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# A Helical Poly(amino acid) Having Carbazole Side Chains: A Candidate for a Photoelectric Liquid Crystal. 3. A Conformational Study

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ABSTRACT: The conformation of a carbazole-substituted poly(α-amino acid), poly($N^{\epsilon}$-(carbazolylcarbonyl)-L-lysine) (PKL), has been studied in solid films and solutions by fourier transform infrared spectroscopy. In all samples investigated the main chain assumes the α-helical conformation. The side chains are strongly hydrogen bonded in the solid state, with approximately 20% unbounded groups. A side-chain conformation is proposed, where the major part of the side chains are stacked in three stacks almost parallel to the molecular axis. The average stack length exceeds 10 units and can in principle be infinite. The carbazole groups in the stacks are efficiently locked-in conformationally in a structure which probably favors effective energy transfer and photoconduction. In solution the hydrogen bonding of the side chains is disrupted.

## Introduction

Carbazole-containing polymers have been extensively studied in recent years with respect to their photoelectrical, mainly photoconductive, properties.[1-3] These investigations have lead to the supposition that the spatial arrangement of the carbazole groups is decisive for the photoconductive properties.[4,5] It is thus desirable to correlate the conformation of these polymers with their photoconductive properties.

The charge carrier transport in photoconductive polymers and the related energy transfer of uncharged, excited electronic states (excitons), which may be studied by fluorescence techniques, are both π-orbital phenomena. Due to the inherent anisotropy of the π-orbital it is expected that the distance between neighboring carbazole groups as well as the angle between the plane normals will determine the orbital overlap and thus the interaction. The Förster theory of exciton diffusion requires a reciprocal sixth power dependence of the distance and a cosine square dependence of the angle.[4] For charge carrier transport one may speculate as to a similar dependence.

Also the macroscopic regularity of the spatial arrangement is important, since the charge carriers have to be transported through the entire sample in order to contribute to the conductivity. It is believed that structural defects act as traps for the carriers, immobilizing and eventually annihilating them,[5-7] leading to recombination.

In this article we present studies on the conformation of a carbazole-substituted polypeptide, poly($N^{\epsilon}$-(carbazolylcarbonyl)-L-lysine) (PKL). The chemical structure of this polymer enables the polypeptide backbone to form an α-helical structure, giving a rod-shaped macromolecule capable of forming liquid-crystalline (LC) solutions. Due to the helical backbone structure, the side-chain conformations are presumably within narrowly defined limits. Furthermore the LC properties are conducive for preparing samples with well-defined orientation and morphology. This polymer is thus suitable for conformational studies by polarized spectroscopy, since the results can be inter-

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pretated unambiguously. Such studies are necessary if the LC properties are to be utilized in materials for nonlinear optics and electronic applications.

In this study we use polarized infrared spectroscopy on oriented solid films of PKL as the main source of information. The solid-state conformational dependence on preparation parameters and solvents, as well as the conformation in solution, is studied.

The synthesis of PKL, investigations of solution properties, and fluorescence studies have been reported previously.[8-13] Energy-transfer studies by fluorescence techniques and photoconductivity measurements will be published subsequently.[14-18]

## Experimental Section

Oriented films of PKL were prepared by either free evaporation or diffusion of a solvent from lyotropic liquid-crystalline cholesteric solutions. Uniaxial nematic orientation was obtained by subjecting the lyotropic solution to shear flow immediately prior to evaporation or diffusion. Alignment of the lyophase by a magnetic field led to a monodomain cholesteric phase, indicating that the magnetic anisotropy is negative for this polymer. Since uniaxial (nematic) orientation is desired for polarized spectroscopy studies, magnetic alignment was not applicable.

Solvents used were tetrahydrofuran (THF), cyclohexanone, tetramethylurea, and isophorone. They were dried by distillation, from Na or $LiAlH_4$. Lyotropic solutions with concentrations in the 20–30 w/v % range were used for film preparation. The lyophases were oriented by spreading a few drops of the solution with the edge of a glass slide or a knife on a plane substrate of either a Teflon surface, a KBr plate, or a glass slide.

For films prepared by free evaporation, rapidity was essential. THF was evaporated at room temperature, while the other solvents, due to their lower vapor pressures, were evaporated at elevated temperature, typically 100–120 °C. The evaporation has to be completed essentially within 1 min, so as to prevent loss of alignment by relaxation to a polydomain lyophase. Sheared solutions of PKL in isophorone and cyclohexanone, evaporated at room temperature in half an hour, thus formed unoriented films.

Oriented films so prepared are transparent, with reasonable mechanical strength in the orientation direction, but with poor strength in the transverse direction. They have the banded texture morphology when seen in a polarizing microscope, as reported for many shear oriented LC polymers.[19-21] The banded texture is indicative of a good but imperfect orientation.

For samples prepared by solvent diffusion, the substrate with the aligned solution is totally immersed in a fluid that is a nonsolvent for the polymer but miscible with the solvent. Upon immersion of the solvent diffuses into the fluid, and the polymer precipitates. Ethanol was found to be suitable for this purpose forming a white, opaque film of the polymer within a few seconds.

For these films no texture was seen in a polarizing microscope except for a few defects, indicating a nearly perfect, uniaxial orientation. The extensive light scattering (which leads to the white appearance) is probably caused by a fibrillar structure of the films. The films are very fragile in the transverse direction but have reasonable mechanical strength in the orientation direction.

The films could be made transparent by a moderate heat treatment at 120–140 °C, provided that minor quantities of residual solvent were present. Such transparent films have fine banded textures, with higher degrees of orientation than those prepared by evaporation, since extinction in these films in a polarizing microscope occurs at smaller angles than for films made by free evaporation.

Film thicknesses of 1–10 μm are readily obtained by both methods.

Infrared spectra were also obtained on lyotropic solutions of PKL in THF, isophorone, or cyclohexanone (30 w/v %) sandwiched between KBr plates. Solvent spectra were subtracted to give differential spectra of the polymer itself. With a high resolution apparatus, the quality of the spectra enables good difference spectra to be obtained over most of the spectral range.

The infrared spectra were recorded on a Bruker IFS 113v FTIR instrument, using a Ge/KBr beam splitter and a $N_2$-cooled MCT detector for the MIR region (4000–550 $cm^{-1}$) and a 6-μm Mylar beam splitter and a DTGS detector for the FIR region (700–200 $cm^{-1}$). The resolution used was 4 $cm^{-1}$. Polarized infrared spectra were obtained by using a Specac wire polarizer (0.2-μm aluminum wires on a KRS-5 substrate). The instrument itself was evacuated, but samples and polarizer were placed in a small compartment, which was purged with dry $N_2$. Each MIR spectrum typically consists of 128 scans and each FIR spectrum of 256 scans. Only a few of the oriented film samples were studied in the FIR range. A 2.5-mm aperture was used in order to minimize effects of thickness variations. All spectra were recorded at room temperature.

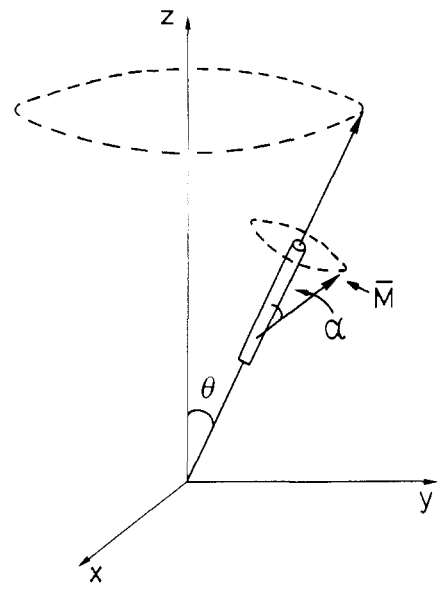


**Figure 1.** Definition of angles for orientation measurements of a partly uniaxially oriented sample. $z$ is the orientational axis, $\theta$ is the angle between $z$ and the long molecular axis, and $\alpha$ is the angle between the molecular axis and the transition moment vector. Radiation propagates in the $x$ direction, and spectra are polarized along the $z$ axis for the parallel and along the $y$ axis for the perpendicular, respectively.

