, 12 H, $(CH_2)_3CH_3$), 1.89 (m, 4 H, OCH_2CH_2), 3.85 (s, 6 H, OCH_3), 4.11 (m, 4 H, OCH_2), 6.95 (d, 4 H, $H_3CO(ArH)$), 7.16 (d, 4 H, $H_3CO(ArH)$), 7.33 (d, 4 H, $O(ArH)O$), 7.60 (m, 2 H, $CO(ArH)CO$).

C16 polyester: ^{1}H-NMR (400 MHz, CDCl$_3$) δ 0.85 (m, 6 H, CH_3), 1.20–1.38 (m, 48 H, $(CH_2)_{12}CH_3$), 1.50 (q, 4 H, $CH_2(CH_2)_{12}$), 1.85 (q, 4 H, OCH_2CH_2), 3.81 (s, 6 H, OCH_3), 4.10 (t, 4 H, OCH_2), 6.95 (d, 4 H, $H_3CO(ArH)$), 7.15 (d, 4 H, $H_3CO(ArH)O$), 7.30 (m, 4 H, $O(ArH)O$), 7.85 (s, 2 H, $CO(ArH)CO$).

The model compounds C6/1 and C16/1 were prepared by the same method from the respective acid dichloride **1** and an excess of 4-methoxyphenol (**2**) in practically quantitative yield. The product was purified by recrystallization from ethanol and dried in vacuo.

C6/1: mp 95.6 °C; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 0.88 (t, 6 H, CH_3), 1.30, 1.48 (m, 12 H, $(CH_2)_6CH_3$), 1.84 (m, 4 H, OCH_2CH_2), 3.81 (s, 6 H, OCH_3), 4.10 (t, 4 H, OCH_2), 6.95 (d, 4 H, $H_3CO(ArH)$), 7.15 (d, 4 H, $H_3CO(ArH)$), 7.55 (s, 2 H, $OCO(ArH)$).

C16/1: mp 76.4 °C; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 0.87 (t, 6 H, CH_3), 1.22 (m, 48 H, $(CH_2)_{12}CH_3$), 1.50 (q, 4 H, $OCH_2CH_2CH_2$), 1.81 (q, 4 H, OCH_2CH_2), 3.81 (s, 6 H, OCH_3), 4.08 (t, 4 H, OCH_2), 6.92 (d, 4 H, $H_3CO(ArH)$), 7.12 (d, 4 H, $H_3CO(ArH)$), 7.52 (s, 2 H, $OCO(ArH)$).

Results and Discussion

Characterization in Solution. The first goal of the present work is a full characterization of the polyesters C6 and C16 with regard to molecular weight and molecular weight distribution. As mentioned in the introduction, the materials under consideration here exhibit a sufficient solubility in a number of organic solvents. Previous

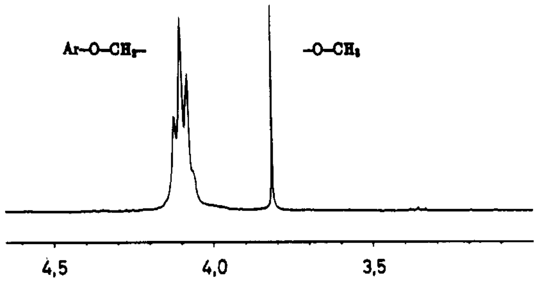


Figure 2. Enlarged part of the ^{1}H-NMR spectra of a C16 polyester. The number-average degree of polymerization $P_{n,NMR}$ is determined from the ratio of the methylene triplet at 4.10 ppm to the singlet of the methoxy end groups at 3.81 ppm.

investigations had shown,[12] however, that association may interfere with the measurements. The solvent must be carefully chosen to avoid gelation. In the course of this investigation it became furthermore apparent that polyesters with open carboxyl end groups behave differently in solution, most probably because of end-to-end association. Therefore all polyesters used in this investigation bear a well-defined 4-methoxyphenol end group, which can be easily monitored by ^{1}H-NMR. Figure 2 displays the enlarged part of a ^{1}H-NMR spectra of the polyester C16/10-2 dissolved in deuterated chloroform.

The singlet of the methoxy protons at 3.81 ppm is clearly separated from the triplet at 4.10 ppm of the first CH_2 group of the side chains. From the ratio of these signals the number-average degree of polymerization $P_{n,NMR}$ (cf. Tables I and II) was calculated. The theoretical number-average degree of polymerization $P_{n,th}$ was calculated from the ratio of hydroquinone to 4-methoxyphenol. Tables I and II contain the respective values for polyesters C6 and C16. Satisfactory agreement of $P_{n,th}$ and $P_{n,NMR}$ is achieved, at least for smaller degrees of polymerization.

