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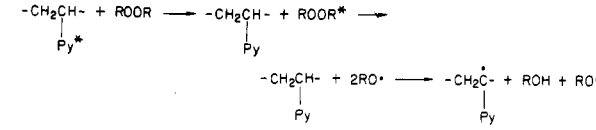


# Investigation of Purity and Fluorescence of Poly[$N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine] Preparations

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ABSTRACT: It is demonstrated that a polymer previously published as a homopolymer of $N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine is in fact a terpolymer of $N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine with $N^6$-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine and $N^6$-(2-methyl-9*H*-carbazol-9-ylcarbonyl)-L-lysine (ratio ca. 200:1:1). Spectroscopy and HPLC and GC/MS analysis on acid hydrolysates were applied for elucidation. The $N^6$-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine is shown to be the cause of the low-energy emission band observed in the fluorescence spectrum of the polymer. Previously published interpretations of fluorescence measurements are thus to be revised. 5*H*-Benzo[*b*]carbazole was synthesized as a reference compound. Commercially available carbazole preparations were found to be markedly heterogeneous.

## Introduction

In recent years carbazole-based polymer systems have been the focus of considerable research due to their unusual electrical and photoelectric properties.[1-3] Several types of carbazole polymers have been synthesized and studied with a view to elucidating the photophysics of excimer formation. By far the most work has been done on poly(*N*-vinyl-9*H*-carbazole) (PVCz), which has well-documented photoelectric and excimer-forming properties.[4-6]

In order to investigate the effect of order on the photoconductive and photovoltaic behavior, Halstrøm and coworkers[7,8] prepared poly[$N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine] (PKL), which was found to have the $\alpha$-helical conformation and to form a lyotropic cholesteric liquid crystal in concentrated solution. Chapoy and coworkers[9-16] used this sample in a recent series of fluorescence and photoconductivity investigations. In the following this material will be referred to as polymer I. The steady-state emission spectrum of I was reported to consist of two well-resolved emission bands at 342 and 390 nm.[9,10,12-16] Time-resolved fluorescence spectra of I were reported to reveal the presence of four emitting species, of which the two low-energy species (emitting at 386 and 408 nm) were believed to be excimers, formed from species emitting in the high-energy band.[11-13,16]

However, subsequently prepared batches of PKL turned out to differ from the first sample with respect to the low-energy emission band positioned at 390 nm. The steady-state fluorescence spectra of all new batches of PKL did only show but one unresolved emission band at 342 nm, except for highly concentrated solutions and solid films, where a shoulder corresponding to the 390-nm emission appeared. One representative of these new batches of PKL will be referred to as polymer II in the following.

This paper will report on the detection and identification of two covalently bound impurities in polymer I, viz., 5*H*-benzo[*b*]carbazole and 2-methyl-9*H*-carbazole. It will be shown that the $N^6$-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine moiety, although it amounts to only 0.5%, is the cause of the low-energy emission band observed in the fluorescence spectra of polymer I.

Since this paper describes the detection of trace impurities in a specific carbazole-containing polymer, the present findings and methodologies are expected to be of special interest to researchers involved with studies of carbazole-based polymer systems. However, this paper should also be of interest to researchers in the field of polymer luminescence, because in all studies on luminescence and energy transfer in polymers the purity of the samples is an outstanding problem.

## Experimental Section

**Apparatus.** $^1$H NMR spectra were recorded at 500 MHz on a Bruker AM 500 spectrometer. $SiMe_4$ was used as internal standard. $^{13}$C NMR spectra were recorded at 22.63 and 125.7 MHz on Bruker WH-90 and AM 500 spectrometers, respectively. $CDCl_3$ and $(CD_3)_2SO$ were used as solvents. IR spectra were recorded on a Perkin-Elmer 157 G spectrophotometer using KBr disks. UV spectra were recorded on a Perkin-Elmer 320 spectrophotometer with THF, MeOH, and $CH_3CN$ as solvents. Fluorescence spectra were recorded on a Perkin-Elmer MPF-2A spectrophotometer with dioxane and MeOH as solvents. Mass spectra were recorded on a VG 7070 F instrument operating at 70 eV using a direct inlet. Elemental analyses were carried out by Novo Microanalytic Laboratory. X-ray fluorescence analysis was carried out with a Philips TW 1410/10 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Amino acid analyses were performed on a Kontron Liquimat III amino acid

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analyzer, using the standard procedure for protein hydrolysates. HPLC analyses and fractionations were performed with a Spectra Physics SP 8000 B liquid chromatograph using a Waters μ-Bondapak C-18 reversed-phase column, 30 cm × 7.8 mm (i.d.). Operating conditions were as follows. Mobile phase 1: $CH_3CN/H_2O$, gradient 60–70% (20 min), 70–100% (10 min), 100% (5 min); mobile phase 2: $MeOH/H_2O$, gradient 70–80% (20 min), 80–100% (10 min), 100% (5 min); flow rate 2.0 mL/min; column temperature 35 °C; UV detection (Spectra Physics SP 8400) at 254 nm and fluorescence detection (Waters 420-AC), excitation at 300–390 nm (Waters filter no. 78154), emission from 420 nm and upward (Waters filter no. 78231); UV and fluorescence flow cells in series, with the UV detector first; retention times and integration for the UV signal only. HPLC-grade solvents were purchased from Rathburn. GC/MS analyses were carried out on a VG Micromass 7070 F instrument (ionization potential 70 eV; ion source temperature 220 °C). A 1.5 m × 2.2 mm (i.d.) glass column packed with 5% DV-101 on 60–80 mesh Chromosorb W, HP, was used. The temperature program was 200 °C (2 min)–280 °C at 8 °C/min. Injector and transfer lines were kept at 250 °C. The carrier gas was He, ~25 mL/min. Mass spectra were stored on a VG 2035 data system.

**Materials. 9*H*-Carbazole** was purchased from Fluka (no. 21790) and from Ferak, Berlin (no. 30363). **2-Aminonaphthalenesulfonic acid** was purchased from Fluka (no. 70840). ***N*-Phenylhydrazine** was obtained from Merck-Schuchardt (no. 807250). Hydrochloric acid (37%, pro analysi) for semimicroscale acid hydrolysis was purchased from Merck (no. 317).

