Investigation of the Thermal and Morphological Behavior of Liquid-Crystalline Acetylene Homo- and Copolymers

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ABSTRACT: The thermal and morphological behavior of the first complete homologous series of liquid-crystalline polyacetylene derivatives has been investigated by means of X-ray diffraction, differential scanning calorimetry, thermogravimetry, and polarizing optical microscopy. The influence of the spacer length on the thermal behavior and on the structure of the mesophases is discussed. All polymers except one form smectic monolayers at room temperature. For one spacer length, the formation of bilayers is observed. Despite the connection of the mesogens to the stiff, conjugated polymer main chain, most polymers exhibit highly ordered mesophases. Copolymerization of the mesogen-containing monomers with 1-octyne leads to a decrease of the supramolecular order with an increasing amount of comonomer in the polymer and finally to the formation of a new phase.

Introduction

Since the breakthrough in the field of side group liquid-crystalline polymers by Finkelmann et al.,[1,2] these materials have gained enormous interest in academic and industrial research because they not only have application potential in a wide range of electro-optic devices[3] but also offer a fascinating challenge in understanding the influence of the chemical structure on the self-organization of the molecules in the liquid-crystalline phase. The effect of variations of the chemical nature of the side group has been intensively investigated and is quite well-understood today.[4−7] However, the influence of the nature of the polymer main chain and the length and parity of the spacer moiety on the phase behavior still has to be fully elucidated. Yet, the synthesis and characterization of rigid main chain polymers often present considerable experimental difficulties because of their restricted solubility and/or high-transition temperatures. Especially in the field of polyacetylenes, only a few research groups have dealt with the these issues. The synthesis of linear polyacetylene with cholesteryl[8] and aromatic[9−14] side groups and the synthesis of liquid-crystalline polyheptadiynes[15−21] has been described by essentially three different groups, but conclusions concerning the role of the spacer and main-chain rigidity on the phase behavior have been drawn from incomplete homologous series. Such extrapolations may have underestimated small but substantial aspects concerning the influence of these structural parameters on mesophase behavior. This situation is mainly caused by difficulties in the synthesis and the availability of key intermediates.

Recently, we have shown a facile and versatile synthetic route to acetylene monomers with mesogenic side groups.[22] The polymerization of these monomers is possible with well-defined *Schrock*-type molybdenum initiators leading to polymers with a relatively narrow molecular-weight distribution.[22,23] These initiator systems also give access to the synthesis of random copolymers with nonmesogenic monomers such as 1-octyne. Furthermore, the synthesis of block copolymers is possible as well.[24] With respect to the interesting features of both polyacetylenes[25−36] and liquid-crystalline polymers[37−48] in membrane processes for gas separation, these new materials are of fundamental interest not only for the investigation of structure−property relationships but also for their potential application in this field.

We now report about our investigations on the thermotropic liquid-crystalline properties of the abovementioned homo- and random copolymers by means of X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetry, and polarizing optical microscopy (POM). The center of our research was the investigation of the structure−property relationships controlling the mesophase formation of these systems, focusing on the question of whether the connection of mesogens to the stiff, conjugated main chain interferes with the formation of highly ordered structures. In addition, we investigated the effect of a stepwise reduction of the molecular order within the condensed phases by the incorporation of increasing amounts of the nonmesogenic comonomer 1-octyne.

Experimental Section

The synthesis of monomers, polymers, and an initiator has been described in a previous publication.[22] Thermal transition characteristics were determined using a Perkin-Elmer DSC 7 in the temperature range from 50 to 190 °C. Thermal stability was investigated by means of a Polymer Laboratories STA 1500 under argon. Degradation temperatures were determined at the temperature of a 5% weight loss. Molecular weights were determined by size-exclusion chromatography (SEC) using chloroform as the solvent, a Merck-Hitachi L 6200 intelligent pump, SDV-gel separation columns of Polymer Standards Service (10^6, 10^4, and 10^2 Å, 5-μm particle size), and

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Scheme 1

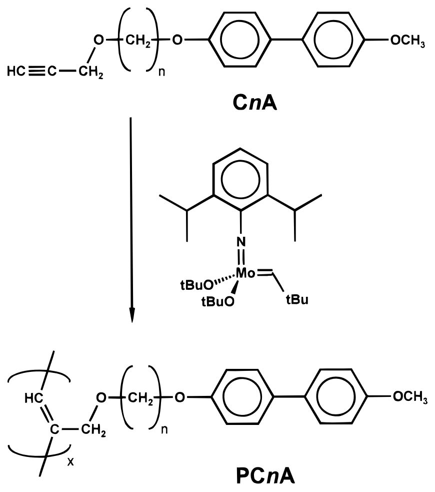

Table 1. Survey of the Synthesized Homo- and Copolymers, Comonomer Content, and Molecular Weights