For degrees of polymerization beyond 30, the signal of the end groups becomes smaller and smaller and the end group analysis is less secure. A further problem of the NMR analysis (cf. Figure 2) is the fact that P_n is overestimated when only one end group is closed, i.e., in the case of an incomplete reaction leading to open carboxyl end groups. Another possible source of error might be a certain loss of oligomers during precipitation into methanol. It is hence of great importance to employ an independent absolute method for determination of the molecular weight.

Unfortunately, the still limited solubility of the C_n polyesters renders the application of the usual methods for measuring molecular weights a very difficult task. It turned out that only membrane osmometry conducted at 50 °C in o-dichlorobenzene is suitable to determine P_n with sufficient accuracy, at least in the case of the C16 materials. Figure 3 gives examples of plots of the reduced osmotic pressure π/c as a function of concentration. In all cases investigated here the solutions of C16 led to linear plots which allowed the extrapolation to vanishing concentration. The resulting values of $P_{n,osm}$ are collected in Table II. Attempts to determine P_n of the C6 polyester under the same conditions failed since the osmotic pressure was not reproducible and plots of π/c versus c were highly nonlinear. The temperature of 50 °C is obviously not yet sufficient for the C6 materials to suppress association to a sufficient degree. The difference between the C6 and the C16 materials must be due to the much shorter side chains of the former polyesters. Higher temperatures could not be employed since the membrane made of regenerated cellulose would not be stable anymore under such conditions. Therefore no data on $P_{n,osm}$ could be recorded for the C6 polyesters.

The $P_{n,osm}$ obtained for the C16 polyesters compare favorably with the data determined previously by ^{1}H-NMR analysis if the P_n does not exceed values of 30. Beyond this point $P_{n,osm}$ are considerably lower than the respective $P_{n,NMR}$. This finding mainly reflects the shortcomings of the NMR analysis already discussed above. On the other hand, for the discussion of $P_{n,osm}$ one has to bear in mind that molecules with small degrees of polymerization may be able to permeate the membrane. Thus the stability of π over an extended period of time (1 h) was checked carefully. Attempts to measure the osmotic pressure of the C16/10 materials (cf. Table II) indeed were unsuccessful because a part of the material obviously permeated the membrane slowly. In this case the molecular weight could be determined by vapor pressure osmometry.

The second virial coefficient A_2 found from the plot of π/c (Figure 3) is of the order of 2×10^{-3} cm^3 mol/g^2 in all cases studied herein. This magnitude is expected for an extended, rodlike polymer.[13,14] Within the present limits of error A_2 was found to be independent of molecular weight. This fact also points to an approximately rodlike structure[14] but the present data are too scarce to allow a more extended interpretation.

The foregoing discussion has demonstrated that the number-average degree of polymerization P_n can be obtained for C6 and C16 with an error increasing with molecular weight. Attempts to employ static light scattering on solutions of C16 in cyclohexane/$CHCl_3$ were unsuccessful since there was the clear indication of strong association. To check the consistency of the present data of the molecular weights and to obtain the respective weight-average degrees of polymerization P_w, a viscosimetric investigation of the C6 and the C16 polyesters was combined with analysis by gel permeation chromatography (GPC). For this purpose the intrinsic viscosities $[\eta]$ of both polyesters were determined at 25 °C in $CHCl_3$ and at 80 and 150 °C in o-dichlorobenzene. In all cases the maximum concentration used was of the order of 1%, and the extrapolation to vanishing concentration according to Huggins[13] provided no difficulties. The Huggins constants were typically located between 0.2 and 0.5 cm^6/g^2. The resulting intrinsic viscosities are gathered in Tables I and II. The analysis of the polyesters by GPC was done by a trial-and-error method as follows: The columns were first calibrated using narrowly distributed polystyrene samples of narrow molecular weight distribution. The P_w values of the polyesters C6 and C16 were estimated from a trial value of the polydispersity P_w/P_n. The maximum of the GPC peak then served for the determination of an approximate calibration curve[13] which in turn could be used for the determination of P_n and improved data of P_w. The P_w also gave access to the cofficient K and the exponent a of the $[\eta]$–M_w (Mark–Houwink) relation. At this point the universal calibration curve could be determined using the polystyrene standards which led to improved data for P_w. In addition to this, the good resolution of the GPC columns allowed the direct determination of the elution volumes of the oligomeric species both for C6 and for C16 polyesters. The assignment of the degree of polymerization was done by comparison with the elution volume of the triads C6/1 and C16/1. The entire process was repeated until full consistency was reached. Figure 4 shows the calibration curve relating to the C16 polyesters. A result of similar accuracy was obtained for the C6 material. The crosses refer to the polystyrene calibration, and the good agreement of the data points of the C16 materials (circles) with the universal calibration curve in the range $10^4 \le M_w \le 10^5$ is evident. In the oligomeric range there is a deviation