No traces of residual solvent and only very small amounts of water were seen. Dichroic ratios were determined by measurements of peak heights on absorbance spectra relative to the base line of well-resolved bands. For partially overlapping peaks, ratios are only approximative since manual deconvolution of partially overlapping bands was performed.

## Results and Discussion

**Model.** For the conformational analysis the strategy was as follows: First the α-helical conformation of the main chain is utilized to calculate an order parameter for the backbone. Once the order parameter is determined, the transition moment angles of the side-chain vibrations relative to the helical axis can be calculated.

Given these angles, some possible conformations of the side chains may be elucidated and discussed.

**Orientation.** The degree of orientation of the sample is expressed by the order parameter, $S_\theta$, defined through the second Legrendre polynomial:

$$S_\theta = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) \quad (1)$$

where $\theta$ is the angle between the long molecular axis and the orientation axis and $\langle\ldots\rangle$ symbolizes an average taken over all molecules. Symbols are defined in Figure 1.

The measured apparent order parameter $S_m$ is calculated from the dichroic ratio $R$ and is given by

$$S_m = \frac{R-1}{R+2} = S_\theta S_\alpha \quad (2)$$

where $R = A_z/A_y$ is the dichroic ratio, i.e., the ratio be-

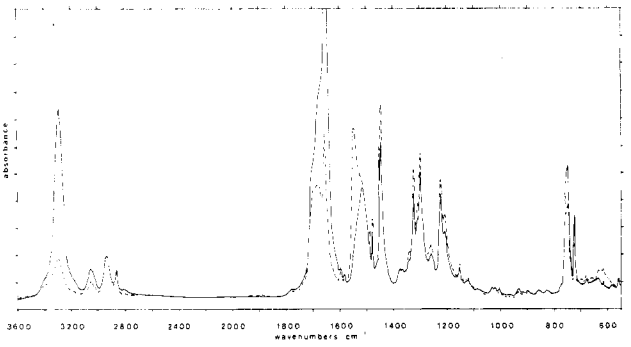


**Figure 2.** Typical polarized infrared absorption spectra of poly($N^{\epsilon}$-(carbazolylcarbonyl)-L-lysine): solid curve, parallel spectrum; dashed curve, perpendicular spectrum. The assignment of the major bands are given in Table I.

tween the absorbances of the parallel and perpendicular spectra, respectively.

$S_\alpha$ is the second Legrendre polynomial analogue of the transition moment angle, where $\alpha$ is the angle between the helical axis and the transition moment vector:

$$S_\alpha = \tfrac{1}{2}(3\cos^2\alpha - 1) \quad (3)$$

Expressing $\alpha$ by the second Legrendre polynomial is compatible with the usual mathematical treatment, where $S_\theta = (R-1)(R_0+2)/(R+2)(R_0-1)$ and $R_0 = 2\cot^2\alpha$. The advantage of using expression 3 is that a distribution of angles $\alpha$ can readily be incorporated.[20]

Unknown transition moment directions may be calculated by using

$$S_\alpha = S_m/S_\theta \quad (4)$$

provided that $S_\theta$ can be determined independently.

**Spectra.** Typical polarized infrared spectra of a PKL film are shown in Figure 2. The assignment of the more important bands is given in Table I. For the sake of simplicity the discussion of the bands is divided into three groups: Those caused by vibrations in the main chain ($\alpha$-helix), the side chain, and the carbazole group.

**The Main Chain.** The main-chain vibrations are those of an amide group in an $\alpha$-helical conformation. The ability to form lyotropic liquid-crystal phases and the circular dichroic spectrum of the polymer further support the $\alpha$-helical structure of the main chain.[8,13]

The assignment of the amide bands and their frequency dependence on conformation has been extensively studied by numerous workers[23-26] and reviewed by Fraser.[27] The polarization of the bands has also been determined.[24,27,28] In addition, direct comparisons with infrared spectra of poly($\gamma$-benzyl-L-glutamate) (PBLG) were made. PBLG is well-known to be in the $\alpha$-helical conformation in the solid state, when cast from an appropriate solvent. Oriented films of PBLG were made by using the evaporation technique, from tetrahydrofuran solution, as described above.

The amide frequencies for PBLG and the PKL main chain were identical within 3 $cm^{-1}$, and the width of the bands was similar. The amide A and B bands of PKL do not show splitting into main-chain and side-chain components, presumeably because they coincidentially appear at the same frequency. In addition to the strong component at 3292 $cm^{-1}$, a weak component of the amide A band is seen at 3420 $cm^{-1}$ for PKL and 3430 $cm^{-1}$ for PBLG, which is ascribed to a free amide A band (see below).

Main-chain amide I and II bands appear at 1655 and 1545 $cm^{-1}$. The amide I band of the side chain consists of two components, the stronger at 1675 $cm^{-1}$ and the weaker at 1705 $cm^{-1}$. The amide II band of the side chain

**Table I**
**Assignment of Important Infrared Bands in Poly($N^{\epsilon}$-(carbazolylcarbonyl)-L-lysine) (PKL)**

| wavenumber, $cm^{-1}$ | intensity | polarization[a] | approx description |
|---|---|---|---|
| 3430 | w (sh) | u | free amide A of side chain |
| 3291 | s | ∥ | amide A of main chain and side chain |
| 3057 | m | ∥ | amide B of main chain |
| 3045 | m (sh) | – | amide B of side chain? |
| 2934 | m | var | asymmetric $CH_2$ stretch |
| 2865 | m | var | symmetric $CH_2$ stretch |
| 1705 | m (sh) | – | side chain amide I, free |
| 1675 | s | ∥ | side chain amide I, hydrogen bonded |
| 1653 | s | ∥ | main chain amide I mode |
| 1547 | s | ⊥ | main chain amide II mode |
| 1516 | s | ∥ | side chain amide II mode |
| 1452 | s | var | carbazole |
| 1445 | s | var | carbazole |
| 1324 | m | ∥ | amide III bands and carbazole, unresolved |
| 1310 | m (sh) | – | |
| 1299 | m | ∥ | |
| 1153 | mw | – | carbazole |
| 749 | s | ∥ | carbazole |
| 725 | s | ∥ | carbazole |
| 698 | w | ⊥ | amide VI? |
| 635 | w | ⊥ | unresolved amide V modes? |
| 615 | mw | ⊥ | |
| 561 | m | ∥ | carbazole |
| 420 | m | ∥ | carbazole |

[a] Symbols: sh, shoulder, u unpolarized, var variable (in different samples), – unknown (due to overlap), ∥ parallel, ⊥ perpendicular polarized.

appears at 1515 $cm^{-1}$ and consists of a single recognizable component. The I and II bands of the main and side groups show some overlap, so deconvolution must be performed to make approximate dichroic ratio determinations. The uncertainty of the ratios is largest for the side chain, since absorbances are smaller.

The amide III bands show too much overlap to distinguish between individual bands, and probably also carbazole bands are present in this region.