sample ID	n	calc. octyne content (%)[a]	exp. octyne content (%)[b]	M_n[c]	M_w/M_n[c]
PC4A	4	0	0	n.d.[d]	n.d.[d]
PC5A	5	0	0	n.d.[d]	n.d.[d]
PC6A	6	0	0	n.d.[d]	n.d.[d]
PC7A	7	0	0	n.d.[d]	n.d.[d]
PC8A	8	0	0	n.d.[d]	n.d.[d]
A135A	6	8	10	n.d.[d]	n.d.[d]
A135B	6	16	17	n.d.[d]	n.d.[d]
A135C	6	24	23	n.d.[d]	n.d.[d]
A137A	4	30	32	20.9	2.6
A137B	5	30	31	19.5	2.2
A137C	6	30	29	18.4	2.2
A137D	7	30	31	21.5	2.1
A137E	8	30	37	23.6	2.1

[a] Octyne content in the monomer feed in mol %. [b] Octyne content in the copolymer in mol % determined by ^{1}H-NMR. [c] In kg/mol, measured by means of GPC. [d] Not determined because of insolubility.

detection at 254 nm with a UV spectrometer LC-55 S (Perkin-Elmer). Polystyrene standards ($M_n = 685-1.8 \times 10^6$, $M_w/M_n < 1.1$, Polymer Standards Service) were used for calibration. Polarized light micrographs were taken with a Olympus BHS POL microscope equipped with an Olympus PM-10 ADS light-measuring unit, a Linkam Scientific Instruments THM 600 heating table, and a Linkam Scientific Instruments TMS thermostat. X-ray diffraction was performed using a custom-made apparatus previously described.[49] NMR spectra were recorded with a Bruker ARX 300 spectrometer using $CDCl_3$ as the solvent at room temperature and 1,2-dichlorobenzene-d_4 for measurements at 80 °C.

Results and Discussion

All homopolymers in this contribution are based on the methoxybiphenyl-substituted monomers C*n*A (Scheme 1). For the random copolymers, 1-octyne was used as the comonomer. Table 1 gives a survey of the investigated homo- and copolymers and their respective abbreviations. NMR and IR spectra have been discussed in a previous publication.[22]

Homopolymers PC*n*A. *Thermal Stability.* Thermal stability of the polymers was detected by means of thermogravimetry. All polymers show a one-step decomposition curve and a well-defined onset of degradation as it is shown exemplarily for PC8A in Figure 1.

The curve shows that the materials possess a significant thermostability. The degradation temperatures cooresponding to a 5% weight loss as a measure of thermal stability of the polymers PC*n*A were 268, 277, 283, 287, and 296 °C, respectively. Thermal stability of the polymers markedly depends on the length of the alkyl chain in the side group. On the average, the onset temperature of thermal degradation increases almost linearly by about 7 K/each additional methylene group as displayed in Figure 2.

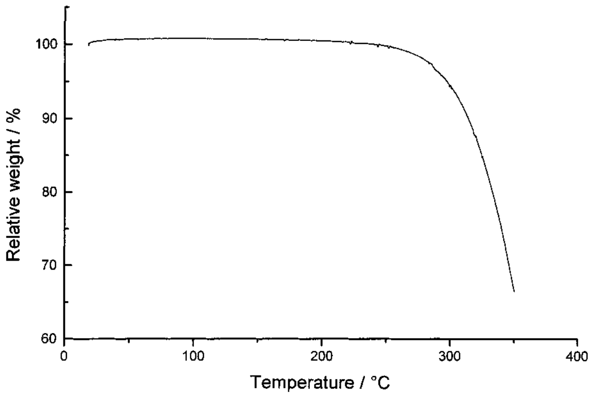

Figure 1. Thermogravimetric analysis of polymer PC8A under argon at a heating rate of 5 K/min.

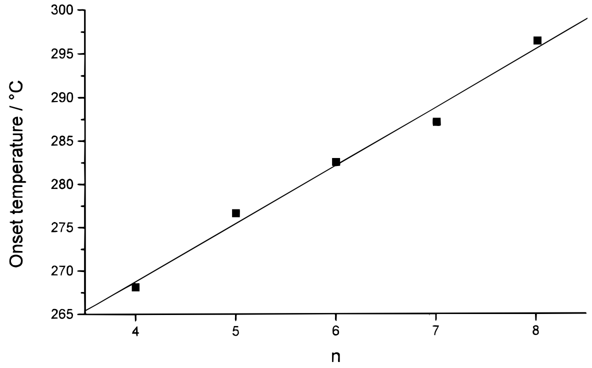

Figure 2. Plot of the dependence of the degradation temperature upon the spacer length for the polymers PC*n*A.