**Poly[$N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine].** Batch I: This sample is identical with that in ref 7–16. The origin of the commercial 9*H*-carbazole preparation used is unknown. Batch II: This sample was prepared according to the method used for I.[7,8] The 9*H*-carbazole used was purchased from Ferak. TLC in THF of I and II gave a longish spot, $R_f \simeq 0.9$. $^1H$ NMR of I and II (25 mg/0.5 mL of $CDCl_3$): δ 7.5–6.5 (9 H, carbazole H, amide NH), 5.85 (1 H, urea NH), 3.8 (1 H, $H^\alpha$), 3.1 (2 H, $H^\epsilon$), 2.0–1.0 (6 H, $H^\beta$, $H^\gamma$, $H^\delta$). $^{13}C$ NMR of I and II (25 mg/0.5 mL of $CDCl_3$, 125.7 MHz): δ 175.9 (amide >C=O), 152.7 (urea >C=O), 137.5 (carbazole, $C_{8a,9a}$), 125.9 (carbazole, $C_{3,6}$), 124.3 (carbazole, $C_{4a,4b}$), 121.5 (carbazole, $C_{4,5}$), 119.2 (carbazole, $C_{2,7}$), 113.0 (carbazole, $C_{1,8}$), 58.0 ($C^\alpha$), 40.6 ($C^\epsilon$), 30.7 ($C^\beta$), 29.0 ($C^\delta$), 24.2 ($C^\gamma$). UV of I (100 mg/L in THF, corresponding to $3.11 \times 10^{-4}$ M of basic unit): $\lambda_{max}$ 370 nm (absorbance 0.0065), 350 (0.0081), 320 (1.076), 310 (1.226), 288 (3.00). UV of II (100 mg/L in THF, corresponding to $3.11 \times 10^{-4}$ M of basic unit): $\lambda_{max}$ 320 nm (absorbance 1.043), 310 (1.193), 288 (3.00). Elemental analysis of I and II: Found for I: C, 70.67; H, 5.95; N, 12.88. Found for II: C, 70.20; H, 5.94; N, 12.71. Calcd for $C_{19}H_{19}N_3O_2$: C, 71.01; H, 5.96; N, 13.08. Elemental analysis of sample II by X-ray fluorescence: Na < 200 ppm, Mg < 50 ppm, Al < 50 ppm, Si < 100 ppm, S ~ 80 ppm (from vacuum oil pump), Cl ~ 420 ppm (from human breath), Cu < 30 ppm, Zn < 20 ppm, all other elements with $Z$ greater than 10 are less than 10 ppm. Specific optical rotation for I: $[\alpha]_{578}$ = +25.6°, $[\alpha]_{546}$ = +27.8°, $[\alpha]_{436}$ = +38.4° (*c* 0.32, dioxane, 25 °C); for II: $[\alpha]_{589}$ = +29.0°, $[\alpha]_{578}$ = +29.7°, $[\alpha]_{546}$ = +32.6°, $[\alpha]_{436}$ = +48.5°, $[\alpha]_{365}$ = +66.0° (*c* 1.0, dioxane, 25 °C).

**5*H*-Benzo[*b*]carbazole.** The compound was prepared according to the method of Bucherer and Sonnenburg[17] and Bucherer and Rauch.[18] 2-Aminonaphthalenesulfonic acid (25.0 g, 0.11 mol), *N*-phenylhydrazine (12.0 g, 0.11 mol), and 200 mL of aqueous $NaHSO_3$ solution (3.5 M) were stirred under reflux for 20 h. After this time a crystalline precipitate had formed. After the mixture cooled to room temperature the precipitate was filtered off. As described by Bucherer and Rauch[18] the precipitate was composed of 7*H*-benzo[*c*]carbazole and 5*H*-benzo[*b*]carbazole-6-sulfonic acid sodium salt.

**7*H*-Benzo[*c*]carbazole** was extracted from the precipitate with 4 × 75 mL of $Et_2O$. The $Et_2O$ phase was dried over $MgSO_4$, filtered, and evaporated. Column chromatography on silica in 50% $Et_2O$/PE followed by crystallization from $Et_2O$ (50 mL)/PE (500 mL) afforded the product as yellowish needles: yield 6.8 g (29%); mp 132–133 °C (lit.[17] mp 134 °C); homogeneous by TLC in 50% $Et_2O$/cyclohexane ($R_f$ 0.44) and in 75% $CH_2Cl_2$/cyclohexane ($R_f$ 0.64); $^1H$ NMR ($Me_2SO$-$d_6$) (assignments were made by COSY experiment[19]) δ 11.80 (1 H, s, NH), 8.76 (1 H, d, *J* = 8 Hz, $H_4$), 8.58 (1 H, d, *J* = 8 Hz, $H_{11}$), 8.08 (1 H, d, *J* = 8 Hz, $H_1$), 7.91 (1 H, d, *J* = 8.5 Hz, $H_5$), 7.80 (1 H, d, *J* = 8.5 Hz, $H_6$), 7.72 (1 H, dd, $H_3$), 7.68 (1 H, d, *J* = 8 Hz, $H_8$), 7.47 (1 H, dd, $H_2$), 7.43 (1 H, dd, $H_9$), 7.34 (1 H, dd, $H_{10}$); $^{13}C$ NMR ($Me_2SO$-$d_6$, 22.63 MHz) δ 138.733, 137.532, 129.480, 129.151, 128.578, 126.904 (two signals), 124.017, 123.014, 122.860, 122.599, 121.604, 119.580, 114.063, 113.487, 111.683; UV (MeOH) $\lambda_{max}$ 360 nm (log ε 3.63), 342 (3.72), 325 (4.16), 285 (4.00), 265 (>4.67), 230 (4.27), 215 (4.38); MS *m/z* 217 ($M^+$, 100%), 189 ($M^+ - H_2CN$, 13).

**5*H*-Benzo[*b*]carbazole-6-sulfonic Acid Sodium Salt.** The insoluble residue from $Et_2O$ extraction was recrystallized from DMF (150 mL)/acetone (300 mL) and then from water with a few milliliters of 2 M NaOH added to yield 5.98 g (17%) of product: homogeneous by TLC in 50% $MeOH/CHCl_3$ ($R_f$ 0.77 ($R_f$ 0 in 50% $Et_2O$/cyclohexane and 75% $CH_2Cl_2$/cyclohexane)); $^1H$ NMR ($Me_2SO$-$d_6$) (assignments were made by COSY experiment[19]) δ 10.83 (1 H, s, NH), 9.06 (1 H, d, *J* = 9 Hz, $H_7$), 8.72 (1 H, s, $H_{11}$), 8.25 (1 H, d, *J* = 7 Hz, $H_1$), 8.06 (1 H, d, *J* = 8 Hz, $H_{10}$), 7.72 (1 H, d, *J* = 8 Hz, $H_4$), 7.50 (1 H, m, $H_8$), 7.45 (1 H, m, $H_3$), 7.39 (1 H, dd, $H_9$), 7.19 (1 H, dd, $H_2$); $^{13}C$ NMR ($Me_2SO$-$d_6$, 22.63 MHz) δ 141.851, 135.624, 128.541, 128.397, 127.795, 127.468, 126.414, 125.382, 124.797, 122.162, 121.834, 121.603, 120.745, 120.375, 118.786, 111.311; UV (MeOH) $\lambda_{max}$ 395 nm (log ε 3.75), 376 (3.65), 322 (4.12), 320 (3.94), 305 (3.69), 285 sh (4.61), 278 (4.89), 268 (4.71), 232 (4.47); fluorescence ($3.44 \times 10^{-6}$ M, MeOH), excitation spectrum (emission monochromator 412 nm, slit width 6 nm) $\lambda_{max}$ 392 nm (intensity (set to 100% at 280 nm) 36), 378 (51), 336 (>100), 322 (60), 280 (100), emission spectrum (excitation monochromator 388 nm, slit width 5 nm) $\lambda_{max}$ ~430 nm (intensity (set to 100% at 411 nm) 68), 411 (100).