The amide V and VI bands are probably located at 700, 635, or 615 $cm^{-1}$, where perpendicular polarized bands appear, but these bands are not well resolved and thus are not applicable for order parameter determination.

The strongly parallel polarized $\alpha$-helix skeletal deformation observed in PBLG at 563 $cm^{-1}$ is probably masked by other bands in PKL in the 600–400-$cm^{-1}$ range.

The polarization of the amide A, I, and II bands of the main chain of typical samples of PKL are shown in Table II, where also PLBG samples are included. As the transition moment directions for the amide groups differ in the literature (ref 27 Table 9.7), we used an internal consistency principle to estimate values of $\alpha$ for the amide bands: The order parameter of a given sample should be identical when calculated from different bands. The estimated values for $\alpha$ for the transition moment directions are shown in Table III. The directions for the amide I and II transitions are based on data from both polymers, assuming that PBLG and PKL have identical main-chain conformations. The directions for the other transitions are based on PBLG data only. Order parameters for the samples calculated from the amide I and II transitions gave consistent values as shown in Table II.

The $\alpha$ values in Table III are in reasonable agreement with those calculated for a standard $\alpha$-helix with a 100° twist and a 1.50-Å (ref 27, Table 9.7) pitch, except for the amide A band, where the value found by Suzuki[28] is better. For the PKL amide A band, main-chain and side-chain

**Table II**
**Dichroic Ratio and Order Parameters for Amide Bands of Films**

| sample | prep[a] | dichroic ratio main-chain amide: A 3291 cm$^{-1}$ | I 1653 cm$^{-1}$ | II[b] 1547 cm$^{-1}$ | measured $S_m$: A | I | II | calcd order param $S_\theta$[c]: A | I | II | order param $S_\theta$ (av) | calcd apparent $S_\alpha$ for amide A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PKL 16 | THF, evap | $3.4_0$ | $2.9_4$ | $0.21_1$ | $0.44_4$ | $0.39_3$ | $-0.35_7$ | | $0.73_5$ | $0.71_8$ | 0.73 | $0.59_2$ |
| PKL 54 | THF, evap | $2.6_8$ | $>1.7_6$ | $0.29_4$ | $0.35_9$ | $>0.20_2$ | $-0.30_8$ | | $(>0.37_9)$ | $0.61_9$ | 0.62 | $0.57_9$ |
| PKL 62 | isoph, diff | $4.7_1$ | $4.3_6$ | $<0.06_8$ | $0.55_3$ | $0.52_9$ | $<-0.45_0$ | | $0.99_1$ | $>0.90_5$ | >0.95 | $0.55_9$ |
| PKL 64 | isoph, diff | $3.7_7$ | $3.4_3$ | $<0.14_3$ | $0.48_0$ | $0.44_8$ | $<-0.40_0$ | | $0.83_9$ | $>0.80_5$ | >0.82 | $0.57_1$ |
| PKL 65 | isoph, evap | $4.5_8$ | $>4.3_4$ | $0.08_2$ | $0.54_4$ | $>0.52_7$ | $-0.44_1$ | | $>0.98_7$ | $0.88_7$ | 0.94 | $0.56_1$ |
| PKL 67 | cyclohex, diff | $4.0_0$ | $3.7_1$ | $<0.08_3$ | $0.50_0$ | $0.47_5$ | $<-0.44_0$ | | $0.89_0$ | $>0.88_5$ | >0.89 | $0.56_2$ |
| PKL 68 | cyclohex, diff | $4.2_8$ | $3.6_3$ | $<0.07_7$ | $0.52_2$ | $0.46_7$ | $<-0.44_4$ | | $0.87_5$ | $>0.89_3$ | 0.88 | $0.58_7$ |
| PKL 77 | cyclohex, diff | $3.2_7$ | $3.1_1$ | $0.15_1$ | $0.43_1$ | $0.41_3$ | $-0.39_5$ | | $0.77_3$ | $0.79_5$ | 0.78 | $0.55_3$ |
| PKL 80 | TMU, diff | $2.5_0$ | $2.3_3$ | $0.34_6$ | $0.33_3$ | $0.30_7$ | $-0.27_9$ | | $0.57_5$ | $0.56_1$ | 0.57 | $0.59_5$ |
| PBLG 32 | THF, evap | $5.4_2$ | $2.7_9$ | $0.18_5$ | $0.59_6$ | $0.37_4$ | $-0.37_3$ | $0.68_7$ | $0.70_0$ | $0.75_1$ | 0.72 | |
| PBLG 2 | THF, evap | $8.3_1$ | $3.3_4$ | $0.13_8$ | $0.70_9$ | $0.43_8$ | $-0.40_3$ | $0.81_8$ | $0.82_0$ | $0.81_1$ | 0.82 | |

[a] Solvent: THF, tetrahydrofuran; isoph, isophorone; cyclohex, cyclohexanone; TMU, tetramethylurea. Preparation by free evaporation (evap) or diffusion of solvent (diff). [b] The parallel absorption of the amide II band is too weak to be measured precisely. [c] Using $\alpha$ and $S_\alpha$ values for an $\alpha$-helix; see Table III.

**Table III**
**Transition Moment Angles $\alpha$ for the $\alpha$-Helix Main-Chain Vibrations**

| band | exptl, this work: $S_\alpha$ | $\alpha$ | calcd[a] $\alpha$ | exptl $\alpha$, ref |
|---|---|---|---|---|
| amide A 3291 cm$^{-1}$ | 0.867 | 17.3° | 22.7° | 17.3°, 26<br>28°, 24 |
| amide I 1653 cm$^{-1}$ | 0.534 | 33.9° | 34.6° | 27.6°, 26<br>39°, 24 |
| amide II 1545 cm$^{-1}$ | −0.497 | 87.5° | 87.5° | 75.3°, 26<br>75°, 24 |
| amide III 1328/1313 cm$^{-1}$ | 0.234 | 45.6° | 45.6° | 40°, 24 |
| amide V 615 cm$^{-1}$ | −0.45 | ~80° | 86.7° | 76.4°, 26<br>>80°, 24 |

[a] Calculated for an $\alpha$-helix with unit pitch of 1.50 Å.[25]

**Table IV**
**Transition Moment Angles $\alpha$ for Side-Chain Amide and Carbazole Bands**

| wavenumber, cm$^{-1}$ | $S_\alpha$ | $\alpha$ | band |
|---|---|---|---|
| 3291 | 0.091[a] | 51° | amide A of side chain |
| 1675 | 0.27 to 0.32 | 42–44°[b] | amide I of side chain |
| 1517 | 0.07 to 0.11 | 52–54° | amide II of side chain |
| 1453 | −0.01 to 0.08 | 52–55°[c] | carbazole |
| 1444 | −0.09 to −0.05 | 52–59° | carbazole |
| 750 | 0.10 to 0.20 | 47–51° | carbazole |
| 725 | 0.19 to 0.26 | 45–47° | carbazole |
| 561 | 0.12 to 0.27 | 44–50° | carbazole |

[a] Calculated from an apparent $S_\alpha$ = 0.573, main-chain $S_\alpha$ = 0.867, and relative absorbance of 0.63; see text. [b] Variations in $\alpha$ due to uncertainty for the amide bands. [c] For the carbazole bands, variations depend on the preparation: The lowest values of $S_\alpha$ are observed in films made by free evaporation of solvent, the high values in diffusion-made films.

contributions are unresolved. The apparent $S_\alpha$ value for the combined amide A band can be calculated by using eq 4 and the order parameter values of Table II. The apparent $S_\alpha$ value was constant, approximately 0.573, implying that the side-chain transition moment direction is fairly constant for all samples.