The dependence of thermostability upon the spacer length can be due to several reasons. Supposing that the degradation process emanates from the polymer main chain, for example, as a back-biting reaction leading to the formation of aromatic species, the volatility of the fragments decreases with increasing lengths of the side groups; thus, the temperature needed for their evaporation increases. Analogue considerations are valid when degradation is due to side group processes. Therefore, the extension of the spacer length seems to be a suitable concept for the synthesis of materials with considerable thermal stability.

Differential Scanning Calorimetry (DSC). Figure 3 shows the DSC thermograms of the polymers PC*n*A.

The DSC traces differ considerably from those of the analogue polymethacrylates.[50,51] In contrast to these, the peaks of the phase transitions are significantly broadened, closer together, and thus, badly resolved. The cooling runs show a similar pattern. As the substituents of the polymethacrylates mentioned above are identical to those of the polyacetylenes discussed here, this difference in the thermal behavior must be due to a main-chain effect. As the conjugated backbone of polyacetylenes is essentially more rigid compared to that of polymethacrylates, peak broadening and the bad separation of the signals coinciding with that can be

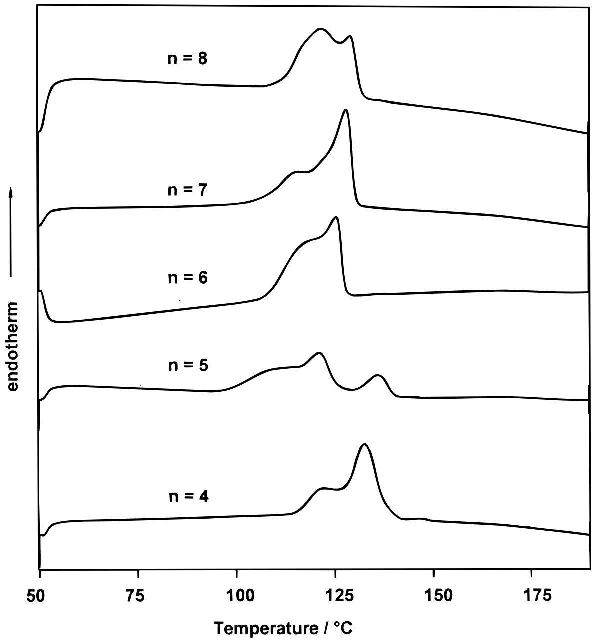

Figure 3. DSC traces of polymers PC*n*A (second heating run at 10 K/min).

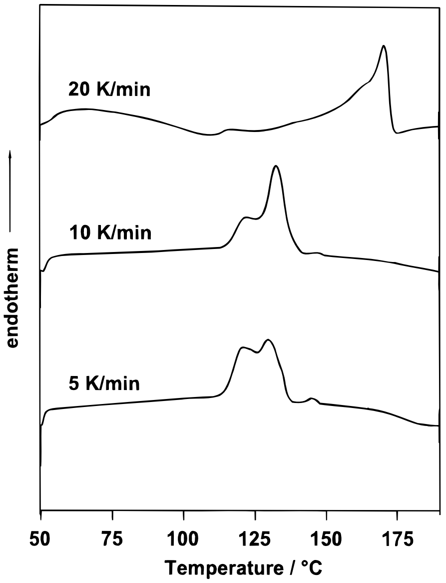

Figure 4. DSC traces of polymer PC4A for different heating rates. Top: first heating run. Center: second heating run. Bottom: third heating run.

attributed to kinetic effects under the conditions of the DSC experiment. This effect can also be demonstrated by recording DSC traces at different heating rates (Figure 4).

The thermograms recorded at different heating rates obviously show two phase transitions. The marked dependence of curve form on the respective heating rate hints at the formation of highly ordered phases. It is striking that at low heating rates the low-temperature phase transition is significantly more intensive than that observed at higher rates. This is a further indication of incomplete phase transitions due to kinetic effects under the conditions of the DSC experiment, which are probably due to the restricted mobility of the mesogenic side groups owing to their connection to the stiff backbone. These effects render the characterization of the liquid crystallization (LC) behavior considerably difficult. Thus, a discussion of liquid-crystalline properties for each spacer length separately is considered not to be sensible.

Table 2. Phase-Transition Enthalpies of the Polyacetylene Homopolymers PC*n*A and the Corresponding Polymethacrylates[50]

	total phase-transition enthalpy[a] (J/g)	
spacer length n	polyacetylenes	polymethacrylates
4	35.5	18.0
5	32.9	38.7
6	40.5	20.6
7	37.6	24.9
8	46.0	15.7

[a] Measured by means of DSC as the average value of the second and third heating run (10 and 5 K/min, respectively) and first, second, and third cooling run (20, 10, and 5 K/min).

