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Donor Acceptor Interactions in Polymeric Systems, 1

Synthesis and Properties of Polyamides Having the Carbazole Group in the Main Chain

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SUMMARY:

Low temperature polymerizations of 3,6-diamino-9-ethylcarbazole (**1b**) with the diacyl dichlorides **2a—e** were investigated. In all cases polyamides of high relative molecular mass ($[\eta] \approx 1 \cdot 10^2$ cm^3 g^{-1}) could be obtained. These polyamides are polymeric electron donors in which the donor units are arranged with regular intervals. Donor acceptor interactions between polyamides and 1,3,5-trinitrobenzene were studied. In comparison with the monomeric model compound 9-ethyl-3,6-bis(propionylamino)carbazole (**1c**) the polymer donor showed a higher stability constant. However, there is no regularity in the sequence of stability constants in respect to the number of methylene units separating two carbazole groups. There is a possibility that donor units in the polymer molecules might be located in such a way that each donor unit could cooperate to form a donor-acceptor complex. No specific interactions between the carbazole groups could, however, be detected by fluorescence spectroscopy. The importance of solvent effects was expressed by the results of absorption and emission spectroscopy.

ZUSAMMENFASSUNG:

Tieftemperatur-Polymerisationen von 3,6-Diamino-9-äthylcarbazol (**1b**) mit den Diacyldichloriden **2a—e** wurden untersucht. In allen Fällen wurden Polyamide mit hoher rel. mol. Masse ($[\eta] \approx 1 \cdot 10^2$ cm^3 g^{-1}) erhalten. Die Polyamide erwiesen sich als polymere Elektronendonatoren, in denen die Donator-Einheiten in regelmäßigen Abständen angeordnet sind. Donator-Acceptor-Wechselwirkungen zwischen Polyamiden und 1,3,5-Trinitrobenzol wurden untersucht. Im Vergleich zur monomeren Modellsubstanz, dem 9-Äthyl-3,6-bis(propionyl amino)carbazol (**1c**) zeigten die polymeren Donatoren eine höhere Stabilitätskonstante. Es besteht jedoch keine Regelmäßigkeit in der Folge der Stabilitätskonstanten im Hinblick auf die Zahl der Methylen-Einheiten, die die Carbazolgruppen trennen. Es ist möglich, daß die Donator-Einheiten in den Polymer-Molekülen derart angeordnet sind, daß jede Donator-Einheit am Aufbau eines Donator-Acceptor-Komplexes beteiligt ist. Spezifische Wechselwirkungen zwischen den Carbazolgruppen konnten mit Hilfe der Fluoreszenz-Spektroskopie nicht festgestellt werden. Die Ergebnisse der Absorptions- und Emissionsspektroskopie bringen die Bedeutung von Lösungsmitteleffekten zum Ausdruck.

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Introduction

Among a variety of intermolecular interactions in polymeric systems, such as COULOMB force and VAN DER WAALS force, charge transfer interactions have been left relatively unsurveyed. Characteristics of charge transfer (CT) interaction in comparison to other intermolecular forces may be expressed as follows.

(A) The CT interaction is very selective so that binding force due to CT interaction is observed only for the combination of a donor with an acceptor.

(B) Since the majority of donors and acceptors are neutral molecules the intermolecular force is induced as a result of approaching of the donor to the acceptor. This is different from the COULOMB interaction between oppositly charged species.

(C) In the extreme case of a weak CT interaction, although the molecular interaction can be observed clearly as contact charge transfer absorption, it contributes no longer to the binding force. Consequently the CT interaction in a polymeric system would provide an approach to the study of the interactions of different molecules without influencing too much the structures and physical states of isolated polymers.