These results show the self-consistency of the universality of the $\alpha$-helical conformation of the main chain and the correct assignment of main-chain and side-chain amide bands.

**Order Parameters.** As the main-chain conformation is independent of sample history, the amide I and II bands of the main chain may be used for order parameter determination of oriented samples of PKL and PBLG.

From the tabulated order parameters it is clearly seen that the qualitative observations in the polarizing microscope are correct: Films prepared by evaporation typically have order parameters of 0.70–0.85, whereas the films made by diffusion can have order parameters in excess of 0.90.

**The Side Chain.** The side chain consists of four methylene groups, an amide-like group, and a carbazole group, the latter being treated separately. The amide-like group is not strictly speaking an amide group, since it is connected to the aromatic nitrogen atom of the carbazole moiety. It is, however, not a genuine urea group, since the carbazole nitrogen is aromatic in nature. Since the carbazole group shows only weak interaction (in the ultraviolet and infrared regions) with the side chain, we will refer to it as an amide group.

The methylene bands at 2935 and 2865 cm$^{-1}$ display an interesting conformational dependence on the casting conditions of the films. Films made by evaporation have unpolarized absorptions, while diffusion-made films have parallel polarized absorptions, with $S_\alpha$ of 0.10 and 0.15, respectively. The methylene bands are polarized perpendicularly to a stretched methylene chain, as seen in polyethylene,[29] implying that diffusion-made samples have more extended methylene side chains than evaporation-made samples. However, the methylene side chains are not totally extended to the all-trans configuration, as this would lead to a larger value of $S_\alpha$.

The side-chain amide band dichroism differs from that of the main chain. As mentioned above, the combined amide A band has a $S_\alpha$ of 0.573, expressing some average of the two amide groups. Using the $S_\alpha$ of the main-chain amide A band for PBLG (from Table III) and the relative absorptivity (0.63) found below, $S_\alpha$ = 0.091 for the side-chain amide A can be calculated. Assuming all side groups identical, this corresponds to an angle $\alpha$ of 51°. From the dichroism of the amide I and II bands, approximate values of $S_\alpha$ for the side chains can also be estimated. Due, however, to partial overlap with the main-chain bands, there is considerable uncertainty. Values are listed in Table IV. No significant differences in transition moment directions of the side-chain amide groups due to casting conditions of the films could be detected.

**Hydrogen Bonding.** The amide group in the side chain is strongly hydrogen bonded as can be elucidated from the frequencies and multiplicity of the side-chain amide A and I transitions. For both bands doublets are seen, the high-wavenumber components being the contribution from

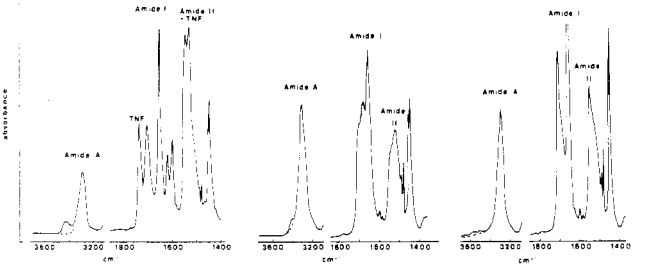


**Figure 3.** Comparison of the amide bands of PKL in the solid state, solution, and charge-transfer complex film: left, PKL/TNF film, 1:1 molar ratio, from THF solution; center; PKL film from THF solution; right, differential spectrum of PKL, in a 30 w/v % THF solution. In the solid state, most of the side chains are hydrogen bonded, as indicated by the weak amide A component at 3430 $cm^{-1}$ and the strong amide I component at 1675 $cm^{-1}$. In both solution and complex the side chains are nonbonded, as indicated by the larger component at 3430 $cm^{-1}$ and the strong amide I component at 1705 $cm^{-1}$.

the free groups. Thus the amide A band has a weak component at 3430 $cm^{-1}$, which is ascribed to a free NH band,[25,28] in addition to the strong hydrogen bonded band at 3291 $cm^{-1}$.

Hydrogen bonding in the side chain of poly($N^{\epsilon}$-carbobenzoxy-L-lysine) (PCLL) has been studied by Sasaki,[30] who also found an unresolved hydrogen-bonded amide A band at 3291 $cm^{-1}$ consisting of contributions from both the main chain and the side chain. The hydrogen bonding of the side chains is between adjacent groups, giving rise to columns of the side chains. By assuming equal absorption coefficients of the main chain, side chain, and free side chain Sasaki found that 82% of the side chains were hydrogen bonded.

This assumption is not used here, but instead we assume that the relative absorbances of the amide A, I, and II bands of the main chain are identical in PBLG and PKL. The main-chain contribution to the amide A band at 3291 $cm^{-1}$ can thus be estimated, leading to the result that the absorption of the hydrogen bonded side chain is 63% of that of the main chain.

In the PKL films the ratio of areas of the free and bonded amide A bands is very constant: 0.030–0.032. Using Sasaki's assumption one can calculate that only 8% of the side groups are free. A more precise estimation requires a knowledge of the extinction coefficient ratio $\epsilon_{S,f}/\epsilon_{S,b}$ of free and bonded groups. The value of this ratio is difficult to obtain unambiguously but has been attempted for polyurethanes and polyamides.[31,32] Based on low molecular weight compounds, a ratio of 1:3.2 has been proposed.[31]

To make an independent determination of this ratio a non-hydrogen-bonded specimen is needed. In solution it is difficult to make quantitative measurements (see subsection Solutions), but this was attempted in a charge-transfer (CT) complex of PKL and 2,4,7-trinitrofluorenone[17,18] (TNF). The IR spectrum of this complex in a 1:1 molar ratio showed almost exclusively the free component of the C=O side-chain amide I band, as seen in Figure 3, indicating that the NH group is also entirely free.

In the CT complex the ratio of areas of the amide A band is 0.234, as seen in Figure 3. Assuming that TNF does not otherwise alter the spectrum, the molar extinction coefficient ratios $\epsilon_{S,f}:\epsilon_{S,b}:\epsilon_{\alpha,b}$ can be calculated to 0.234:0.79:1. The $\epsilon_{S,f}:\epsilon_{S,b}$ ratio is then 0.297:1 or 1:3.37, in agreement with that cited above for low molecular analogues.[31]

**Table V**
**Frequencies for Amide Bands and Hydrogen Bond Length**

| polymer | band | $\nu_A$, $cm^{-1}$ | $\nu_B$, $cm^{-1}$ | $\nu_{II}$, $cm^{-1}$ | $\nu_{NH}$, $cm^{-1}$ | N···O dist, Å |
|---|---|---|---|---|---|---|
| PKL | main chain | 3291 | 3057 | 1547 | 3254 | 2.84 |
| | side chain, bonded | 3291 | 3045 | 1517 | 3302 | 2.93 |
| | side chain, free | 3430 | 3057? | 1517? | 3453 | |
| PCCL | main chain | 3300 | 3065 | 1540 | 3285 | 2.90[a] |
| | side chain, bonded | 3300 | 3050 | 1520 | 3310 | 2.94[a] |
| | side chain, free | 3430 | 3065 | 1520 | 3455 | *a* |

[a] From Sasaki.[28] Relations used, see Fraser:[25] distn(N···O) = $0.001825\nu_{NH} - 3.10$ Å; $\nu_{NH} = \nu_A + \nu_B - 2\nu_{II}$ unpertubed NH stretch frequency; $\nu^0_{NH} = 3457$ $cm^{-1}$, for free unpertubed NH stretch.