Figure 4 shows another aspect which is important for the discussion of the phase behavior. The first heating run (trace at 20 K/min) shows an unusually unstable baseline. In the following heating runs (center and bottom of Figure 4) the baseline is stable. This is attributed to a cis−trans isomerization in the polymer backbone upon the first heating, leading to a broad exotherm in the DSC thermogram. It is known from literature that the cis configuration can readily be thermally transformed into the trans form which is thermodynamically more stable.[52] This result is of considerable importance because each of the analysis methods of this contribution comprises a melting process of the sample. Thus, this observation shows that the properties discussed in the following are those of the pure trans system. Nevertheless, the exact assignment of the individual peaks remains unclear. The cooling runs do not supply any additional information.

Irrespective of the difficulties coinciding with peak broadening, the DSC experiments supply the following results:

(1) All materials show first-order phase transitions and thus are either liquid-crystalline or crystalline. The connection of mesogens to the rigid polymer backbone does not suppress the formation of ordered phases.

(2) None of the materials show any ΔC_p steps assignable to a glass transition. This is, in analogy to the polymethacrylates,[50,51] indicative of the formation of highly ordered smectic or crystalline phases.

(3) The total phase-transition enthalpy for the transition from the isotropic melt to the low-temperature phase is subjected to a distinct odd−even effect as is characteristic for LC phases (Table 2).

(4) The enthalpies are comparable to those of the polymethacrylates.[50] Nevertheless, it is interesting that, for these polymers, the odd-numbered spacer moieties exhibit the higher enthalpies, whereas for the polyacetylene series, the higher values are found for the polymers with an even number of methylene groups in the alkyl spacer. Furthermore, the transition enthalpy seems to increase with increasing spacer lengths for the polyacetylenes, whereas for the polymethacrylates, the opposite tendency is observed. In most cases, distinctly higher enthalpies are determined for the polyacetylenes. This trend is shown in Figure 5.

Polarizing Optical Microscopy (POM). Under the crossed polarizers of a microscope, the homopolymers PC*n*A develop textures of different quality and stability. Figure 6 shows the *schlieren* texture at room temperature formed by polymer PC6A. This texture develops from the isotropic melt upon cooling and does not

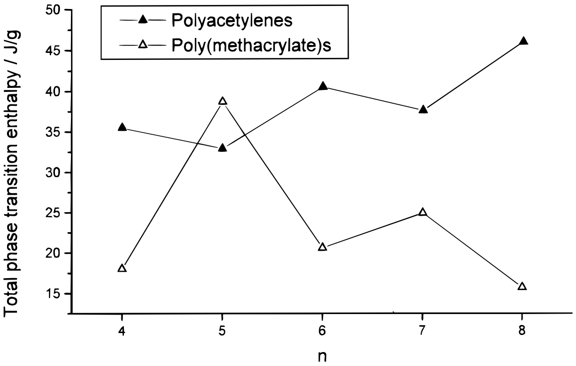

Figure 5. Plot of the dependence of the total phase-transition enthalpy on *n* for polyacetylene and polymethacrylate[50] homopolymers with methoxybiphenyl substituents.

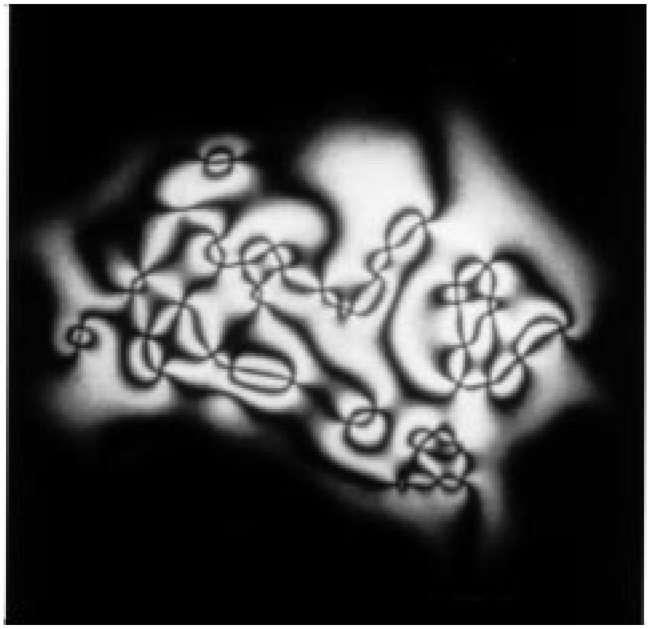

Figure 6. *Schlieren* texture of polymer PC6A (photograph taken at room temperature).

undergo any further change. Such behavior is frequently observed for LC polymers because of the increase of viscosity upon cooling, especially when a phase of higher order develops at a lower temperature.