There are several reports on CT interaction in polymeric systems. A line of research is oriented to a practical application such as semiconductor or photoconductor$^{1)}$. Also the improvement of mechanical properties was reported to be brought about by the interaction between a donor polymer and an acceptor polymer$^{2)}$. Another direction of research is to study the polymeric CT complex in comparison to a relevant monomeric complex. Quantitative studies are mostly confined to ethylenic polymers with electron donating groups which interact with electron accepting small molecules$^{3-5)}$. Then the results are compared with reference experiments with monomeric donors. The advantage of working with ethylenic polymers consists in the ease of choosing a variety of samples which are in general commercially available. There are, however, several limitations. Firstly, the ambiguity of a monomeric model must be considered. For example, toluene was used as a model for polystyrene, *N*-ethylcarbazole as a model for poly(*N*-vinylcarbazole). Although the functional part of the donor molecules is indeed the same as in the polymer, these models do not represent the skeletal configuration of the corresponding polymers. Secondly, it is difficult to synthesize oligomeric models with well-defined end groups. Thirdly, strong electron acceptor polymers are extremely difficult to synthesize by vinyl polymerization, since good electron accepting groups are always radical inhibitors. They react with carbanions and reduce the reactivity of the vinyl group toward cationic propagation. Fourthly, the choice of backbone structure is limited. When homopolymers are used, functional groups are separated always by three carbon atoms and the distances between functional groups are not controllable.

In this article the synthesis of polyamides having the carbazole group in the main chain and the investigation of the properties as electron donors are described. By the use of a condensation polymer more freedom in molecular design is expected and monomeric model compounds simulated closely to the polymer can be obtained. On the other hand, the choice of solvent is limited due to the poor solubility of polyamide in common solvents. The number of quantitative measurements of the CT interaction in polymeric systems using condensation polymers as donor or acceptor, is very limited. A recent article investigating the CT complex formation of tetracyanoethylene with an oligomeric polyester having the spiro[cyclopropane-1,9′-fluorene] unit as side group⁶⁾ is probably the only example.

Experimental Part

Materials:

3,6-Diamino-9-ethylcarbazole (**1b**): 20 g of 9-ethylcarbazole (**1a**) (ECZ) was dissolved in 350 cm^3 of glacial acetic acid and a stoichiometric amount of nitric acid ($d = 1,38$) mixed with 60 cm^3 of glacial acetic acid was added dropwise at 20°C. After reaction at 40°C for 15 h, another 8,2 cm^3 of nitric acid together with 60 cm^3 of glacial acetic acid was added at 80°C. Nitration was continued at 80°C for 2 h, then at 100°C for 30 min. After cooling, precipitated nitrated **1a** was filtered off and washed with water. Yellowish fine crystals (mp. > 300°C) were considered as dinitro derivatives. Without further purification the crude products were reduced by crystalline stannous chloride in conc. hydrochloric acid. Residual stannous and stannic salts were removed in the form of sulfide by bubbling hydrogen sulfide through the reaction mixture. The reduction products were precipitated by neutralization. After two recrystallizations from ligroin, **1b** was obtained as pale-yellow needles; mp. 189,0–192,0°C.

$C_{14}H_{15}N_3$ (225,3) Calc. N 18,65 Found N 18,40

Overall yield from ECZ was about 20%. Since **1b** is very sensitive to light and air in polar organic media, more convenient method of reduction using organic solvents could not be applied. Recrystallization from polar solvents must also be avoided. Pure diamine was obtained by recrystallization from ligroin. The purified diamine was kept in dark in a nitrogen atmosphere.

Diacyl chlorides: Adipoyl chloride and sebacoyl chloride were commercial reagents and purified by vacuum distillation. Succinyl dichloride, glutaroyl dichloride and suberoyl dichloride were prepared from corresponding carboxylic acids⁷⁾ ⁸⁾.

Polyamides from **1b**: A general method for polymer preparation by low temperature solution polycondensation⁹⁾ is described as follows:

837 mg of **1b** ($3{,}72 \cdot 10^{-3}$ mol) and 1,04 cm^3 of triethylamine (dried over KOH and dist.) were dissolved in 80 cm^3 of dry **1a**. An equivalent amount of desired diacyl dichloride ($3{,}72 \cdot 10^{-3}$ mol) dissolved in 20 cm^3 of **1a** was added at once to the amine solution and the mixture was rigorously stirred by a homogenizer. As the reaction proceeded, the temp. went up gradually to 45—50°C. The polymer started to precipitate from the beginning of reaction· After stirring for 15 min in dark, the polymer was precipitated in methanol, filtered off, washed well with methanol, water and finally with hexane and dried *i. vac.* The polymer sample was kept in dark in a nitrogen atmosphere. The results are summarized in Tab. 1.