**5*H*-Benzo[*b*]carbazole.** To 5*H*-benzo[*b*]carbazole-6-sulfonic acid sodium salt (3.0 g, $9.4 \times 10^{-3}$ mol) was added 100 mL of concentrated HCl (36%), and the mixture was refluxed for 1 h. After the mixture cooled to room temperature 200 mL of water was added and the precipitate was filtered off and washed with water. The solid material was dried under vacuum in a desiccator and then recrystallized from toluene (250 mL)/aniline (30 mL) to afford 1.52 g (74%) of greenish crystalline material, mp 335–337 °C (dec) (lit.[17] mp 332 °C); homogeneous by TLC in 50% $Et_2O$/cyclohexane ($R_f$ 0.49) and in 75% $CH_2Cl_2$/cyclohexane ($R_f$ 0.74); HPLC (mobile phase 1), $R_t$ 16.72 min, HPLC (mobile phase 2), $R_t$ 16.73 min; $^1H$ NMR ($Me_2SO$-$d_6$) (assignments were made by COSY experiment[19]) δ 11.20 (1 H, s, NH), 8.68 (1 H, s, $H_4$), 8.26 (1 H, d, *J* = 7.5 Hz, $H_1$), 8.06 (1 H, d, *J* = 8 Hz, $H_7$), 8.00 (1 H, d, *J* = 8 Hz, $H_{10}$), 7.88 (1 H, s, $H_6$), 7.52 (2 H, m, $H_{3,4}$), 7.46 (1 H, dd, $H_9$), 7.36 (1 H, dd, $H_8$), 7.18 (1 H, dd, $H_2$); $^{13}C$ NMR ($Me_2SO$-$d_6$, 22.63 MHz) δ 142.487, 139.672, 132.247, 128.280, 127.508, 127.285, 126.905, 125.158, 124.766, 122.297, 121.021, 118.570, 118.262, 110.551, 105.081; UV (MeOH) $\lambda_{max}$ 390 nm (log ε 3.49), 370 (3.48), 329 (3.93), 314 (3.84), 290 (4.34), 280 (4.52), 270 (4.59), 228 (4.45); fluorescence ($9.68 \times 10^{-6}$ M, MeOH), excitation spectrum (emission monochromator 406 nm, slit width 5 nm) $\lambda_{max}$ 390 nm (intensity (set to 100% at 332 nm) 41), 373 (56), 332 (100), 318 (68), 294 (91), 283 (83), emission spectrum (excitation monochromator 334 nm, slit width 5 nm) $\lambda_{max}$ 425 nm (intensity (set to 100% at 405 nm) 69), 405 (100); MS *m/z* 217 ($M^+$, 100%), 189 ($M^+ - H_2CN$, 11).

**Microscale Acid Hydrolysis of Sample II (Hydrolysis Time 24, 48, and 72 h).** The samples (1.79–2.83 mg) were hydrolyzed in 4 mL of 6 M hydrochloric acid in evacuated, sealed vials at 110 °C for 24, 48, and 72 h, respectively. The acid was then removed under reduced pressure, and the hydrolysates were prepared for quantitative amino acid analysis by dissolving in 25–50 mL of sodium citrate buffer (pH 2.20).

**Semimicroscale Acid Hydrolysis of Samples I and II (Hydrolysis Time 24 and 48 h).** The hydrolysis of I is used as an example. Sample I (25.0 mg, $7.78 \times 10^{-5}$ mol of basic unit) was heated with 50 mL of 6 M hydrochloric acid in an evacuated, sealed ampule at 110 °C for 24 h with frequent vigorous shaking. After the mixture cooled to room temperature the ampule was opened and the precipitate was filtered off on a sintered-glass filter (G-3) followed by washings with water. The precipitate was extracted with MeOH and used for UV spectroscopy, TLC analysis, HPLC analysis (see section on HPLC analysis), and GC/MS analysis (see section on GC/MS analysis). TLC was performed on silica plates in 50% $Et_2O$/PE and in 25% THF/PE

with 9H-carbazole as a reference, $R_f$ 0.44 and 0.80, respectively. The residue, which was insoluble in MeOH, was dissolved in DMF. TLC in 50% $Et_2O$/PE and 25% THF/PE gave $R_f$ 0. The HCl filtrate was evaporated on a rotatory evaporator at 30 °C. The hydrolysate was taken up in 100 mL of 0.05 M hydrochloric acid, and 5 mL of the solution was diluted to 25 mL with sodium citrate buffer (pH 2.20) and subjected to quantitative amino acid analysis.

**HPLC Analysis of the Precipitates from Semimicroscale Acid Hydrolysis of Samples I and II.** The precipitate from acid hydrolysis was dissolved in 10.0 mL of $CH_3CN$. Samples of 100 μL were analyzed on the HPLC chromatograph using mobile phase 1. A 9H-carbazole preparation (Ferak, 1.56 mg/mL of $CH_3CN$) was used as reference. The $CH_3CN$ solution was then evaporated, and the residue was redissolved in 10.0 mL of MeOH. Samples of 100 μL were analyzed on the HPLC chromatograph using mobile phase 2. A 9H-carbazole preparation (Ferak, 1.24 mg/mL of MeOH) was used as reference.