Table I
Characterization of the Polyesters C6

	$P_{n,th}$	$P_{n,NMR}$	$M_{n,GPC}$	$M_{w,GPC}$	$(M_w/M_n)_{GPC}$	[η] ($CHCl_3$, 25 °C)	[η] (DCB, 80 °C)
C6/10-1	10	13	6 300	18 200	2.9	0.42	0.22
C6/10-2	10	13	4 100	15 300	3.7	0.35	0.20
C6/10-3	10	12	3 400	13 200	3.9	0.29	0.16
C6/10-4	10	12	4 200	15 000	3.6		
C6/20-1	20	25	7 700	29 100	3.8	0.67	0.38
C6/20-2	20	22	9 400	34 600	3.7	0.78	0.44
C6/20-3	20	21	12 700	40 900	3.2	0.91	0.52
C6/30-1	30	35	17 700	54 000	3.1	1.14	0.85
C6/30-2	30	30	21 700	60 000	2.8	1.21	0.87
C6/30-3	30	32	19 000	58 200	3.1	1.25	0.69
C6/30-4	30	31	10 000	35 800	3.6		
C6/40-1	40	40	18 100	53 800	3.0	1.20	0.90
C6/40-2	40	36	23 700	69 600	2.9	1.59	1.12
C6/40-3	40	(42)	9 200	39 500	4.3	0.84	0.48
C6/50-1	50	(49)	15 400	52 900	3.4	1.19	0.70
C6/50-2	50	(60)	10 100	38 900	3.9	0.90	0.52
C6/50-3	50	(48)	10 600	49 200	4.7	1.06	0.64
C6/50-4	50	(52)	6 400	22 800	3.5		
C6/70-1	70	(80)	11 900	47 500	4.0		

Table II
Characterization of the Polyesters C16

	$P_{n,th}$	$P_{n,NMR}$	$M_{n,osm}$	$M_{n,GPC}$	$M_{w,GPC}$	$(M_w/M_n)_{GPC}$	$[\eta]^b$	$[\eta]^c$	$[\eta]^d$	$[\eta]^e$
C16/10-1	10	10	6 200[a]	6 400	20 900	3.3	0.36	0.25		0.27
C16/10-2	10	10		6 200	18 600	3.0	0.28	0.24	0.19	0.26
C16/20-1	20	20	12 200	10 200	35 300	3.5	0.52		0.32	0.48
C16/30-1	30	29					0.88			
C16/40-1	40	37	20 800	16 500	57 700	3.5	0.91	0.60	0.56	
C16/50-1	50	51	28 000	25 200	89 100	3.5	1.30	0.83	0.65	
C16/50-2	50	49	23 000	14 400	56 900	4.0	0.84	0.62	0.58	0.77
C16/70-1	70	(80)	17 300	12 900	50 400	3.9	0.69	0.54	0.40	0.62
C16/80-1	80	(68)	30 500	26 200	99 000	3.8	1.32	1.02	0.86	1.24

[a] Determined by vapor pressure osmometry. [b] Chloroform, 25 °C. [c] o-Dichlorobenzene, 80 °C. [d] o-Dichlorobenzene, 150 °C. [e] Chloroform/cyclohexane (50:50 by volume), 25 °C. Unit of the intrinsic viscosity: dL/g.

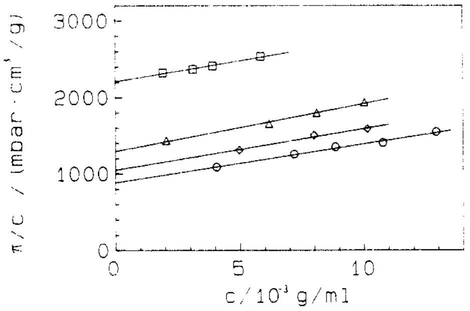


Figure 3. Reduced osmotic pressure π/c as a function of concentration c for several C16 polyesters. The measurements have been done in o-dichlorobenzene at 50 °C. (□) C16/20-1; (△) C16/40-1; (◇) C16/50-1; (○) C16/70-1.