9-Ethyl-3,6-bis(propionylamino)carbazole (**1c**): Under the same reaction conditions as described for the polyamide synthesis, **1c** was prepared by reaction of **1b** with propionyl chloride. The reaction products were precipitated in hexane, washed well with water and purified by reprecipitation from acetone/hexane; mp 213,5—215°C.

$C_{20}H_{23}N_3O_2$ (337,4)	Calc.	C 71,19	H 6,87	N 12,45	O 9,48
	Found	C 71,02	H 6,92	N 12,17	O 9,45

Acceptors: 1,3,5-Trinitrobenzene (TNB) was recrystallized twice from ethanol. Mp 121°C (Lit.¹⁰⁾: 120°C).

Solvents for spectroscopy: m-Cresol (Guaranteed Reagent Grade) was distilled once under reduced pressure. Hexane and carbon tetrachloride were spectro-grade reagents and used without further purification.

Spectroscopy: Absorption and emission spectroscopy were carried out with Shimadzu MPS-50 spectrophotometer and Hitachi MPF-3 Fluorescence Spectrophotometer, respectively. For the purpose of determining stability constant of complex formed between carbazole derivatives and TNB the sample compartment of spectrophotometer was thermostated at 43°C and a series of measurements to determine a set of values of K and ε was repeated at least twice. The solution containing 0,32 mol/dm^3 of TNB and $1{,}6 \cdot 10^{-2}$ mol/dm^3 of carbazole derivative was successively diluted by solvent and the change in optical density was plotted according to SCOTT's Eq. (1). The values obtained from two repeated measurements were then averaged.

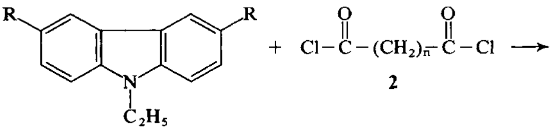
$$[A][D]/\mathrm{O.D.} = 1/\varepsilon\,[A] + 1/\varepsilon K \qquad (1)$$

[A] and [D] are concentrations of acceptor and donor (in mol/dm^3), respectively. O.D. is optical density (I_0/I), ε is the molar extinction coefficient (in mol/dm^3) and K is the stability constant of charge transfer complex (in dm^3/mol).

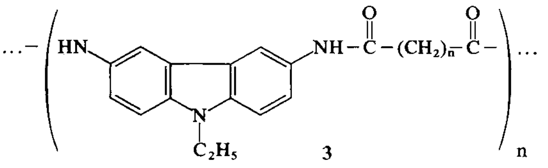
Results and Discussion

Synthesis of polymers

Low temperature solution polycondensation of **1b** with **2a—e** provided polyamides **3a—e** of reasonably high relative molecular mass. The dependence of the intrinsic viscosity of polymer **3e** on the feed ratio of sebacoyl dichloride to diamine is shown in Fig. 1.



1a: R = H
1b: R = NH_2
1c: R = $NHCOC_2H_5$



2,3	n
a	2
b	3
c	4
d	6
e	8

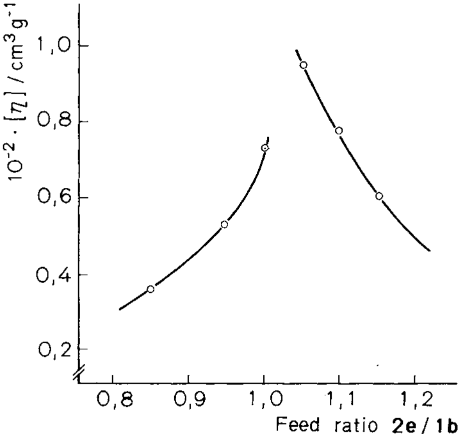


Fig. 1. Intrinsic viscosity $[\eta]$ of polyamide **3e** plotted against the feed ratio of sebacoyl dichloride (**2e**)/diamine **1b**. $[\eta]$ was measured at 45°C in *m*-cresol

The maximum rel. molecular mass of polymer **3e** was obtained at a feed ratio of slightly higher than 1. The yield of the polymer was nearly constant at 80 % independent of the feed ratio. Although a higher rel. molecular mass of the polymer provides a favourable condition for the study of the polymeric CT complex, the polymer prepared with the monomer feed ratio of 1 would have free amine as end groups.