The other polymers PC*n*A exhibit similar textures. Although *schlieren* textures are often observed in the presence of nematic phases, the micrographs cannot be assigned unequivocally to a nematic structure since only four disclination lines meet in the singularities as observed also, for instance, for smectic C mesophases. However, we are sure that the texture has to be assigned to a liquid-crystalline phase.

The stability of the phases differs significantly for the individual spacer lengths. The *schlieren* texture of polymer PC6A shown in Figure 6 does not change even at room temperature over several days. Polymer PC4A, yet, forms very similar textures when the isotropic melt is cooled below the transition temperature, but these textures collapse within a few seconds to give an ill-defined structure which cannot be assigned to any type of phase. In summary, it can be stated that each homopolymer forms POM textures which are typical of liquid-crystalline phases. However, an unequivocal assignment based upon these micrographs is not possible.

X-ray Diffraction. The low-temperature phases of the homopolymers PC*n*A with $n = 4-7$ can readily be characterized by means of X-ray diffraction. Figure 7 exemplarily shows the diffraction pattern of a mechanically oriented fiber from PC7A at room temperature.

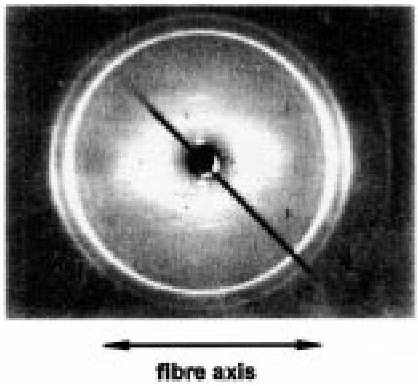

Figure 7. X-ray diffraction pattern of a PC7A fiber at room temperature.

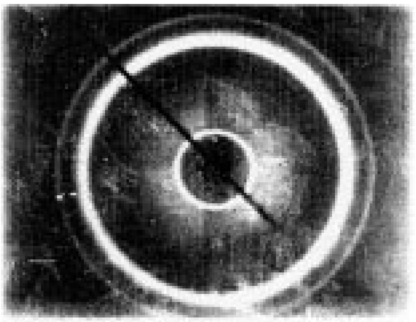

Figure 8. X-ray diffraction pattern of polymer PC8A at room temperature.

The diffraction pattern clearly shows the presence of a mesophase of the E-type (formerly referred to as smectic E). In the small-angle region, the first three orders of the (001) reflection can be noticed. As in the case of the polymethacrylates, the second-order reflex is by far the most intensive one, which can be interpreted as a hint at interdigitation of the mesogenic side groups. In the wide-angle region, the (110), (200), and (210) reflections with their decreasing intensities typical of E-phases can be perceived. The same pattern is also found for the polymers with butylene, pentylene, and hexylene spacers. The diffraction pattern of polymer PC8A deviates markedly from these results. As shown in Figure 8, the reflection assigned as (110) is significantly broadened compared to the other ones. The intensity of the reflection assigned as (210) is very low; thus, it is no more visible in the reproduction shown here.

The reason for this deviation is not totally clear. A consideration of the layer planes in the orthorhombic systems shows that it is not possible to disturb the order of the (110) planes without affecting the (200) and (210) planes. Yet, the reflections assigned to these planes are sharp. However, when the spacer length is increased, the probability for the alkyl chain to adopt a conformation different from the *all-trans* conformation increases as well. This might induce a reduction of order within the phase. Table 4 states calculated monomer lengths, experimentally determined layer plane distances, and where possible, the lattice parameters of the orthorhombic arrangement.

The data show that for all polymers capable of forming an E-phase the arrangement of the mesogens

Table 3. Layer Plane Distances and Lattice Parameters of the Low-Temperature Phases of Polymers PC*n*A[a]

n	monomer length (Å)[b]	lattice parameter *a* (Å)	lattice parameter *b* (Å)	lattice parameter *c* (Å)	$d_{(110)}$ (Å)	$d_{(200)}$ (Å)	$d_{(210)}$ (Å)	$d_{(210)}$ (calc.) (Å)[c]	Δ*d* (Å)[d]
4	21.0	7.82	5.42	37.9	4.46	3.91	3.18	3.17	0.01
5	23.1	7.83	5.41	24.2	4.45	3.92	3.15	3.17	0.02
6	23.6	7.84	5.41	25.7	4.46	3.92	3.20	3.18	0.02
7	25.6	7.86	5.39	26.9	4.44	3.93	3.19	3.17	0.01
8	26.1	n.d.[e]	n.d.[e]	27.7	n.d.[e]	n.d.[e]	n.d.[e]	n.d.[e]	n.d.[e]

[a] Determined by means of X-ray diffraction at room temperature. [b] According to *molecular modeling* estimations. [c] Calculated value for the (210) reflection based upon those determined for the (110) and (200) reflections, taking into account more figures than those shown here. [d] Difference of calculated and experimentally obtained values for d_{210}, taking into account more figures than those shown here. [e] Not detected.