The degree of hydrogen bonding can then be recalculated to 78–80%, leaving 20–22% free NH groups in the side chain. Note that this degree of bonding is constant and does not depend on sample history. All free groups are assumed to originate from the side chains, since in PBLG less than 1% of the main-chain NH groups are free. If in the CT complex some groups are hydrogen bonded, the calculation will lead to an even higher degree of bonding in the pure polymer. Thus 78–80% bonded groups is a lower estimate.

Evidence of free groups may also be seen by the weak polarization of the 1705-$cm^{-1}$ component of the amide I band, compared to the polarization of the 1675-$cm^{-1}$ component.

The hydrogen bond distance may be estimated from the frequencies of the bonded and free groups. As reviewed by Fraser[27] the hydrogen bond length is correlated to the unperturbed NH stretch frequency, which can be calculated from the amide A, B, and II frequencies. These results are shown in Table V. It is seen that the unperturbed NH frequency calculated from the free side chain bands is practically identical with the teoretical value of 3457 $cm^{-1}$. The hydrogen bonding length of 2.93 Å is only 0.1 Å longer than that for the main-chain $\alpha$-helix. This bond length combined with the high degree of hydrogen bonding imposes severe restrictions on the conformational possibilities of the side chains.

This calculation has only been experimentally verified for the $\alpha$-helical amide, but any given hydrogen bond length would still impose a severe restriction on the conformation. Lengths above 3.2 Å are energetically unfavorable, thus inadmissible, and further restricting the number of possible conformations.

**The Carbazole Group.** The carbazole bands are easily discernible, being sharp with narrow line widths. Most prominent are bands at 1450, 750, 725, 561, and 420 $cm^{-1}$, but several weaker bands are also observed. All the strong bands and most of the weaker ones are observed within a few reciprocal centimeters with respect to those in the carbazole crystal,[33] carbazole solutions,[34] and solid poly(*N*-vinylcarbazole).[35,36] Evidently the carbazole moiety shows only weak coupling with the surroundings and frequencies are definitely not affected by conformational changes.

The polarization of the bands may be seen in Table IV. All bands cited are weakly polarized and well resolved, making a very precise determination of the dichroic ratio possible. As may be seen the $S_\alpha$ values are dependent on preparation conditions: The 1450-$cm^{-1}$ in-plane bands having positive $S_\alpha$ in diffusion prepared films and negative values in evaporated films. The changes are, however, rather small and only correspond to smaller angular changes of the carbazole group.

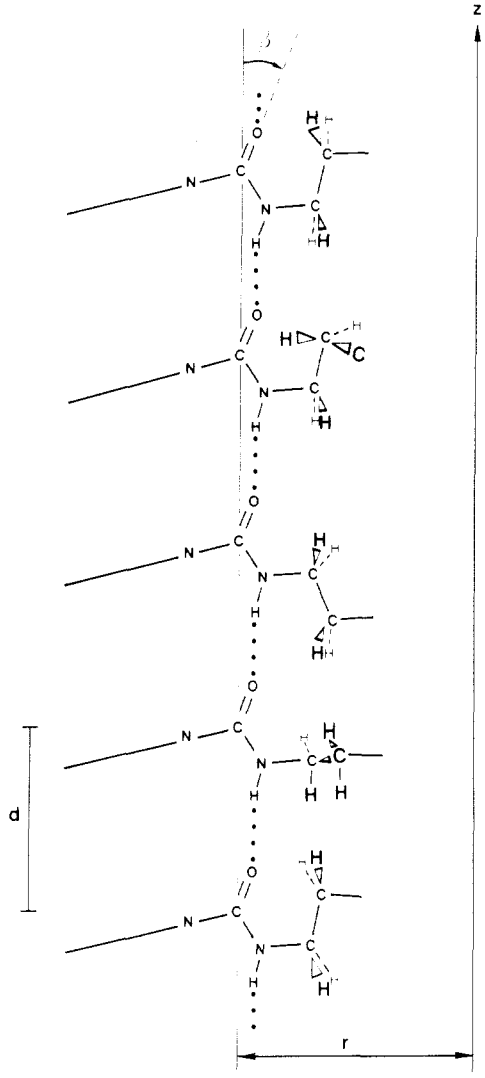


**Figure 4.** Schematic representation of a stack of hydrogen-bonded side chains. The amide group plane is in the drawing plane, while the carbazole plane is normal to this plane. The helical backbone has been omitted for clarity, only the center axis defined by $z$ is shown. The terms $r$, $d$, and $\beta$ as used in the text are shown.

The 750 and 725 $cm^{-1}$ out-of-plane vibrations are stronger and always parallel polarized, with identical changes in $S_\alpha$.

Assignments for transition moment directions in carbazole have been performed in the carbazole crystal,[33] but only in part for carbazole polymers,[35] thus precluding a quantitative treatment regarding spatial placement.

Summarizing, one finds small but significant changes in carbazole spatial disposition in PKL, depending on the sample history.

**Conformation of the Side Chains.** So far, results presented have been extracted from the measurements directly. Trying to make models of possible conformational arrangements is, however, an interpretation of data and may be subjected to debate as to whether they uniquely and unambiguously account for the experimental data.

Here are evaluated various conformations obtained only by allowable rotations about single bonds, thus preserving the dihedral angles of the methylene groups and the planarity of the amide and carbazole groups. Arrangements have been constructed with a molecular model kit to ensure the geometrical ability of forming such conformations.

**Stacking of the Side Groups.** The fact that 80% of the side chains are hydrogen bonded implies that there is stacking of the side chains with on the average five per stack. As elucidated below this fact imposes severe restrictions on the possible conformations. A stack structure as shown in Figure 4 must be formed to account for the hydrogen bonding, though not necessarily as regular in distance and angles as depicted. A molecule consisting of three such stacks is depicted in Figure 5.

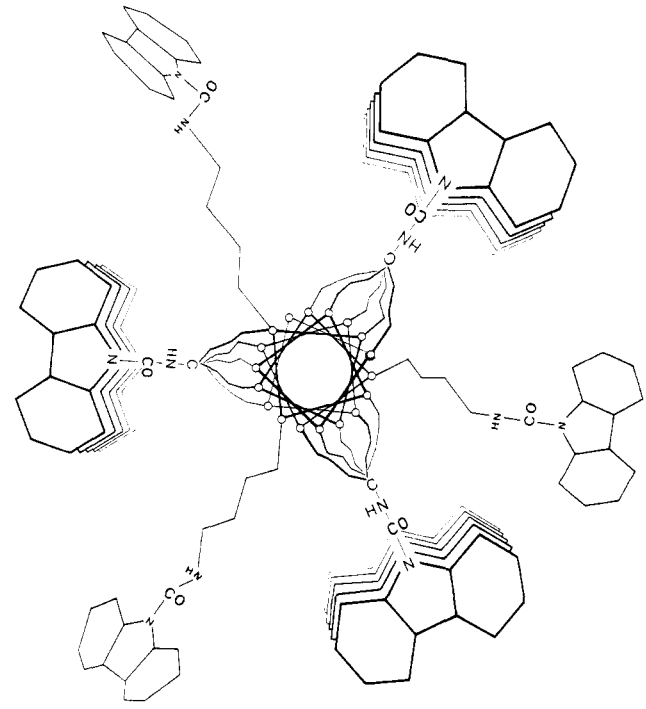

**Figure 5.** A possible molecular conformation of PKL, viewed along the helical axis. In this model the side chains are hydrogen bonded to form three stacks parallel to the helical axis. A small fraction of the side groups cannot be incorporated in the stacks and are thus shown as nonbonded.