The colouration of the polyamide under photoirradiation is shown in Fig. 2. A polyamide with carboxylate end groups is apparently much more stable than that with amine end groups. It is understandable that the amine group attached to electron donating carbazole group is susceptible to oxidation.

For a spectroscopic determination of the stability constant the polyamides were prepared with a 15 % excess of diacyl dichloride over diamine as shown in Tab. 1. Using polymers with carboxylate end groups, the contribution of free amine to the CT interaction is eliminated and a good stability of the polymers during the measurements is attained. The relatively low yield of polymer in the condensation polymerization is probably due to the loss of polymers of low rel. molecular mass during the precipitation and washing of the products. These polymers are only soluble in *m*-cresol.

There is a possibility that the amino group could attach in part to 1,6-positions of the carbazole ring. In the case of the nitration of carbazole, a contamination by the 1,6-disubstituted isomer has been discussed[11], such a contamination can not be important in the present case since both **1b** and **1c** show relatively sharp melting points.

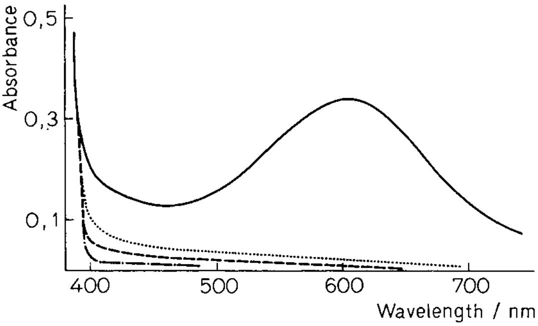


Fig. 2. Photochemical colour formation of the polyamide **3e** with different end groups. Irradiated by a high pressure mercury lamp (300 W) at $\lambda > 365$ nm. Preparative conditions: feed ratio diacyl dichloride/diamine = 1: ——— irradiation for 5 min, – – – without irradiation; feed ratio diacyl dichloride/diamine = 1,15: ······ irradiation for 20 min, —·—·—·— without irradiation

Tab. 1. Preparation of polyamides

Polyamide	% Yield[a]	Viscosity[b] $10^{-2}\cdot[\eta]/\mathrm{cm}^3\,\mathrm{g}^{-1}$	Colour of the polymer
Poly[(9-ethyl-3,6-carbazoldiyl)imino-succinylimino] (**3a**)	53,8	0,37	pale yellow
Poly[(9-ethyl-3,6-carbazoldiyl)imino-glutarylimino] (**3b**)	80,7	0,25	white
Poly[(9-ethyl-3,6-carbazoldiyl)imino-adipoylimino] (**3c**)	78.4	0,28	white
Poly[(9-ethyl-3,6-carbazoldiyl)imino-suberoylimino] (**3d**)	73,5	0,25	white
Poly[(9-ethyl-3,6-carbazoldiyl)imino-sebacoylimino] (**3e**)	81,2	0,60	white

[a] feed ratio: diacyl dichloride/diamine = 1,15.
[b] in m-cresol at 45 °C.

Complex formation of polyamides, of a monomeric model compound and of ethylcarbazole with sym-trinitrobenzene

The complex formation of carbazole derivatives with TNB results from Fig. 3.

Although no charge transfer absorption band can be observed as an independent peak, the shift of the absorption is large enough for the determination of the stability constant. *m*-Cresol, used as solvent, is a relatively strong electron donor interacting with TNB as indicated by the long tailing of the absorption of TNB upto ≈ 600 nm, whereas on the other hand the solvent acts as electron acceptor in the sense of a hydrogen bonding solvent. The shape of the absorption spectra is the same for **1a**, a polyamide and the monomer model compound.