**HPLC Fractionation of the Precipitate from Semimicroscale Hydrolysis (48 h) of Sample I.** The precipitate from 48-h acid hydrolysis of sample I was dissolved in 2.0 mL of $CH_3CN$, and samples of 100 μL were fractionated on the HPLC chromatograph using mobile phase 1. The peaks with retention times 11.87 min (peak 1), 13.88 min (peak 2), 16.02 min (peak 3), 16.72 min (peak 4), and 34.37 min (peak 5) were collected. The collected fractions were concentrated and rechromatographed using mobile phase 2. In this system the following retention times were observed: 10.98 min (peak 1), 13.10 min (peak 2), 16.73 min (peaks 3 and 4), and 34.03 min (peak 5). The collected fractions were evaporated and analyzed by UV and fluorescence spectroscopy and mass spectrometry. Peak 1: identified as 9H-carbazole by its retention time. Peak 2: UV (MeOH/$H_2O$) $\lambda_{max}$ 335 nm (absorbance 0.025), 322 (0.035), 295 (0.160), 259 (0.171), 245 sh (0.215), 235 (0.412); fluorescence (MeOH/$H_2O$), excitation spectrum (emission monochromator 360 nm, slit width 5 nm) $\lambda_{max}$ 335 nm (intensity (set to 100% at 298 nm) 43), 323 (50), 298 (100), 260 (16), emission spectrum (excitation monochromator 323 nm, slit width 5 nm) $\lambda_{max}$ 375 nm sh (intensity (set to 100% at 354 nm) ~47), 358 (100), 345 (95); MS $m/z$ 181 (100%), 180 (66), 152 (10), 90 (16). Peak 3: UV (MeOH/$H_2O$) $\lambda_{max}$ 325 nm (absorbance 0.008), 295 (0.044), 290 (0.040), 260 (0.065), 245 (0.070), 236 (0.099); fluorescence (MeOH/$H_2O$), excitation spectrum (emission monochromator 360 nm, slit width 10 nm) $\lambda_{max}$ 332 nm sh (intensity (set to 100% at 295 nm) 62), 325 (64), 295 (100), 258 (18), emission spectrum (excitation monochromator 326 nm, slit width 10 nm) $\lambda_{max}$ 358 nm (intensity (set to 100% at 358 nm) 100), 345 (94); MS $m/z$ 247 (100%), 245 (100), 167 (98), 139 (35). Peak 4: UV ($CH_3CN$) $\lambda_{max}$ 390 nm (absorbance 0.004), 370 (0.003), 330 (0.011), 315 (0.010), 290 (0.028), 279 (0.045), ~265 (0.077), 230 (0.055); fluorescence (MeOH), excitation spectrum (emission monochromator 404 nm, slit width 6 nm) $\lambda_{max}$ 390 nm (intensity (set to 100% at 283 nm) 43), 372 (54), 332 (97), 317 (67), 294 (97), 283 (100), ~270 sh (86), emission spectrum (excitation monochromator 334 nm, slit width 6 nm), $\lambda_{max}$ 424 nm (intensity (set to 100% at 405 nm) 72), 405 (100); MS $m/z$ 217 (100%), 189 (6), 109 (6), 108 (21). Peak 5: UV (MeOH/$H_2O$) $\lambda_{max}$ 400 nm (absorbance 0.008), 380 (0.005), 332 (0.009), 318 (0.010), 295 (0.037), 282 (0.056), 272 (0.085), 266 (0.086), 232 (0.038); fluorescence (MeOH/$H_2O$), excitation spectrum (emission monochromator 420 nm, slit width 10 nm) $\lambda_{max}$ 378 nm (intensity (set to 100% at 285 nm) 54), 332 (69), 320 (60), 293 sh (93), 285 (100), emission spectrum (excitation monochromator 380 nm, slit width 10 nm) $\lambda_{max}$ 420 nm; MS $m/z$ 469 (~55%), 432 (65), 181 (55), 180 (43), 149 (100).

**Quantification of 5H-Benzo[b]carbazole Content in the Precipitates from Semimicroscale Hydrolysis (48 h) of Samples I and II. External Standard Method.** Three solutions of the synthesized 5H-benzo[b]carbazole (21 μg/mL, 2.1 μg/mL, and 0.21 μg/mL) were chromatographed (50–100-μL injection) using mobile phase 1. Calibration plots of UV and fluorescence peak heights vs. amount injected were made. The HPLC chromatograms of the semimicroscale hydrolysates of I and II were used for quantification of 5H-benzo[b]carbazole. In the hydrolysate of polymer I was found a total of $7.9 \times 10^{-5}$ g of 5H-benzo[b]carbazole, corresponding to 0.43% (mol/mol) of the 9H-carbazole amount (theory: $8.46 \times 10^{-5}$ mol). In the hydrolysate of polymer II was found $2.3 \times 10^{-6}$ g of 5H-benzo[b]carbazole, corresponding to 0.012% (mol/mol) of the 9H-carbazole amount (theory: $8.71 \times 10^{-5}$ mol).

**Component Addition Method.** For quantification of 5H-benzo[b]carbazole in the hydrolysate from I, 100 μL of a 10.0-mL $CH_3CN$ solution of precipitate from hydrolysis of I was mixed with 50 μL of a 21 μg/mL solution of the synthesized 5H-benzo[b]carbazole. From this solution 75 μL was injected on the HPLC chromatograph using mobile phase 1. Similarly, 100 μL of a 10.0-mL $CH_3CN$ solution of precipitate from hydrolysis of II was mixed with 100 μL of a 0.21 μg/mL solution of the synthesized 5H-benzo[b]carbazole, and from this solution 100 μL was injected on the HPLC chromatograph. In the hydrolysate of polymer I was found $9.4 \times 10^{-5}$ g of 5H-benzo[b]carbazole, corresponding to 0.51% (mol/mol) relative to 9H-carbazole. In the hydrolysate of polymer II was found $2.3 \times 10^{-6}$ g of 5H-benzo[b]carbazole, corresponding to 0.012% (mol/mol) relative to 9H-carbazole.

**HPLC Analysis of the Filtrates from Semimicroscale Acid Hydrolysis (48 h) of Samples I and II.** The 0.05 M HCl solutions were evaporated and the residues dissolved in 15 mL of MeOH/$H_2O$ (2:1). HPLC on 100-μL samples were performed with mobile phase 2.

**HPLC Analysis of Commercial 9H-Carbazole Preparations for Content of 5H-Benzo[b]carbazole:** Fluka, 1.72 mg/mL of MeOH, 50-μL injection, mobile phase 2; Ferak, 1.24 mg/mL of MeOH, 100-μL injection, mobile phase 2. The calibration curve (fluorescence peak height vs. amount injected) was obtained from 100-μL injections of 21, 2.1, and 0.21 μg/mL of the synthesized 5H-benzo[b]carbazole, mobile phase 2.

**GC/MS Analysis of the Precipitates from Semimicroscale Acid Hydrolysis (48 h) of Samples I and II. Hydrolysate of Sample I: Injection ~100 μg in Acetone.** The following retention times/mass spectral data were obtained: 155 s ($m/z$ 167 (100), 139 (12), 84 (16), 197 s (181 (100), 180 (68), 167 (55), 152 (10), 139 (8)), 245 s (247 (25), 245 (25), 181 (10), 167 (100), 139 (15)), 329 s (247 (97), 245 (100), 167 (90), 166 (75), 139 (30)), 509 s (217 (100), 189 (10), 167 (15), 108 (22)).