In this presentation cylindrical coordinates are used, $z$ defining the helical axis, $r$ *the distance* from the $z$ axis to the carbonyl carbon of the side chain. The distance between succesive side groups, more specifically the distance between succesive carbonyl carbons of the side chain, in a stack is termed *the repeat distance* $d$. The lengths $r$ and $d$ of the side chains are assumed equal for all chains in a stack. The relative spatial positioning of two succesive side groups in the stack is described by the *vertical displacement* $\Delta z$ and the *angular displacement* $\phi$. The simple geometrical equations relating $d$, $r$, $\Delta z$, and $\phi$ are shown in Figure 6. Using the bond angles and distances for a standard amide group in the trans conformation[27] and the hydrogen bond length of 1.93 Å determined from the IR frequencies, a repeat distance $d$ of 5.02 Å can be calculated. Even if a slight distorsion of bond angles, e.g., to 126° for the N–C–N angle as opposed to 120°, and a hydrogen bond length of 2.2 Å are allowed (resembling the rippled or parallel $\beta$-sheet structure), the repeat distance $d$ is not allowed to exceed 5.38 Å.

From a molecular model it can be deduced that the side-chain length $r$ may vary from 5.5 Å for the most compressed conformation of the side chains to 9.3 Å for the all-trans conformation of the methylene groups.

Due to the $\alpha$-helical structure, there is a correlation between the angular displacement $\phi$ and the vertical displacement $\Delta z$, provided that one looks for a stack of infinite length:

$$\Delta z = \frac{360° + \phi}{100°} 1.50 \text{ Å} \qquad (5)$$

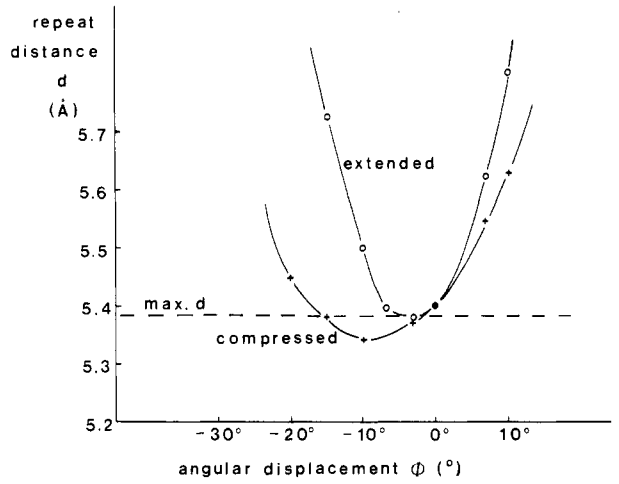


**Figure 6.** Relations between the repeat distance $d$ and the angular displacement $\phi$, defined in the text, for compressed and extended conformations of the side chains, for infinite stacks. The maximal $d$ of 5.38 Å corresponds to a hydrogen bond length of 2.20 Å. Geometrical relations: $\Delta xy = r(2 - 2\cos\phi)^{1/2}$ and $d = (\Delta z^2 + \Delta xy^2)^{1/2}$. The $\alpha$-helical restriction is that of eq 5. For the compressed conformation $r = 5.5$ Å, and for the extended conformation $r = 9.3$ Å. For given values of $\phi$ and $r$, one can thus calculate $d$.

This condition gives restrictions on the repeat distance $d$ as shown on Figure 6 for different $\phi$ and $r$.

It is seen that the limitation $d$ less than 5.38 Å imposes very severe restrictions on the angular displacement, $\phi$, which should be between −15° and 0° in order to get realistic repeat distances.

**Stack Length.** One may argue that eq 5 relating $\phi$ and $\Delta z$ need not be fulfilled. Shorter stacks with a smaller repeat distance can be formed by bending the methylene chains toward one another. The chains can, however, maximally be displaced by approximately 4.2 Å (from the all-trans conformation) when the dihedral angles are preserved.

The question then arises of whether the "free" groups are totally free or whether they are simply at the ends of the bonded stacks. The more totally "free" groups, the larger the average stack length. The free groups at the end of the stacks should have a dichroism similar to the bonded groups, while totally free groups should be randomly placed giving unpolarized bands. Thus, the polarization of the 3420- and 1705-cm$^{-1}$ bands should provide information on the nature of the free groups.

It was not possible to measure the precise polarization of these bands, but the qualitative result is that the free bands are nearly depolarized, in contrast to the corresponding bonded bands, in agreement with the above-mentioned hypothesis. Thus contributions from both totally free and stack-end groups are present.

The percentage cannot be determined exactly; however, estimates[37] are that 65–70% of the free groups are unpolarized, corresponding to 12–14% of the total number of side groups. Then 7–9% of the side groups should be at the end of the stacks. This gives an average length of 10–15 units. Of course statistically a few very long regular stacks must thus be formed.

These long stacks must have very small angular displacements, as indicated in Figure 6. Some short stacks without these restrictions may be made by proper bending of the methylene chains toward one another, but such stacks can only comprise a minor part of the chains, since the number of stack ends is limited.

The model proposed in Figure 5 has the features of a small angular displacement and low content of free groups, typically 11–17%. In this model the structure regularly repeats after a period of 18 units. Bonding occurs for example between the units $i$, $i + 4$, $i + 8$, $i + 11$, $i + 15$, and $i + 18$, where $i = 1, 2, 3$. This gives three stacks which may be of infinite length and three free groups per 18 units (in this example no. 4, 8, and 15). Some of the free groups (no. 4 and 8) may also form a hydrogen bond.

The major proportion of the side chains are placed in three stacks which are virtually parallel to the helical axis. The resulting free chains are not involved in stacks, implying that the stacking will contain structural defects. However, the possibility of infinitely long stacks in the sense of percolation theory exists.

These above facts can be utilized to evaluate the possibility of other arrangements: A four-stack model where the $i$th repeat unit is bonded to the $(i + 4)$th, $(i + 8)$th, etc. units, forming four regular stacks twisting around the molecule, is possible only for short stacks, as the vertical displacement $\Delta z$ is 6.0 Å and the angular displacement $\phi$ is 40° for each repeat unit, thus giving a repeat distance $d$ between 7.1 and 8.7 Å (for the compressed and extended arrangement, respectively), which greatly exceeds the maximum allowable based on the hydrogen bond length. Shorter stacks can be formed where the methylene chains are bent toward one another to get closer contact of the amide groups. The chains may, however, maximally be displaced by approximately 4.2 Å so stacks with an average length exceeding five units cannot be formed.

A three-stack arrangement with bonding between the $i$th, $(i + 3)$th, $(i + 6)$th, etc. repeat unit is possible for short stacks only, since the vertical displacement of 4.5 Å and the angular displacement of −60° lead to a repeat distance of 7.1–10.3 Å for the stack. Here also some five units is the limit.

In PBLG an intermolecular stacking has been proposed[38,39] for concentrated solutions and films where twisted stacks of benzene groups are placed in an regular manner between neighboring molecules. A similar carbazole stacking may in principle be realized in PKL but will lead to a large content of free NH groups, since intermolecular hydrogen bonding is not possible due to steric considerations.

An arrangement of intercalated, intermolecular carbazole stacks with highly extended methylene stacks may be admitted in principle. Since intermolecular hydrogen bonding is not possible when carbazole groups are stacked, this can only account for a very small proportion of the side chains (as 80% are determined to be bonded).