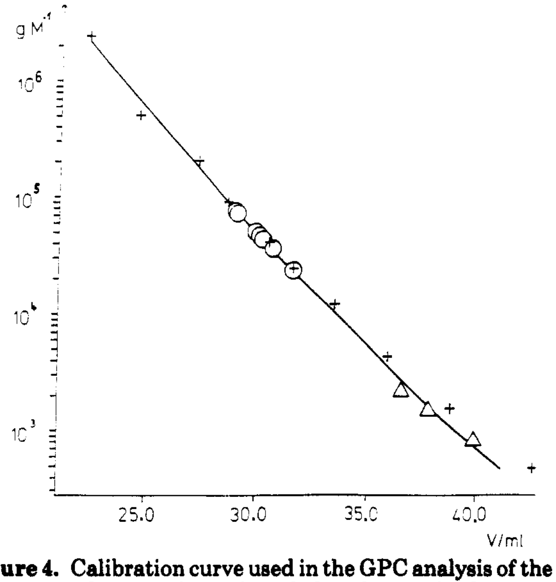


Figure 4. Calibration curve used in the GPC analysis of the C16 polyesters. Open circles, values deduced from the C16 samples; crosses, values deduced from the polystyrene calibration; open triangles, elution volumes of defined oligomers. See text for further explanation.

of the polystyrene calibration and the measured elution volumes (triangles). Here only the directly measured elution volumes of the oligomers which could be resolved by GPC have been used for calibration. In the region of high molecular weights ($M_w > 10^5$) the present calibration rests on the polystyrene points and the validity of the concept of universal calibration. The good agreement found in the intermediate range, however, suggests that the calibration curve certainly may be used in this range, too. Since the calibration curve covers the full range of elution volumes, the values of the weight-average molecular weight M_w obtained from the above GPC analysis present a data base of sufficient accuracy for the subsequent discussion. Also, the $P_{n,GPC}$ data, which are in sufficient agreement with the results of the end group analysis and membrane osmosis, lead to the conclusion that the analysis is self-consistent within the limits of error. All results of the GPC analysis are collected in Tables I and II.

The polydispersity P_w/P_n is in all cases considerably higher than 2. A possible explanation of this observation may be sought in a change of reactivity with molecular weight (cf. the discussion of this point in ref 15). Recently, a careful experimental study of the polydispersity of nylon

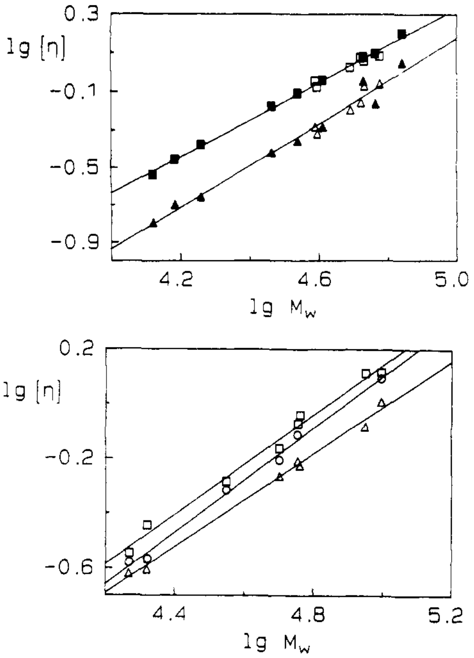


Figure 5. Mark–Houwink plot of polyesters C6 (a, top) and of polyesters C16 (b, bottom) (a): (□) $CHCl_3$, 25 °C; (△) o-dichlorobenzene, 80 °C. (b): (□) $CHCl_3$, 25 °C; (△) o-dichlorobenzene, 80 °C; (○) $CHCl_3$/cyclohexane, 25 °C. Filled symbols in (a): data used for GPC calibration.

610 as a function of the different methods of polycondensation has been presented by Arai et al.[16] These authors could show that a high-temperature melt polycondensation indeed leads to values of P_w/P_n of the order of 2 as expected from theory. However, a low-temperature polycondensation using the free amine and the acid dichloride together with an acid acceptor resulted in polydispersities up to 6.52. The study by Arai et al. therefore demonstrates clearly that a low-temperature method similar to the one employed herein is followed by a much broader molecular weight distribution.