**Hydrolysate of Sample II: Injection ~35 μg in Acetone.** The following retention times/mass spectral data were obtained: 149 s ($m/z$ 167 (100), 139 (12), 84 (16)), 197 s (181 (100), 180 (68), 167 (55), 152 (10), 139 (8)), 340 s (247 (90), 245 (90), 167 (100), 166 (80), 139 (35)).

## Results and Discussion

**1. Characterization of Polymers I and II by TLC, Spectroscopy, and Elemental Analysis.** TLC analysis gave identical $R_f$ values for samples I and II. However, when viewed under 254- and 360-nm UV light the spot from polymer I showed strong fluorescence (uniform emission from the entire spot) compared to the spot from polymer II. The $^1H$ NMR spectra of samples I and II showed the expected signals. The only significant difference between the two compounds was observed in the aromatic region, where sample I showed a subspectrum. In the $^{13}C$ NMR spectra the expected signals were observed, and practically no difference between samples I and II could be observed. In the IR spectra no differences could be observed. Two, weak, but well-defined absorption bands were observed in the UV spectrum for sample I at ~350 and ~370 nm. Otherwise, the UV spectra of I and II showed the expected $\lambda_{max}$ and absorbance values. The steady-state fluorescence emission spectra of samples I and II (Figure 1) differed significantly as mentioned in the introduction of this paper. Elemental analyses (C, H, N) of the two samples were in agreement with the theoretical values. The X-ray fluorescence analysis of sample II showed very low levels of contamination by elements with $Z > 10$. The specific optical rotations of polymer I were somewhat smaller than those for polymer II. Samples I and II were both found to form lyotropic liquid crystals in 15% (w/v) THF solutions. The differences between the two polymer preparations I and II as observed by TLC, $^1H$ NMR, UV, and steady-state fluorescence spectroscopy

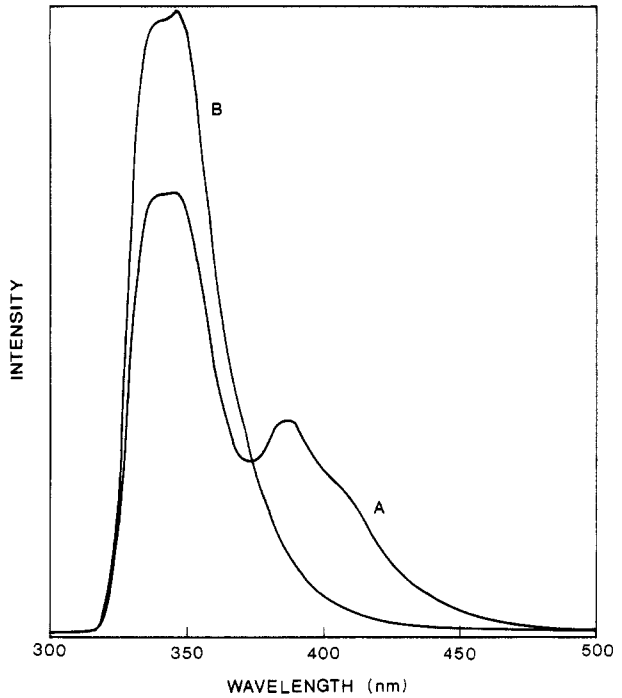


**Figure 1.** Fluorescence emission spectra of samples I (A) and II (B) in dioxane at 293 K recorded under identical experimental conditions. The spectra have the same intensity scale. Excitation wavelength 322 nm, slit width 4 nm. Concentration of I: 18.1 mg/L ($5.63 \times 10^{-5}$ M of basic unit); concentration of II: 17.2 mg/L ($5.35 \times 10^{-5}$ M of basic unit).

**Table I**
**Amino Acid Analysis Results from Microscale Acid Hydrolysis of Sample II**

| amt hydrolyzed, mg | hydrolysis time, h | lysine,[a] nmol | | |
|---|---|---|---|---|
| | | injected, theory | found | % |
| 2.00 | 24 | 12.44 | 11.43 | 91.9 |
| 1.79 | 48 | 22.27 | 22.35 | 100.4 |
| 2.83 | 72 | 17.60 | 17.47 | 99.3 |

[a] Amino acid analysis.

indicated the presence of one or more covalently bound impurities in sample I.

**2. Acid Hydrolysis of Samples I and II and Analysis of Hydrolysates.** In order to determine the composition of polymer samples I and II they were subjected to acid hydrolysis. The overall reaction scheme of the hydrolysis is shown in Figure 2. Initially the polymer floated atop the hydrochloric acid, but gradually it disintegrated and a blue-greenish powderlike precipitate was formed. The precipitate was filtered off before amino acid analysis.

In order to find the minimum time for complete hydrolysis microscale hydrolysis experiments were carried out for 24, 48, and 72 h. As seen from Table I only partial hydrolysis had occurred after 24 h, but complete hydrolysis

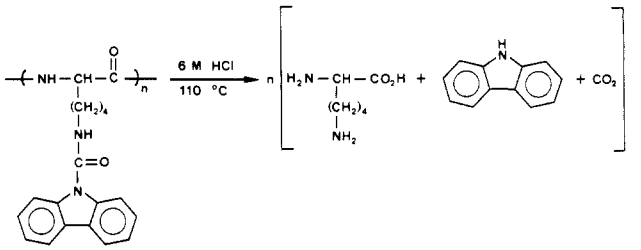


**Figure 2.** Overall reaction scheme of acid hydrolysis of poly-[$N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine].

was accomplished within 48 h.

A more thorough investigation of the composition of polymer samples I and II was carried out by hydrolyzing larger amounts for 24 and 48 h. The amino acid analysis results from 24-h hydrolysis of I and II are presented in Table II. The relatively lower lysine values in the hydrolysates (53.3% for I, 49.1% for II) as compared to the figures for the microscale 24-h hydrolysis experiment (91.9%) are mostly likely due to incomplete mixing in the semimicroscale experiment. The main component of the MeOH-soluble part of the precipitate was identified as 9*H*-carbazole by UV, TLC, and HPLC analyses. The amount of 9*H*-carbazole was determined from the UV spectra by using the extinction coefficients for 9*H*-carbazole at 323 and 336 nm[20] (Table II). The figures for lysine and 9*H*-carbazole indicate incomplete hydrolysis of the >N–C(O)–N< bonds of the urea groups in the polymer side chains (9*H*-carbazole content in hydrolysate 62–64% of theory) as well as the peptide bonds of the backbone (lysine content in hydrolysate, 49.1–53.3% of theory). Apparently the side-chain urea bonds are hydrolyzed more rapidly than the peptide bonds of the backbone. The MeOH-insoluble residue was soluble in DMF, and on the basis of the above-mentioned results this residue is suggested to be composed of polymer fragments with some of the side-chain urea bonds hydrolyzed.