Stability constants of the complexes were determined using the optical density at 600 nm at which photoabsorption is almost entirely due to the com-

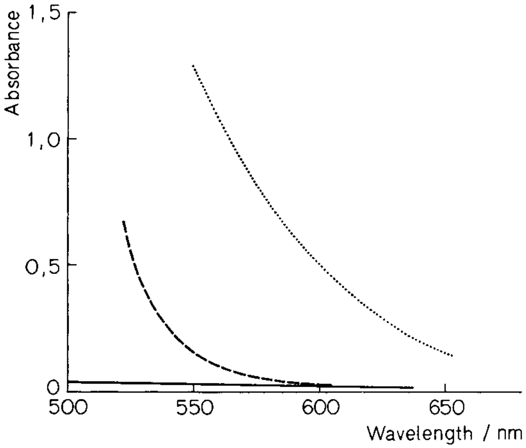


Fig. 3. Absorption spectra of the monomeric model compound **1c** in the presence of 1,3,5-trinitrobenzene (TNB) in *m*-cresol. ——— [**1c**] = $1{,}6\cdot10^{-2}$ mol/dm^3. – – – [TNB] = 0,32 mol/dm^3; ····· [**1c**] = $1{,}6\cdot10^{-2}$ mol/dm^3, [TNB] = 0,32 mol/dm^3

Tab. 2. Stability constant (K) and molar extinction coefficient (ε) of complexes formed between TNB and carbazole derivatives in *m*-cresol

Donor		εK	$\varepsilon_{600\ \mathrm{nm}}$	K at 43 °C
Ethylcarbazole	(**1a**)	109	48,4	2,26
Monomer model	(**1c**)	99,1	236	0,42
Polymer n = 2	(**3a**)	56,8	35,1	1,62
Polymer n = 3	(**3b**)	92,5	105	0,88
Polymer n = 4	(**3c**)	70,3	84	0,84
Polymer n = 6	(**3d**)	86,2	62	1,39
Polymer n = 8	(**3e**)	114	146	0,78

plex. Stability constants and molar extinction coefficients based on the SCOTT's equation are summarized in Tab. 2. Typical SCOTT's plots are depicted in Fig. 4.

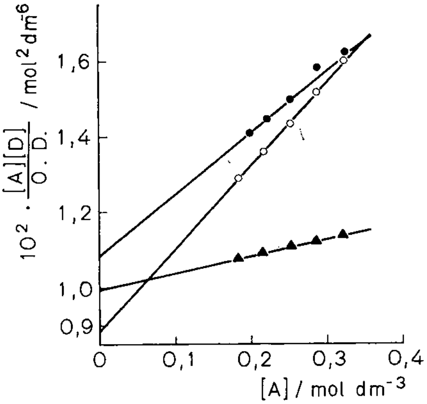


Fig. 4. SCOTT's plots. ● : polymer **3e** (n = 8); ○: **1a**; ▲: monomeric model compound **1c**

The determined values of K are independent of the wavelength of measurements between 550 and 650 nm.

The sequence of the stability constant is in the order **1a** > polymer > monomer model compound. Provided that the difference in K for **1a** and the monomer model compound reflects donor strength of two carbazole derivatives, the results seem to contradict the expected order of donor strength. Electron donating properties of the amide group should enhance the donor strength of the monomer model compound **1c**. A specific interaction of *m*-cresol with **1c** is indicated by the solvent effect on the fluorescence spectra as discussed later.

The difference between polymer and monomer model compound is a main point of discussion. Unexpectedly, any systematic trend of K as a function of the distance between the carbazole groups could not be observed. Possible factors causing the difference in K and ε between the polymers and **1c** are as follows.

i) Since carbazole groups in the polymers are connected to each other, the carbazole group might act as an aggregate. Consequently, the donor strength of the carbazole group in the polymers would be essentially different from **1c**. Moreover, the ratio D/A in the polymer complex might be higher than unity.

ii) If the solvation is different for the polymeric and monomeric systems, the degree of solvation would sensitively reflect on the apparent donor strength.

iii) The contribution of the contact charge transfer complex would also differ for the polymers and **1c**. As far as absorption and emission spectroscopy are concerned, the polymers and **1c** seem to have identical electronic energy levels. The difference in K for the polymers and **1c** could therefore not be attributed to the difference in donor character of carbazole groups in the polymers and **1c**. The possibility of forming higher complexes in the polymeric systems seems to be unlikely. The SCOTT's plots which assume a 1:1 complex alone fall on a straight line for the polymeric systems as well as for **1c**. Apparently, the cooperative action of the neighbouring donor unit to form higher complexes should be further investigated using polymers of different flexibility of the main chain.