**Spatial Placement of the Side Chains.** The positioning of both the main-chain and side-chain amide group relative to the helical axis is shown in Figure 7. Both amide plane normals are essentially perpendicular to the helical axis. Based on the angles for the main-chain amide vibrations, tabulated in Table III, the angle $\gamma$ between the transition moment vector and, for example, the C=O direction can be found for the main-chain amide group. From the dichroic absorption measurements, more than one possibility of the angle $\gamma$ exists. These are shown in Table VI. From the $\gamma$ values the angle $\beta$ in Figures 4 and 7 may be estimated to 20° for the amide A and II bands and to 6° for the amide I band. Based on the arrangement shown in Figure 4 with a colinear hydrogen bond (C=O···H—N linear) an angle of $\beta$ equal to 13° is expected. The distorted arrangement where the hydrogen bond is not completely linear and has a length of 2.2 Å gives a 21° angle.

It should be noted that the measured transition moment angles can be explained by an arrangement with tilted

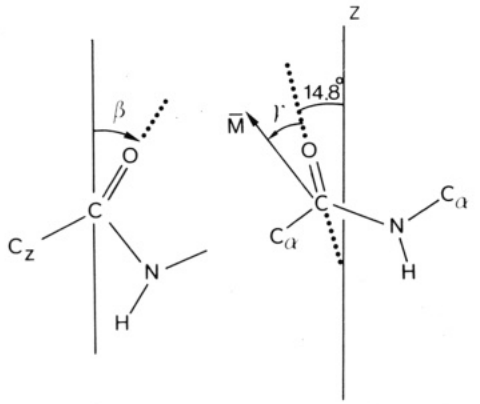


**Figure 7.** Angle between the helical axis and the carbonyl bond of the amide group, for both the main chain and the side chain. Both amide plane normals are essentially perpendicular to the helical axis. The angle for the main chain is calculated for a standard $\alpha$-helix;[27] the value $\beta$ for the side chain is discussed in the text. The sign of the angle $\gamma$ between the carbonyl bond and the transition moment vector is also indicated. $\bar{M}$ is the transition moment vector, $C_\alpha$ the main-chain tetragonal carbon, and $C_z$ signifies the carbazole group.

**Table VI**
**Angular Assignment of Side-Chain Amide Group**

| band | main chain obsd $\alpha$ | possible angles $\gamma^{a,d}$ 1 | 2 | side chain obsd $\alpha^b$ | angle $\beta$ from$^{c,d}$ 1 | 2 |
|---|---|---|---|---|---|---|
| A | 17.3° | 2.5° | −32.1° | 51° ± 2° | 48° | 19° |
| I | 33.9° | 19.1° | −48.7° | 43° ± 1° | −24° | 6° |
| II | 87.5° | 72.7° | 77.7° | 53° ± 1° | 20° | 49° |

[a] $\gamma$ is the angle between C=O and the transition moment vector; see Figure 7. [b] $\alpha$ is determined from eq 2–4. [c] $\beta$ is the angle between the C=O of the side-chain amide and the helix axis; see Figure 6. [d] 1 and 2: The $\alpha$ angle is by convention given in the 0–90° range but may as well lie in the 90–180° range. The two possibilities are listed as 1 and 2, respectively.

amide groups,[27] for which the plane normals are not perpendicular to the helical axis, but tilted some 50°. Though this may be compatible with the four-stack model, it can be excluded on account of the large repeat distance which precludes the formation of hydrogen bonds. The possibility also exists that the transition moment vectors do not have the same directions in the main-chain and side-chain amide as these are not identical in nature. Fraser[27] has noted that such vectors in simple and in $\alpha$-helical amides do not have identical directions. The unexpected $\beta$-value in Table VI for the amide I band cannot, however, be satisfactorily explained.

The carbazole groups are locked-in conformationally due to the stacking. As seen in Figure 4, the bulky groups cannot rotate freely around the N–C bond between the carbazole and the amide. The carbazole planes are inclined 69–77° to the helical axis. Thus, the distance between adjacent planes is 5.0–5.5 Å. On the basis of the van der Waals half-thickness of aromatics (1.85 Å) the groups can only tilt 40–45° from the position perpendicular to the amide plane and even less if the carbazole planes are not parallel. An uncorrelated tilt of a single carbazole group can only be 10–11°. The carbazole and amide groups are thus efficiently locked-in. Small variations in the tilts for samples prepared from different solvents may be indicated by small differences in the dichroic ratio of the carbazole band.

The stacking requires that the four methylene groups in the side chain can adjust their conformation by rotation to gauche or skew conformations. Hence some groups are bent forward and others backward with respect to their position at the $\alpha$-helical backbone. Thus a compressed rather than an extended version of the side-chain conformation is expected. The density of the solid films is 1.49 g/cm$^3$. Assuming hexagonal packing of rods, one finds a radius of the molecule equal to 8.3 Å. This is even lower than expected from spatial considerations where the most compressed version gives a radius of 10.6 Å, and the all-trans extended version gives a radius of 14.3 Å. Evidently the arrangement in three stacks gives a noncylindrical molecule, possibly a hexagonal rod which is able to pack in a more condensed way.

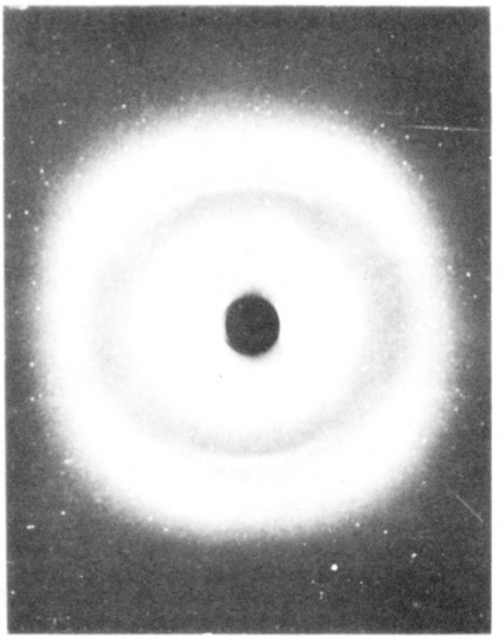

**Figure 8.** Flat-film X-ray diffraction photograph of a shear-oriented film of PKL. Cu K$\alpha$ radiation; sample to film distance 83 mm; helix and shear directions vertical; 59 layers with approximately 400-$\mu$m total thickness.

The arrangement in three stacks parallel to the helical axis diminishes the effects of chirality in the solid state, as both left-handed and right-handed helices would give identical arrangements of the side chains. This may be an explanation of the fact that it has not been possible to prepare films of PKL with a "frozen-in" cholesteric structure,[18] though a such structure is easily obtainable with PBLG.[40]

**X-ray Scattering.** X-ray diffraction has been performed on shear-oriented films of PKL, made by diffusion of the isophorone solvent. To achieve sufficient scatter it was necessary to make sandwiches of 15 or 60 layers of films, which reduced the macroscopic order due to misalignment of the layers. A typical flat film X-ray photograph is shown in Figure 8. Only a few arc reflections are seen, indicating the orientation is far from perfect.

A sharp meridional reflection of 5.2 ± 0.1 Å is observed, which may correspond to the repeat distance of the carbazole stacks. Two prominent broadened equatorial reflections are observed, corresponding to 7.2–8.3 Å and 18.0–20.0 Å, the broadening being due to the lattice rather than uncertainty in the measurements on the film, which is 0.1–0.2 Å. The 8-Å reflection could indicate an average distance between the carbazole groups and the helical backbone and the 19-Å reflection the average distance between the rods in the (assumed hexagonal) packing. This distance is larger than the helix center distance of 16.6 Å found from the density calculations, but the density was determined on films prepared by free evaporation,

which were found to have a more compressed conformation of the methylene groups of the side chain than diffusion-prepared films used for the X-ray scattering. The effective radius of the molecules may therefore be somewhat larger in these films. The broad diffuse reflection corresponding to 3.5–4.4 Å is probably indicative of van der Waals contacts of atomic groups.