The amino acid analysis results from 48-h acid hydrolysis of I and II are presented in Table II. The precipitate was completely soluble in MeOH. The main component of the precipitate was identified as 9*H*-carbazole by UV, TLC, and HPLC analyses. The 9*H*-carbazole amount was determined from the UV spectra, and the results are presented in Table II. The figures for lysine and 9*H*-carbazole indicate a practically complete hydrolysis of the side-chain urea bonds as well as the peptide bonds of the backbone.

**3. HPLC Analysis and Fractionation of Hydrolysates.** In Figure 3 are shown the HPLC chromatograms of the precipitates from 48-h hydrolysis of samples I and II using $CH_3CN/H_2O$ as mobile phase. Peak 1 ($R_t$ 11.87 min) corresponds to 9*H*-carbazole. Less intense peaks with retention times 13.88 min (peak 2) and 16.02 min (peak 3) are observed in the chromatograms of both hydrolysates. Peak 4 ($R_t$ 16.72 min), which is very intense in the fluorescence chromatogram but of relatively small intensity

**Table II**
**Amounts of Lysine and 9*H*-Carbazole Found in Semimicroscale Hydrolysates of Samples I and II**

| sample | amt hydrolyzed, mg | hydrolysis time, h | lysine,[a] nmol | | | 9*H*-carbazole, mol × $10^{-5}$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | injected, theory | found | % | theory[b] | found[c] | % |
| I | 25.0 | 24 | 18.67 | 9.95 | 53.3 | 7.78 | 4.95 | 64 |
| | 27.2 | 48 | 16.92 | 16.44 | 97.2 | 8.46 | 8.3 | 98 |
| II | 25.0 | 24 | 18.67 | 9.16 | 49.1 | 7.78 | 4.84 | 62 |
| | 28.0 | 48 | 17.42 | 16.94 | 97.2 | 8.71 | 8.5 | 98 |

[a] Amino acid analysis of filtrate from hydrolysis. [b] Amount expected from total hydrolysis of the samples assuming that the polymers are homopolymers of $N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine. [c] UV analysis of precipitate from hydrolysis.

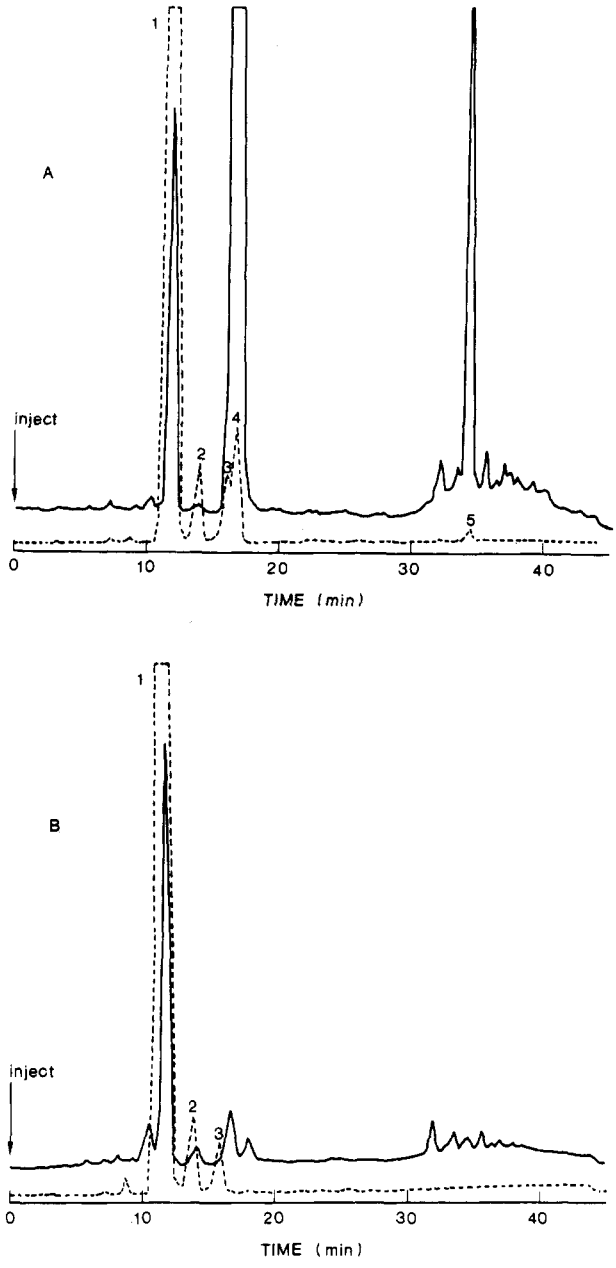


**Figure 3.** HPLC chromatograms of the precipitates from 48-h semimicroscale hydrolysis of samples I (A) and II (B): mobile phase $CH_3CN/H_2O$; gradient 60–70% (20 min), 70–100% (10 min), 100% (5 min); flow 2.0 mL/min; column temperature 35 °C. Chromatograms obtained by fluorescence detection (—) and by UV detection (- - -). Peak 1, $R_t$ 11.87 min; peak 2, 13.88 min; peak 3, 16.02 min; peak 4, 16.72 min; peak 5, 34.37 min.

in the UV chromatogram, is present in the chromatograms of both hydrolysates. However, it is much more abundant in the hydrolysate of I. Another peak of high fluorescence intensity but small UV intensity with retention time 34.37 min (peak 5) is observed in the chromatograms of both hydrolysates. Again, it is much more abundant in the hydrolysate of I. HPLC analysis was also carried out with $MeOH/H_2O$ as mobile phase, which gave essentially the same results.

The MeOH-soluble precipitates from 24-h hydrolysis of samples I and II were also chromatographed in the two HPLC systems. The same peaks were observed. However, peaks 4 and 5 were markedly smaller as compared to the corresponding peaks in the chromatograms from 48-h hydrolysates. This indicates that the strongly fluorescent compounds were liberated more slowly than 9H-carbazole during hydrolysis.