In the recent article by BRAUN$^{6)}$ on CT complexes between an electron donating oligo ester and tetracyanoquinodimethane (TCNQ), a higher stability constant of the oligomer system than that of a monomeric model system has been discussed, assuming formation of higher complexes in which two or more electron donating side groups of the polymer hold a TCNQ molecule cooperatively as sandwich-like complex. However, the stoichiometry of the complex is 1:1, as observed by the method of continuous variation. Since the concentrations of the employed donor and acceptor for the continuous variation method are not identical with those employed for the determination of stability constants, the stoichiometry of the complex formation might be different from that predicted from the continuous variation method. An interpretation of the different stability constants for the polymers and the monomer is still a puzzling problem.

A higher value of ε for **1c** than that for the polymers would account for the contribution of a contact CT complex. A larger contribution of the contact CT complex in the monomeric system would certainly bring about a higher value of ε than that for the polymer.

Determination of stability constants by NMR spectroscopy

Stability constants determined by absorption spectroscopy are not necessarily identical with the values obtained by other methods. Molecular complexes detected by absorption spectra may not be detected by other methods or *vice versa*. This is due to the fact that the binding force of a molecular complex is not always a charge transfer interaction. A recent reinvestigation of "charge transfer" complexes led to the conclusion that the CT force may play only a minor rôle even in "typical" CT complexes such as the benzene-iodine system$^{12)}$. The benzene/hexafluorobenzene system is an another example of a non charge transfer binding$^{13)}$. Consequently, absorption spectroscopy may not represent the total binding force. There might be an extreme case in which the CT absorption is observed as a result of a close approach of donor to acceptor, caused by intermolecular forces other than CT.

As an alternative method of determining K, NMR spectroscopy was applied. The shift of the proton signal due to complex formation has theoretically nothing to do with a CT interaction. Nevertheless, the qualitative conclusion that the polymeric complex is more stable than the monomeric complex was again supported by the results of NMR spectroscopy. Since the shift of the proton signal (singlet) of TNB is very small even with a 220 MHz NMR spectrometer, the accuracy of determining K is not good. Approximate values of K calculated from Fig. 5 using Eq. (2)[14] are 1,4 and 0,3–0,4 for the polymer **3c** and for **1c**, respectively.

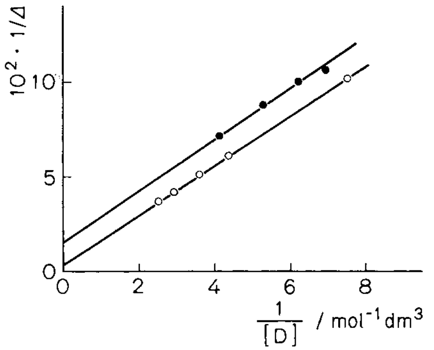


Fig. 5. NMR shift of the proton signal of TNB by complex formation at room temp. (220 MHZ). Solvent: *m*-cresol. Donor: ●: polymer **3c**, ○: monomeric model compound **1c**

$$1/\Delta = 1/K \; 1/\Delta_0 \; 1/[D] + 1/\Delta_0 \qquad (2)$$

In Eq. (2), Δ_0 is ($\delta_A - \delta_{AD}$), namely the shift for the pure complex in solution relative to the shift for the pure acceptor A in solution and Δ is ($\delta_A - \delta$) which is the observed shift for the system in equilibrium at the donor concentration [D] relative to the shift for the pure acceptor A in solution.

It is important to note the difference in the experimental conditions for UV and NMR spectroscopy. Contrary to the UV spectroscopy, the concentration of the donor D is very much in excess of that of TNB in the case of NMR measurements. Qualitative agreement of the K values for both measurements would consequently indicate that the contribution of higher complexes is not important.