The Mark–Houwink relations of both types of polyesters in different solvents may now be discussed. Parts a and b of Figure 5 show the data for C6 and C16, respectively. In the case of C6 (Figure 5a) only the filled triangles had been used to determine the $[\eta]$–M_w relation as discussed above. The plots show that the entire set of data can be described by the following Mark–Houwink relations ($[\eta]$ in dL/g):

C6/*n* in $CHCl_3$ at 25 °C:

$$[\eta] = 3.08 \times 10^{-3} M_w^{0.97}$$

C6/*n* in o-dichlorobenzene at 80 °C:

$$[\eta] = 4.05 \times 10^{-4} M_w^{1.12}$$

C16/*n* in $CHCl_3$ at 25 °C:

$$[\eta] = 3.9 \times 10^{-3} M_w^{0.91}$$

C16/*n* o-dichlorobenzene at 80 °C:

$$[\eta] = 5.5 \times 10^{-3} M_w^{0.85}$$

The respective values for the C16 polyesters in o-dichlorobenzene at 150 °C are $K = 3.6 \times 10^{-3}$ and $a = 0.87$, but these figures are less secure than the above results. Since possible association might inflict these results, a mixture of $CHCl_3$ and cyclohexane (50:50 vol %) was also employed for the C16/*n* in addition to the above one-component systems. The reason for the choice of this mixed solvent is given by the fact that the tendency for gelation at lower temperatures was found to be very low in these solutions.

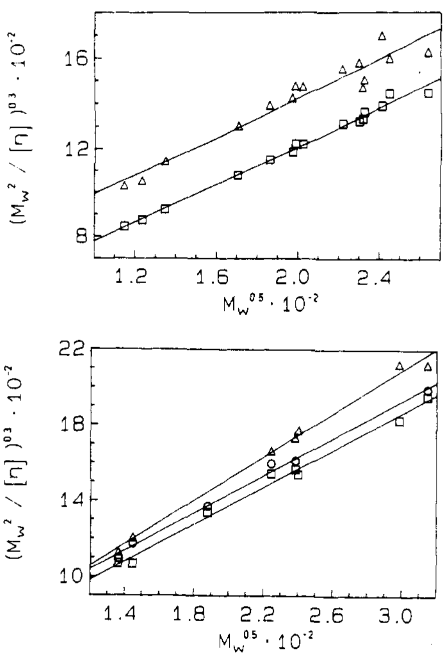


Figure 6. Bohdanecky plots of polyesters C6 (a, top) and of polyesters C16 (b, bottom). (a): (□) $CHCl_3$, 25 °C; (△) o-dichlorobenzene, 80 °C. (b) (□) $CHCl_3$, 25 °C; (△) o-dichlorobenzene, 80 °C; (○) $CHCl_3$/cyclohexane, 25 °C.

The resulting Mark–Houwink relation is

C16/*n* in $CHCl_3/C_6H_{12}$ at 25 °C:

$$[\eta] = 2.2 \times 10^{-3} M_w^{0.95}$$

All data are subject to the uncertainties mainly caused by errors in the determination of M_w.

The present data of the exponent a are slightly lower than the values obtained previously for the poly(3-alkyl-4-hydroxybenzoate)s.[17] They are located in a range typical for semiflexible polymers. As expected, the intrinsic viscosity decreases with increasing temperature, which reflects a certain loss of chain stiffness.

A more quantitative discussion of the hydrodynamic data can be done in terms of the wormlike chain model developed by Yamakawa and Fuji,[18] which allows the calculation of the Kuhn length l_K from $[\eta]$. Bohdanecky[19] has shown that this evaluation can be done elegantly by the following plot:

$$(M^2/[\eta])^{1/3} = A_\eta + B_\eta M^{1/2}$$

where A_η is a quantity depending on the hydrodynamic diameter of the chains and B_η is a quantity depending on the hydrodynamic diameter of the chains and B_η can be expressed as

$$B_\eta = B_0 \Phi_{0,\infty}^{-1/3} (\langle r^2 \rangle_0 / M)_\infty^{-1/2}$$

where $\langle r^2 \rangle_0$ is the unperturbed mean-square end-to-end distance and the subscript ∞ indicates that the ratio of $\langle r^2 \rangle_0$ and M is taken in the random-coil limit. The quantity $\Phi_{0,\infty}$ is the viscosity function for infinite chain length. The value used by Bohdanecky ($\Phi_{0,\infty} = 2.86 \times 10^{23}$) was taken for all calculations. The quantity B_0 varies between 1.10 and 1.00 and can be approximated by the mean value of 1.05 at the present level of accuracy.

Parts a and b of Figure 6 display the Bohdanecky plots for C6 and C16. In all plots the weight-average molecular weight obtained above has been used. The plots displayed in Figure 6 show that the Bohdanecky relation is fulfilled within the given limits of error. Hence the slope may be used to evaluate the Kuhn length $l_K = \langle r^2 \rangle_0 / N l_u$, where

$N = M/M_u$, with M_u and l_u being the mass per unit length and the length of the monomer unit (l_u = 12.6 Å[20]), respectively. The data for C16 in $CHCl_3$ and for the mixed solvent chloroform/cyclohexane thus lead to $l_K \sim 130$ Å, whereas the respective value for C6 results in ~100 Å. In *o*-dichlorobenzene at 80 °C a Kuhn length of approximately 100 Å results for both systems, whereas the data in the same solvent at 150 °C point to a reduction of the Kuhn length.