In order to identify the impurities observed in the hydrolysates of the polymers the precipitate from 48-h semimicroscale hydrolysis of I was fractionated using mobile phase 1. Peaks 2–5 were collected and rechromatographed in HPLC system 2. Based on UV and fluorescence spectroscopic and mass spectrometric data of the isolated compounds the following structure assignments were made. Peak 2: 2-methyl-9H-carbazole. Molecular ion 181 and fragments 180 ($M^+ - H$) and 152 ($M^+ - H - H_2CN$) indicate a methyl-9H-carbazole, in accordance with the literature.[21] UV data are only in agreement with those of 2-methyl-9H-carbazole when comparing with published UV data for methyl-9H-carbazoles.[22,23] Peak 3: bromo-9H-carbazole. Molecular ion and isotope peak 245/247 of almost equal intensity indicate a bromo-9H-carbazole. A definite assignment was not attempted. Peak 4: 5H-benzo[b]carbazole. Molecular ion 217 and fragment 189 ($M^+ - H_2CN$) indicate a benzocarbazole, in accordance with the literature.[21] UV and fluorescence data are only in agreement with those of 5H-benzo[b]carbazole when comparing with published data for benzocarbazoles.[24,25] As a final check of the validity of the structure assignment 5H-benzo[b]carbazole was synthesized according to Bucherer and coworkers[17,18] and obtained in 13% yield. 7H-Benzo[c]carbazole was obtained as a side product in 29% yield. HPLC spiking experiments served as a further confirmation that peak 4 corresponds to 5H-benzo[b]carbazole. Peak 5: no definite assignment is made. However, the close similarity of its UV and fluorescence spectra with those of 5H-benzo[b]carbazole suggest a compound closely related. On the basis of the assumption that 432 is the molecular ion, the compound may be a dimer of 5H-benzo[b]carbazole.

The filtrates from acid hydrolysis were checked by HPLC and the chromatograms showed no peaks at all.

The amount of 5H-benzo[b]carbazole in the precipitates from semimicroscale hydrolysis (48 h) of polymers I and II was determined by the external standard method and the component addition (spiking) method. As a better separation was obtained by using mobile phase 1 this system was applied for quantification. By the external standard method a content of 0.43% (mol/mol) relative to 9H-carbazole was found for the hydrolysate of I. In polymer II 0.012% (mol/mol) was found. By the component addition method 0.51% (mol/mol) was found in hydrolysate I and 0.012% for II.

The amounts of 2-methyl-9H-carbazole, bromo-9H-carbazole, and the compound corresponding to peak 5 were estimated from the HPLC chromatograms assuming that the proportion between the molar extinction coefficients at 254 nm for compounds 2–5 are approximately as 1:1:2:4. In the hydrolysate of I a content of approximately 0.5% 2-methyl-9H-carbazole, 0.5% bromo-9H-carbazole, and 0.02% compound 5 relative to 9H-carbazole was estimated. In the hydrolysate of II approximately 0.5% 2-methyl-9H-carbazole and 0.5% bromo-9H-carbazole relative to 9H-carbazole was estimated.

**4. HPLC Analysis of Commercial Preparations of 9H-Carbazole.** HPLC analysis of two commercial carbazole preparations (Fluka and Ferak) revealed that they are highly heterogeneous. Among the impurity peaks two were identified as 2-methyl-9H-carbazole and 5H-benzo[b]carbazole. No bromo-9H-carbazole or compound 5 could be detected. Quantification of 5H-benzo[b]carbazole by the external standard method yielded 0.04% and 0.02% (mol/mol) relative to the 9H-carbazole amount of the Fluka and Ferak products, respectively.

**5. GC/MS Analysis of Hydrolysates and Crude 9H-Carbazole.** GC/MS analysis of the precipitates from

48-h hydrolysis of the polymer samples I and II confirmed qualitatively the results obtained by HPLC. In the hydrolysate of I methylcarbazole, two bromocarbazoles, and benzocarbazole were detected besides carbazole. In the hydrolysate of II methylcarbazole and bromocarbazole were detected besides carbazole. GC/MS analysis of the Ferak carbazole preparation gave a variety of peaks, among which methylcarbazole and benzocarbazole could be identified. However, no bromocarbazole could be detected.

## Conclusions

As mentioned earlier, the bromine content in polymer sample II was determined by X-ray fluorescence spectroscopy to be less than 10 ppm. The considerable amount of bromo-9*H*-carbazole found in the hydrolysate of II (ca. $4 \times 10^{-7}$ mol from 28.0 mg of II) can then only be accounted for if it is assumed that a reaction has taken place between 9*H*-carbazole and some brominating reagent, possibly $Br_2$, present in the hydrochloric acid used for hydrolysis. In fact the content of bromine in the hydrochloric acid used (Merck, pro analysi, 37%) is only guaranteed to be less than 0.005% (w/w), which, however, would correspond to $1.9 \times 10^{-5}$ mol of Br in the 50 mL of 6 M hydrochloric acid used for hydrolysis. It is therefore concluded that bromo-9*H*-carbazole was formed as an artifact during acid hydrolysis of both polymer samples. To our knowledge none of the bromo-9*H*-carbazoles has been found as constituents of coal tar based carbazole.

It is suggested that of the three remaining carbazole derivatives found in the hydrolysate of polymer samples I and II, two, viz., 2-methyl-9*H*-carbazole and 5*H*-benzo[*b*]carbazole, have been covalently bound in the polymers. Evidently 2-methyl-9*H*-carbazole and 5*H*-benzo[*b*]carbazole, which are present to various extents in carbazole preparations originating from coal tar,[26,27] as for example the Fluka and Ferak preparations analyzed in this investigation, underwent the same reaction steps as did 9*H*-carbazole in the synthesis of the monomer $N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine *N*-carboxyanhydride. This led to the formation of the comonomers $N^6$-(5*H*-benzo[*b*]-carbazol-5-ylcarbonyl)-L-lysine *N*-carboxyanhydride and $N^6$-(2-methyl-9*H*-carbazol-9-ylcarbonyl)-L-lysine *N*-carboxyanhydride which copolymerized with $N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine *N*-carboxyanhydride to form the terpolymers of $N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine with $N^6$-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine and $N^6$-(2-methyl-9*H*-benzo[*b*]carbazol-9-ylcarbonyl)-L-lysine, in the approximate ratios 100:0.5:0.5 for polymer I and 100:0.5:0.01 for polymer II. The UV spectroscopic data support that 5*H*-benzo[*b*]carbazole is bound to poly(L-lysine) in the same way as 9*H*-carbazole. The hypso- and hyperchromic effects observed for the first and second electronic transitions when comparing 9*H*-carbazole (in MeOH) with poly[$N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine] (in THF) (as exemplified by polymer II) are approximately 15 nm and 107%. By analogy the first and second electronic transitions of polymer-bound 5*H*-benzo[*b*]carbazole are expected to have $\lambda_{max}$ at 370 and 355 nm with $\epsilon$ values $3.32 \times 10^3$ and $3.2 \times 10^3$, respectively. The two bands observed in the UV spectrum of polymer I at approximately 370 and 350 nm are in reasonably well agreement with the prediction. The corresponding absorbances of $6.5 \times 10^{-3}$ and $8.1 \times 10^{-3}$, found for a solution with a concentration of 100 mg/L ($3.1 \times 10^{-4}$ M of basic unit) give a concentration of 5*H*-benzo[*b*]carbazol-5-ylcarbonyl units of $2.0 \times 10^{-6}$ M (ca. 0.6% relative to 9*H*-carbazole) based on the 370-nm band, and $2.5 \times 10^{-6}$ M (ca. 0.8% relative to 9*H*-carbazole) based on the 350-nm band. These values are thus in good agreement with the values found by HPLC experiments, 0.43 and 0.51%. The subspectrum observed in the aromatic region of the $^1$H NMR spectrum of I may be accounted for by the presence of approximately 0.5% of $N^6$-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine units in the poly[$N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine] macrochain. The presence of approximately 0.5% of $N^6$-(2-methyl-9*H*-carbazol-9-ylcarbonyl)-L-lysine in both polymers might also give rise to extra signals, but the spectra of I and II would not differ, since the relative amounts of 2-methyl-9*H*-carbazole are equal in the two samples.