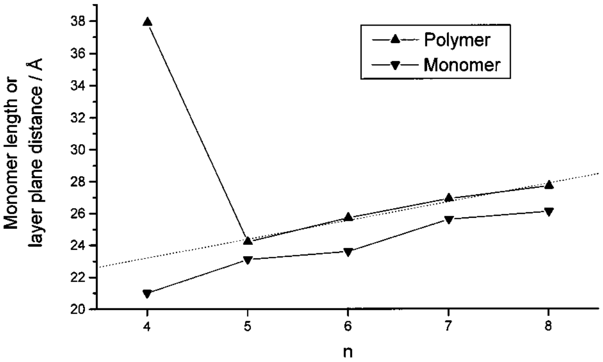

Figure 9. Plot of the dependence of the monomer length and polymer layer plane distance on spacer length *n*.

within the layer is essentially equal. The lattice parameters *a* and *b* vary within the experimental error only. Calculated and experimentally determined values for the (210) reflection correspond very well for $n < 7$, thus supporting the assignment to an E-phase.

At first glance, variation of the layer plane distances (lattice parameter *c*) with the spacer lengths looks surprising. The value for $n = 4$ is markedly higher than for the other homopolymers (Figure 9).

These results suggest that the low-temperature phase of PC4A is a bilayer structure of the E_2-type, whereas all other homopolymers exhibit E_1-phases (or a corresponding monolayer structure for PC8A). Figure 10 shows a possible arrangement of the mesogenic side groups for polymers PC4A and PC6A, taking the monomers as model compounds for the polymer's side groups.

From this figure it becomes clear why for $n = 4$ there does not exist an interdigitating monolayer but a head-to-head arrangement of the mesogens: For this spacer length, steric hindrance of the aromatic rings of the mesogens prevents a monolayer arrangement.

It is interesting to notice the analogue polymethacrylate forms interdigitating monolayers for $n = 4$.[50] This is probably due to steric effects which can be related to the different backbone. The layer plane distances of both polyacetylenes and polymethacrylates investigated are, with the exception of the polymethacrylate with $n = 5$, larger than the (calculated) axial extension of the corresponding monomers (see Table 3 of this paper and Table 3 of ref 50). The mean difference of monomer length and polymer layer plane distance amounts to 0.64 Å (or 0.85 Å without consideration of the structurally deviating pentylene homologue, respectively) for the polymethacrylates, and to 1.53 Å for the polyacetylene backbone. This difference can be interpreted as the spacial extension of the polymer main chain. The deviating behavior of the two polymers is probably due to a distinctly different arrangement of the polyacetylene main chain between the layers or to its bigger sterical demands. Thus, there is considerably less space available for the mesogens, and the transition to a bilayer structure takes place for the butylene homologue already.

X-ray diffraction at higher temperatures was rendered difficult by the overlapping and ill-resolved phase transitions. Therefore, we did not have any access to an investigation of the mesophase(s) between the E-phases and the isotropic melt. In an analogy to the phase behavior of the corresponding polymethacrylates, it seems plausible to expect the formation of a smectic A and/or nematic phase. Nevertheless, this supposal remains speculative.

Random Copolymers with 1-Octyne. There were several motivations for the synthesis of the random copolymers described here: From the synthetic point of view, copolymerization gives access to materials that are soluble in common organic solvents at room temperature once the comonomer content exceeds a critical value which simplifies the analytic investigations. From the theoretical point of view, it is interesting to study the influence of a stepwise reduction of the supramolecular order by diluting the mesogen concentration in the material on kinds and stabilities of the mesophases formed. Random copolymers based upon polyacetylenes have not yet been described in the literature before. Therefore, we synthesized random copolymers of the mesogenic monomers C*n*A with the nonmesogenic monomer 1-octyne, the homopolymer of which is completely amorphous, in addition to the homopolymers described above. A survey of the materials has been given in Table 1.