Fluorescence spectroscopy

Fluorescence spectra of **1c** and the polymers **3a–e** in *m*-cresol are exactly identical as expressed by a single curve in Fig. 6b. The primary aim of fluorescence spectroscopy is to find out excimer emission of polymers. If several donor units could cooperatively act in complex formation, there would be a possibility of excimer formation. No excimer emission was detected, however. Specific solvent interactions are indicated by Fig. 6 and 7. Fluorescence spectra of **1a** shift only by 8 nm, whereas that of **1c** is as large as 50 nm, as a result of changing the solvent from hexane to *m*-cresol. At the same time the shape of the spectra is considerably distorted in the case of **1c**. The specific solvent interaction must be a hydrogen bonding of the phenolic OH with the amide group.

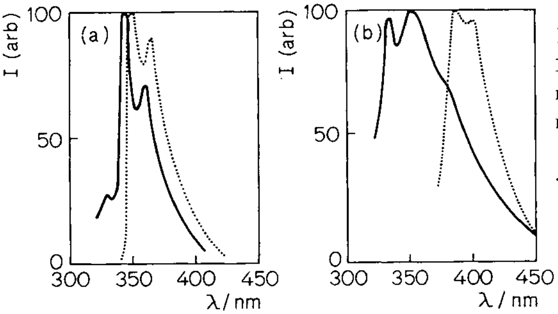


Fig. 6. Fluorescence spectra (a) of **1a**, (b) of the polymers **3a—e** and the monomeric model compound **1c** measured in hexane and in *m*-cresol. — in hexane, $\lambda^{\text{excitation}} = 300$ nm; ····· in *m*-cresol, $\lambda^{\text{excitation}} = 360$ nm. [Fluorescer] = 10^{-3} to 10^{-6} mol/dm^3

Quenching experiments to study the difference of donor properties are depicted in Fig. 7. The formation of a ground state complex of carbon tetrachloride with the carbazole group is negligible under the present conditions. Stern-Volmer plots for **1c** and the polymers as fluorescers fall on a single line. The quenching constant could be a relative measure of donor-acceptor interaction provided that the fluorescer is quenched by a charge transfer interaction with a rate much less than a diffusion controlled process. There is no positive evidence that the donor property of the carbazole group is enhanced

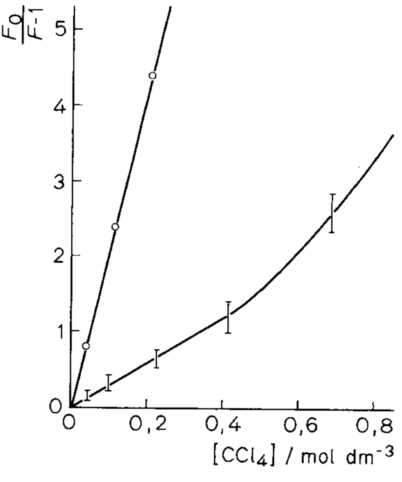


Fig. 7. Stern-Volmer plots of carbazole derivatives/CCl$_4$ systems. Solvent: *m*-cresol, [fluorescer] = $4 \cdot 10^{-4}$ mol/dm^3, $\lambda^{\text{excitation}} = 360$ nm, F determined at the peak intensity. ○: **1a**, I: polymers **3a—e** and the monomeric model compound **1c**

in the polymeric systems. The apparent quenching constant of **1a** is larger than that of both **1c** and the polymers. This does not mean that the absolute rate constant of the quenching process is faster for **1a**, since the quenching constant is a function of life time of the fluorescence and the quenching rate constant.

The specificity of a polymeric quencher to a low molecular weight fluorescer was recently reported 15). Since the effective quenching diameter of a quencher overlaps if quenchers and the polymer molecules are bound close to each other, the quenching constant of a polymeric quencher decreases with decreasing distance between the quenching groups. In the present study, the fluorescer is bound to the polymer and a specific polymer effect is not expected.

The authors are greatly indebted to Professors S. OKAMURA and T. HIGASHIMURA of Kyoto University for their encouragements.

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