These values are of the same order of magnitude as found previously for the related poly(3-alkyl-4-hydroxybenzoate)s.[17] As already discussed in ref 15, all these data support the prediction of Jung and Schürmann[21] that the Kuhn length of the polyesters under consideration here are mainly limited by bond-angle fluctuations of the ester group. Therefore l_K is greatly reduced when compared to values calculated[20] with neglect of the out-of-plane fluctuation of the ester groups. It has to be noted, however, that the values of the persistence length as obtained from the Bohdanecky procedure must be regarded as a lower bound.[22] This is in agreement with a recent study by Krömer et al.[23] on a polyester with a very related structure by light scattering. Here a Kuhn length of the order of 240 Å has been found by application of a much more direct method.

Despite these uncertainties the present data show that l_K is not solely a property of the isolated chain but depends also on the interaction with the solvent. Similar effects have been observed[24] on poly(*n*-hexyl isocyanate)s and explained by local interactions of the solvent with the polymer chains.[25] An explanation in terms of coil expansion or contraction due to the excluded volume effect as a function of solvent power seems not to be feasible, since even the longest chains contain only up to 10 Kuhn segments (cf. also ref 22 for a discussion of this point).

To assess the interaction of the polyesters with the different solvents in more detail, the hydrodynamic diameter d of the chains was evaluated from the intercept A_η. According to Bohdanecky[19]

$$d_r^2/A_0 = (4\Phi_{0,\infty}/1.215\pi N_A)(\bar{v}/A_\eta)B_\eta^4$$

with $d_r = d/l_K$ being the reduced hydrodynamic diameter of the chain and $\bar{v}$ the partial specific volume of the polymer in solution. The ratio A_0 is related to d_r by

$$\log(d_r^2/A_0) = 0.173 + 2.158\log(d_r)$$

The partial specific volume $\bar{v}$ has been measured for solutions of C16 in *o*-dichlorobenzene and results to 1.00 cm^3/g. Within the limits of error this value can be assumed for the other solutions, too. From these relations and data we obtain for C6 in $CHCl_3$ at 25 °C a hydrodynamic diameter of approximately 7.4 Å; the respective value for C16 is 11.1 Å; and for the mixed solvent d_r results to 10.6 Å. In *o*-dichlorobenzene at 80 °C d is found to be ~6 Å for C6 and ~12 Å for C16; the respective data at 150 °C coincide within given limits of error. These values are reasonable figures for the structures under consideration here and agree more or less with the results deduced previously for the poly(3-alkyl-4-hydroxybenzoate)s.[17] The strong increase of d_r with longer side chains shows up for solutions in chloroform as well as in *o*-dichlorobenzene. The accuracy of the present data is not yet sufficient to discuss the influence of solvent power and temperature quantitatively because the difference is too small as compared to the limits of error. All data demonstrate that the polyesters under consideration here must be regarded as semiflexible chains.

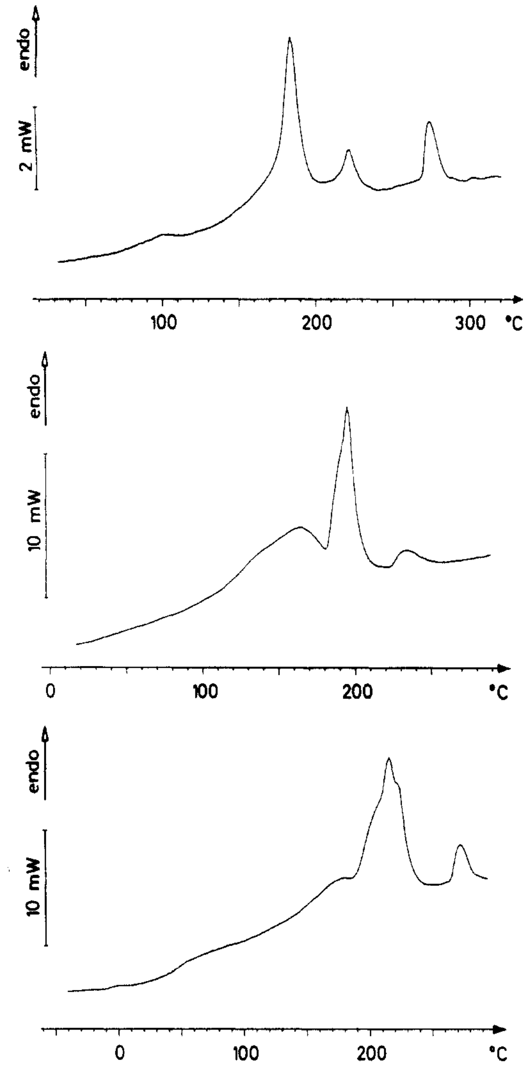


Figure 7. Thermal analysis of polyesters C6/*n* monitored by heating runs with 20 K/min: (a, top), C6/40-1 (M_w = 53 800); (b, middle) C6/10-1 (M_w = 18 200); (c, bottom) C6/70-1 after annealing at 210 °C for 1 min (M_w = 47 500).