Differential Scanning Calorimetry (DSC). In an analogy to the homopolymers PC*n*A, all copolymers show broad and ill-resolved peaks in the DSC trace. One of the most important features of these measurements is the fact that despite the incorporation of 1-octyne the copolymers still undergo first-order phase transitions; so, the materials are not amorphous even when the octyne content reaches 37 mol %. As in the case of the homopolymers, transition enthalpies are subject to a distinct odd−even effect. The numerical data are presented in Table 4.

As could be expected, the transition enthalpies of the copolymers are considerably decreased in comparison to those of the homopolymers. Yet, an analysis of the experiment series A135, in which the comonomer content was increased stepwise at a constant spacer length, shows that this decrease is not continuous. The data in Table 4 clearly show that the decrease of the transition enthalpies upon an increasing comonomer content is not linear. This indicates that there is a critical comonomer content in the range between 8 and 16 mol % 1-octyne. Upon passing this point, the supramolecular order of the mesophases is disturbed significantly, which is

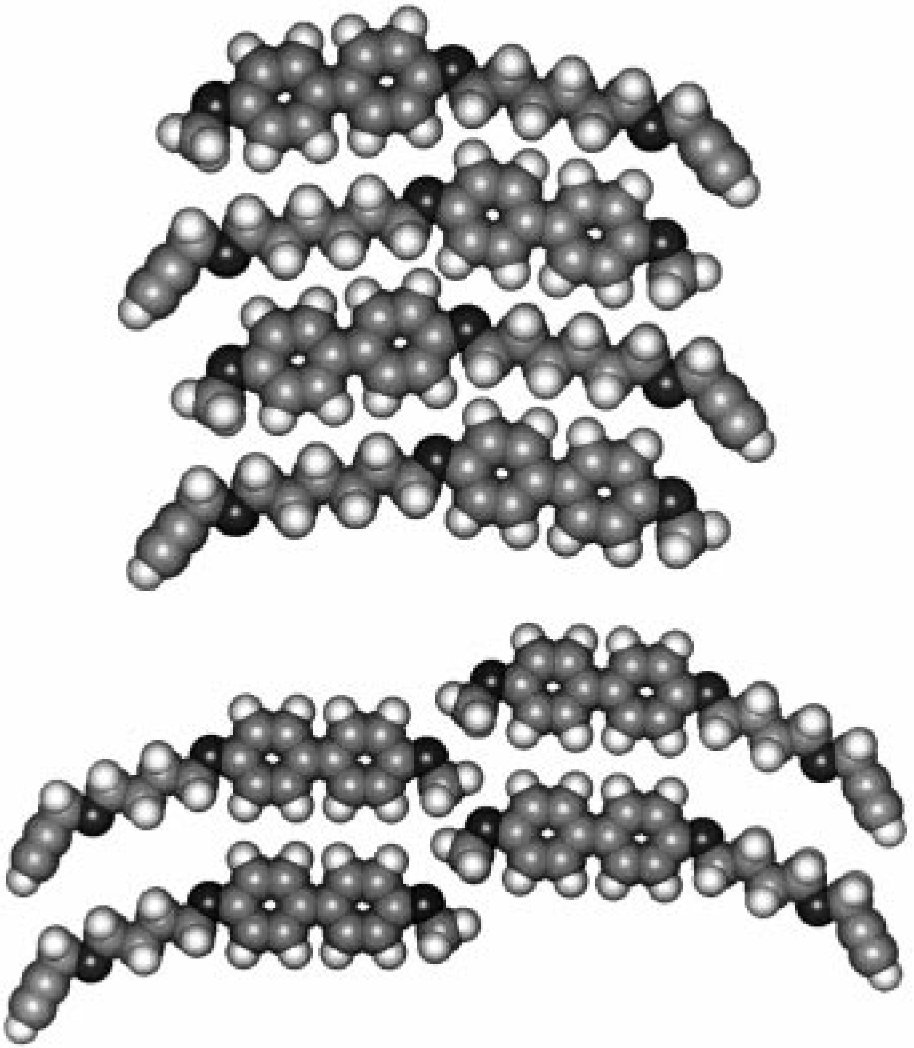

Figure 10. Possible arrangement of the mesogenic side groups in the E_2-phase of polymer PC4A (top) and the E_1-phase of PC6A (bottom).

Table 4. Total Phase-Transition Enthalpies of the Copolymers Poly(C*n*A-*co*-1-octyne)[a]

sample ID	*n*	exp. octyne content[a] (%)	total phase-transition enthalpy (J/g)[b]
A135A	6	10	40.5
A135B	6	17	35.0
A135C	6	23	35.8
A137A	4	32	30.9
A137B	5	31	24.3
A137C	6	29	34.3
A137D	7	31	31.9
A137E	8	37	36.7

[a] Octyne content in the copolymer in mol % determined by ^{1}H-NMR. [b] Measured by means of DSC as the average value of the second and third heating run (10 and 5 K/min, respectively) and first, second, and third cooling run (20, 10, and 5 K/min).

reflected in lower enthalpy changes at the phase transition.