The X-ray scattering results do not conflict with the proposed conformation of PKL, though the samples were not sufficiently oriented to provide new information. The absence of more distinct reflections may possibly indicate that the helical conformation of the main chain is not totally regular but could be considered as a distorted $\alpha$-helix.

**Energy Considerations.** Qualitative energy considerations may also be used to estimate the side-chain conformation. Sources of conformational energy to be considered are hydrogen-bonding energy of the amide groups, rotational energy of the methylene groups, $\pi$-orbital repulsive energy of the carbazole groups, and torsional energy of the amide group.

Hydrogen bonds have an energy of approximately 80 kJ/mol,[27] while the gauche conformation of a methylene group has a 3.3 kJ/mol higher energy than the trans conformer and a 30° torsion from a trans or gauche configuration requires less than 7.5 kJ/mol.[41] Distorted conformations of the methylene groups can therefore be tolerated in order to faciliate hydrogen bonding.

By the stacking model proposed here, only the methylene groups are required to deviate from their lowest conformational energy. The amide groups remain planar, and the carbazole moieties are parallel and too distant to show van der Waals repulsion.

**Solutions.** All main-chain amide bands and carbazole bands in solution are unchanged in frequency compared to film spectra and had comparable width and relative absorptivity.

Only the amide vibrations of the side group were changed, as seen in Figure 3. Apparently the free component of the amide A band is broadened in the 3400–3600-cm$^{-1}$ range. As trace amounts of water also absorb in this region, quantitative measurements of the free content have not been made.

The C=O amide I band was shifted toward the free component at 1705 cm$^{-1}$. The amide II band showed some change in the relative absorbance, but not shift in frequency.

The interpretation of these findings is that the $\alpha$-helix is preserved in solution, not surprising as this is a precondition for the formation of a lyotropic liquid-crystalline phase, and that the carbazole group shows no specific interaction with the solvent or the side-chain amide group. The side-chain hydrogen bonds are, however, effected. An explanation could be that the intramolecular hydrogen bonds are totally broken by the solvent. The capability of a solvent to break the hydrogen bonds might be a precondition for dissolving PKL, thus explaining why many common solvents are not effective for the polymer.[18] In solution the side chains are thus more mobile, tending to randomize the side-chain conformation. A more extended side-chain conformation might be expected due to solvent interpenetration.

The absence of stacks parallel to the molecular axis can be implied from observations of a finite cholesteric pitch height in lyotropic solutions. A noninfinite pitch requires chirality, viz., a molecule shaped as a right-handed screw rather than a cylinder. Pitch measurements on PKL are reported elsewhere,[43] where large solvent- and temperature-dependent variations in the pitch are observed, comparable to that of PBLG.

Generally the side-chain conformation in solution can be varied by factors such as temperature, concentration, and solvent. These variations are reflected in the solid films, where small but significant changes in the methylene and carbazole conformations are seen in samples cast from different solvents.

## Conclusions

Polarized infrared studies show that the main chain of PKL is in the $\alpha$-helical conformation, in both solid films and liquid crystalline solutions. The side chains are strongly hydrogen bonded in the solid state, possibly forming three stacks parallel to the helical axis. A few side groups are free, i.e., cannot be incorporated in the stacks, and are probably more mobile. The carbazole groups are thus due to hydrogen bonding and stacking, conformationally locked-in in positions which are conducive for energy transfer and electronic conduction.

The conformational structure resembles that of isotactic poly(vinylcarbazole) (PVK) in the crystalline state,[42] believed to have favorable positioning of the carbazole groups with respect to photoconductive[1,2,7] and energy-transferring properties.[6] The very regular structure of the photoactive groups in PKL makes this polymer an interesting model material for the study of the photoconduction mechanism. This should be seen in contrast to atactic, amorphous, and isotropic PVK, the subject of much previous study, which is dominated by conformational and stereoisomeric irregularities which can serve as defect trap sites.

However, as in PVK, structural defects, here the free side groups, may act as traps, impeding the photoconduction and energy-transfer processes.

**Acknowledgment.** We express our gratitude to the Danish Natural Science Research Council for making the infrared equipment available for this project. We also thank J. Halstrøm and K. Kovacs, both no longer with the group at IKI, for generously supplying the samples of PKL with which this work was carried out. Sincere thanks are due to Professor R. Norrestam at the Chemical Laboratory B of the Technical University of Denmark for performing the X-ray scattering measurements.

**Registry No.** PKL (homopolymer), 84110-21-4; PKL (SRU), 84117-59-9.

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# Water-Soluble Polymers. 28. Ampholytic Copolymers of Sodium 2-Acrylamido-2-methylpropanesulfonate with (2-Acrylamido-2-methylpropyl)dimethylammonium Chloride: Synthesis and Characterization

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ABSTRACT: Copolymers of (2-acrylamido-2-methylpropyl)dimethylammonium chloride (AMPDAC) and 2-acrylamido-2-methylpropanesulfonate (NaAMPS) were prepared by free radical polymerization employing potassium persulfate as the initiator. Copolymer compositions were determined from elemental analysis and $^{13}C$ NMR data. Reactivity ratio studies yielded $r_1$ and $r_2$ values of 0.22 and 0.31 for the AMPDAC ($M_1$) and NaAMPS ($M_2$) monomer pair. Molecular weights, determined by using low-angle laser light scattering, were found to decrease with AMPDAC content and ranged from 1.6 to $9.5 \times 10^6$ g/mol. Copolymer microstructures were predicted by calculation of reactivity ratios. The viscosity behavior is interpreted in terms of polymer composition, molecular weight, and microstructure in the following paper in this series.

## Introduction

Ampholytic copolymers represent a special class of polyelectrolytes which contain both positive and negative charges along the macromolecular backbone. Solution behavior of ampholytic copolymers is often difficult to predict since a number of parameters including charge type and distribution, polymer microstructure, molecular weight, hydrophobic/hydrophilic balance, solvent type, pH, and ionic strength are operative. In our continuing efforts to prepare electrolyte-tolerant, water-soluble copolymers[1-11] we now report the synthesis and characterization of high charge density polyampholytes.

Although extensive research has been conducted on ordinary polyelectrolytes, very few studies have been conducted on ampholytic polymers, particularly in neutral salt solutions. Peiffer and Lundberg[12] reported the synthesis and viscometric properties of high and low charge density polyampholytes. Sodium styrenesulfonate was copolymerized with (methacrylamidopropyl)trimethylammonium chloride (MAPTAC) and terpolymerized with MAPTAC and acrylamide. The viscometric properties of the high charge density polymers were found to be a function of intramolecular ionic interactions in pure water and neutral salt solutions. In contrast, the viscometric properties of low charge density terpolymers were found to be highly dependent on intermolecular interactions, particularly at polymer concentrations in the region of chain overlap ($C^*$).

Salamone et al.[13,14] reported the synthesis of polyampholytes derived from cationic–anionic monomer pairs. These high charge density copolymers incorporated equal amounts of the comonomers and were found to display viscosity behavior in salt solution that is quite different from that of classical polyelectrolytes. In a more recent study, Salamone et al. reported the spontaneous polymerization and aqueous solution behavior of several ion pair comonomers.[15] The viscosities of the copolymers increased with increasing potassium chloride concentration in the

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