Phase Behavior of the C6 Polyesters. Having characterized the C6 and C16 polyesters with respect to molecular weight and chain stiffness, we deal in the following section with the phase behavior of these materials. Figure 7a displays the DSC trace recorded with a heating rate of 20 K/min of polyester C6/40-1 having a weight-average molecular weight of 53 800. At lower temperature a glass transition is clearly discernible which has not been detected in previous studies[7,8,11] of this material. Wide-angle X-ray (WAXS) diffractograms clearly show that Figure 7a refers to a specimen in modification A (see Introduction and the discussion of the different modifications in ref 8) which transforms into the smectic-like mesophase at a rather sharp transition at 185 °C. A further first-order transition at 223 °C leads to a nematic phase.[11] Above the third transition at 272 °C the polyester C6/40-1 is isotropic.

Lowering the molecular weight to 18 200 (C6/10-1, Figure 7b) leads to a decrease of all transition temperatures. The glass transition is difficult to see since the peak of the first transition is very broad. Therefore the region where the smectic phase occurs has become rather small. In addition to this, the S–N transition is lowered to 196 °C and the N–I temperature to 234 °C.

A further point of interest is the transition of the C6/*n* crystallized in modification B (cf. ref 8). Figure 7c contains the DSC trace of C6/70-1 after annealing at 210 °C for 1

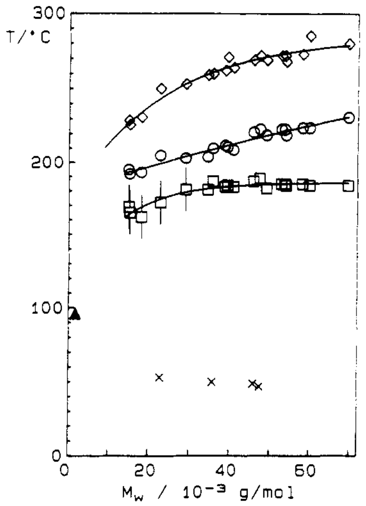


Figure 8. Transition temperatures of polyesters C6/*n* as a function of weight-average molecular weight: (□) crystalline–smectic; (○) smectic–nematic; (◇) nematic–isotropic; (▲) C6/1 (melting point); (×) glass temperature.

min. WAXS diffractograms show that most of the material has been transformed from modification A to modification B. Since the transition temperature of the latter highly crystalline[8] modification is considerably higher, the broad peak refers to the transformation of the solid material to the nematic phase. The transition to the isotropic state is located in the same range of temperature as observed in Figure 7a. Therefore the smectic phase can be observed in the C6/*n* only if the material is converted to modification A; the much higher melting point of B renders the S–N transition monotropic. The sequence of phase transitions thus obtained is (glass transition of amorphous part), modification A–smectic (layered) mesophase–nematic mesophase–isotropic phase; modification B–nematic mesophase–isotropic phase. Figure 8 gathers all data as a function of molecular weight.

The above discussion clearly demonstrates the M_w dependence of the first-order transitions for polyesters C6/*n*, which is particularly pronounced for the mesophase transitions. In agreement with previous deductions,[1] one may conclude that the stability of the structural organization in the solid state and even more in the mesophase depends on the steric interaction of the rodlike main chains. Figure 8, however, shows furthermore that all temperatures go to a finite value with increasing molecular weight. Truly rigid rod polymers would exhibit divergent transition temperatures as can be inferred from studies of oligomeric compounds.[26] But the characterization in solution has revealed the semiflexible nature of the main chain, and the finite transition temperature point to the fact that the persistence length in bulk will be of the same order of magnitude as in solution.

Phase Behavior of the C16 Polyesters. A typical DSC trace of a C16 polyester (C16/50-1), again recorded with 20 K/min, is shown in Figure 9, where the lower part refers to modification A as can be shown from the WAXS analysis. The upper part displays a DSC trace of a specimen crystallized in modification B which has been obtained by annealing the pristine material for 45 min at 60 °C.