Polarizing Optical Microscopy (POM). Among the copolymers described in Table 1, only that with the lowest octyne content (A135A) develops well-defined textures under crossed polarizers which are very similar to that shown in Figure 6. From these textures, one can conclude that the polymer does form LC phases; nevertheless, the exact type of mesophase cannot be assigned either. At higher comonomer contents, the formation of finely structured textures is observed. No conclusion concerning the mesophase present is possible based upon those. The difference in behavior of homo- and copolymers coincides with the DSC result which indicates a change of the phase type for copolymers with a comonomer content above 8 mol %.

X-ray Diffraction. The investigation of the copolymers by means of X-ray diffraction confirms the supposition that copolymers with more than 8 mol % 1-octyne do not exhibit highly ordered phases anymore. Surprisingly, the diffraction pattern obtained resembles very much that of the homopolymer PC8A shown in Figure 8: In the wide-angle region several reflections are visible, one of which is considerably broadened. An exact structure determination is not possible. Nevertheless, sharp reflections in the small-angle region are indicative of the presence of a smectic phase. However, it is sensible that these phases are liquid-crystalline phases as it appears illogical that by means of a reduction of the order of the homopolymer's LC phase a crystalline phase could be induced.

Conclusion

The LC behavior of homo- and copolymers based upon polyacetylene has been investigated. Thermal investigations are rendered difficult by kinetic effects under the conditions of the DSC experiment. However, transition enthalpies are subject to a distinct odd−even effect as it is commonly observed for liquid crystals. The first heating trace shows a curve form indicative of a thermal cis−trans isomerization of the double bonds in the polymer backbone.

A crucial aspect of our research is the application of X-ray diffraction to these materials. By means of that technique, it could be shown that the restriction of mobility of the mesogenic side groups due to their connection to the very stiff polyacetylene backbone does not suppress the formation of highly ordered mesophases. With the exception of the octylene homologue, the homopolymers form layered structures of the E-type at lower temperatures. The analogy to the identically substituted polymethacrylates indicates that the formation of this phase is characteristic of the methoxybiphenyl mesogen. Polymer PC4A is the only one for which the formation of bilayers is detected by means of X-ray diffraction. This can be explained by means of steric considerations. From the comparison with the analogous polymethacrylates one can conclude that the unsaturated polyacetylene backbone is sterically much more demanding than the polymethacrylate backbone. The homopolymer with $n = 8$ gives an X-ray diffraction pattern of a layered structure with reduced order (compared to the E-phase) which so far could not be assigned. The reduced order of this polymer might be due to several reasons: First, the mesogen density (referred to as weight) decreases when the spacer length is increased, thus diluting the mesogen concentration just like the incorporation of octyne; second, a long alkyl spacer tends to adopt a conformation which differs from the *all-trans* one, thus disturbing the regular arrangement of the mesogenic side groups. Third, polymer PC8A shows the largest isotropization enthalpy of all polymers, which normally would have to be interpreted as a sign of relatively high order. Therefore, the low-temperature phase of this homologue remains obscure.

Up to now, we do not have any information on the high-temperature phase(s) between the E-phase and the isotropic melt. Textures from POM are typical of LC phases but cannot be assigned unambiguously to a certain mesophase. In an analogy to the corresponding polymethacrylates it appears plausible to suppose the presence of smectic A and/or nematic phases.

The investigation of random copolymers of the mesogenic acetylene monomers with 1-octyne as the comonomer shows that the ability to form highly ordered liquid-crystalline phases disappears when the octyne content is increased above 8 mol %. At higher comonomer contents, the supramolecular order is considerably disturbed and thus hinders the formation of E-phases. However, the copolymers exhibit layered mesophases. Even at high comonomer contents the transition enthalpies are subject to a distinct odd−even effect.

It is interesting to notice that the X-ray diffraction patterns of the copolymers, which are indicative of disturbed low-temperature phases, resemble significantly that of the homopolymer PC8A. Therefore, both structures are supposed to be disordered smectic liquid crystals.

The results presented here are the first comprehensive investigation of linear LC polyacetylenes in which, by means of a continuous variation of the spacer moiety, the influence of the structural parameter could be analyzed. The incorporation of 1-octyne shows the effect of a dilution of the mesogen concentration within the phases. The comparison to the otherwise identical polymethacrylates shows the influence of main-chain rigidity on the thermal and morphological properties of this class of materials.

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