Since the last impurity present in the hydrolysates (peak 5) was not detected in the Ferak carbazole preparation used for synthesis of II, it must have formed either in the reaction sequence leading to the polymers or, more likely, during hydrolysis.

The difference in fluorescence behavior of polymers I and II can now be explained on basis of the proportion of $N^6$-(5*H*-benzo[*b*]carbazol-5-ylcarbonyl)-L-lysine groups in poly[$N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine], for I approximately 0.5% and for II approximately 0.01%. The $N^6$-(2-methyl-9*H*-carbazol-9-ylcarbonyl)-L-lysine units present in both polymers are assumed to have only minimal effect on the overall fluorescence of the present polymers, and since the concentration of the impurity is almost equal in the two polymers, the difference in fluorescence behavior is not caused by this impurity.

A detailed assignment of the fluorescence spectra of polymers I and II will not be carried out in this paper. It is, however, relevant to compare the present fluorescence spectra with, on one hand, those of the homopolymers poly(*N*-vinyl-9*H*-carbazole) (PVCz)[4,28-30] and poly(*N*-vinyl-5*H*-benzo[*b*]carbazole) (PV5BCz)[28,31] and, on the other hand, those of copolymers of *N*-vinyl-9*H*-carbazole (VCz) with *N*-vinyl-5*H*-benzo[*b*]carbazole (V5BCz).[30,32,33] For PVCz the long-wavelength ($\lambda_{max} \sim 420$ nm) emission was attributed to an intrachain excimer state[4,28,30] and the shorter wavelength ($\lambda_{max} \sim 380$ nm) emission was attributed to either a normal carbazole molecular flourescence[4,30] or a second excimer emission.[4,28] Depending on the polymerization conditions (radical or cationic) different fluorescence spectra were obtained for PV5BCz. For the radical polymers the spectra were composed of a second excimer fluorescence at the shorter wavelength ($\lambda$ = 443 nm) and a sandwich-like excimer fluorescence at the longer wavelength ($\lambda$ = 491 nm).[28,31] The cationic polymers did not show the second excimer fluorescence, but a monomer-like structured fluorescence, at the shorter wavelength, although it did show the sandwich-like excimer fluorescence at the longer wavelength.[28,31] The fluorescence behavior of a series of copolymers of VCz with V5BCz (concentration of V5BCz in PVCz ranging from 0.1 to 4.1%) has been studied by Slobodyanik et al.[30,32,33] In dioxane solution the host PVCz (monomer ($\lambda$ = 370 nm) plus excimer ($\lambda$ = 410 nm) type) fluorescence was quenched by V5BCz guest units and the guest emission appeared. The guest emission spectrum was found to include two components: the monomer-type of emission of guest V5BCz units ($\lambda$ = 412 nm) and the emission of intramolecular exciplexes formed between the neighbouring VCz and V5BCz units ($\lambda$ = 430 nm). By analogy, the fluorescence emission band at 342 nm of polymers I and II can be attributed to the emission from poly[$N^6$-(9*H*-carbazol-9-ylcarbonyl)-L-lysine]. Whether this emission is of excimeric or monomeric nature cannot be decided on the basis of the present experiments. The additional low-energy bands observed in the fluorescence spectrum of I at 386 and 408 nm might be attributed to monomer-

type of guest ($N^6$-(5H-benzo[b]carbazol-5-ylcarbonyl)-L-lysine) emission arising from host–guest energy transfer and an exciplex between neighboring $N^6$-(5H-benzo[b]-carbazol-5-ylcarbonyl)-L-lysine and $N^6$-(9H-carbazol-9-ylcarbonyl)-L-lysine units. Fluorescence due to direct excitation of guest units may be discarded since no emission was observed at 386 and 408 nm when sample I was excited at wavelengths greater than 340 nm. Because of the very low concentration of 5H-benzo[b]carbazole in II the fluoresence due to this impurity is negligible.

It has thus been shown that the previous interpretation[11-13] regarding the low-energy bands of polymer I as being attributable to excimer formation in the homopolymer poly[$N^6$-(9H-carbazol-9-ylcarbonyl)-L-lysine] must be revised in light of the above-mentioned facts that the measurements were in fact performed on a host–guest copolymer.

In order to study the characteristics of the homopolymer of $N^6$-(9H-carbazol-9-ylcarbonyl)-L-lysine a new synthesis using ultrapure starting materials will be carried out.

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**Registry No.** 5H-Benzo[b]carbazole, 243-28-7; 7H-benzo[c]-carbazole, 205-25-4; 5H-benzo[b]carbazole-6-sulfonic acid sodium salt, 2125-66-8; 9H-carbazole, 86-74-8; ($N^6$-(5H-benzo[b]carbazol-5-carbonyl)-L-lysine N-carboxyanhydride)·($N^6$-(2-methyl-9H-carbazol-9-ylcarbonyl)-L-lysine N-carboxyanhydride)·($N^6$-(9H-carbazol-9-ylcarbonyl)-L-lysine N-carboxyanhydride) (copolymer), 103203-29-8; ($N^6$-(9H-carbazol-9-ylcarbonyl)-L-lysine)·($N^6$-(5H-benzo[b]carbazol-5-ylcarbonyl)-L-lysine)·($N^6$-(2-methyl-9H-benzo[b]carbazol-9-ylcarbonyl)-L-lysine) (copolymer), 103203-32-3.

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