The first transition of the lower curve is assigned to a "side chain melting" (cf. refs 1 and 27 for a further discussion of this point), whereas the first-order transition of B at approximately 100 °C refers to a melting of a fully crystalline structure. WAXS diffractograms demonstrate that in both cases a disordered structure with a layer spacing of modification A results which transformed at

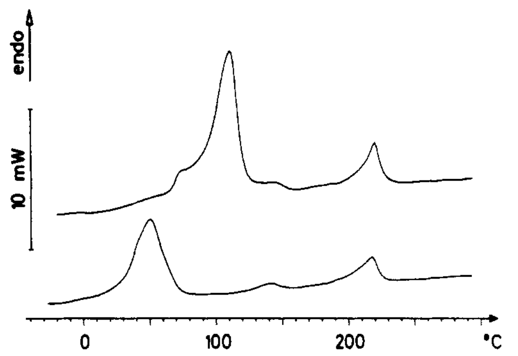


Figure 9. Thermal analysis of polyester C16/50-1 (M_w = 89 100) monitored by heating runs with 20 K/min: lower curve, modification A; upper curve, modification B, obtained from C16/50-1 after annealing at 60 °C for 45 min.

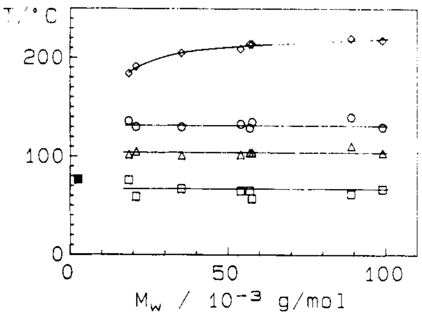


Figure 10. Transition temperatures of polyesters C16/*n* as a function of weight-average molecular weight: (□) side chain melting of A to A′; (△) transition of modification B to A′; (◇) smectic–isotropic transition; (○) transition of modification A′ to the layered mesophase; (■) melting point (crystalline–isotropic) of C16/1.

temperatures around 140 °C to the smectic-like mesophase already described previously.[8] ^{13}C-MAS experiments conducted by Whittaker, Falk, and Spiess[28] showed that the "side chain melting" leads to a pronounced decrease of the fraction of the trans bonds in the alkyl side chains. This transition, which leads only to inconclusive changes in the WAXS pattern, can be therefore identified as an order–disorder transition of the side chains which proceeds virtually without change of layer spacing. The disordered phase termed A′ by Whittaker et al.[28] also results from the melting process of phase B. In consequence, there is a weak endothermic signal in both DSC traces (see Figure 9) at approximately 140 °C referring to the transition of A′ to the layered mesophase. The Bragg spacing of the layered structure undergoes only a very small change at this transition, and the small latent heat originates from the fact that only residual order of the main and side chains is vanishing at this point.

All C16/*n* directly exhibit only a smectic mesophase independent of molecular weight; there is no indication of a nematic phase as observed in case of the C6/*n* polyesters. The transition to the isotropic phase is much lower than in the case of the C6/*n* (cf. Figure 9). Thus one observes the following sequence of phases: A–A′–A (mesophase)–isotropic phase; or B–A′–A (mesophase)–isotropic phase. Figure 10 displays all transition temperatures of the C16/*n* as a function of M$_w$.

All transitions are considerably lowered when compared to the C6 polyester, reflecting the diluent effect[7,8] of the side chains. A further point commanding attention is the rather small dependence of the transition temperatures on molecular weight. This obviously indicates that the demixing of the main and side chains is now the main driving force for the molecular organization; the steric interaction between the main chains being lowered in any case by the longer side chains seems to be of minor importance. In accordance with this interpretation is the fact that the layered mesophase is stable up to approximately 200 °C, whereas in the case of C6/*n* the transition to the nematic mesophase already takes place around 180 °C. On the other hand, the decreased steric interaction between the main chains in the case of the C16 materials directly leads to the transition from the layered liquid crystalline state to the isotropic phase; no nematic phase intervenes.

Conclusion

The above analysis of polyesters C6/*n* and C16/*n* in solution and in bulk shows that these materials are semiflexible, which leads to limiting values of the transition temperatures with increasing molecular weight. The main factor governing the organization in the bulk is the demixing tendency of the main and the side chains, in particular for long side chains. Here the transition temperatures are found to be nearly independent of the molecular weight of the main chains, whereas the C6/*n* exhibit a more pronounced dependence on the molecular weight of the main chain.

Acknowledgment. Financial support by the Bundesministerium für Forschung und Technologie, Projekt "Steife Makromoleküle", by the AIF (Grant 8528), and by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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