of his potentials are too high. (b) The approximations used by Tonelli suppress the flexibility of the backbone. That means that during rotation of the phenyl group neither valence angles nor dihedral angles are allowed to change. These facts may cause the extremely high reported activation energies.

In addition, we recalculated the three sequences reported by Tonelli and found no energy minimum in the range of these conformations. That means that for these conformations activation energies do not exist.

The apparent stability of Tonelli's conformations is forced by the rigid backbone (cf. *b*) and disappears for a nonrigid backbone with interactions between the atoms.

(2) Phenyl Group Rotation in Isotactic Polystyrene. The investigations of the mobility of the phenyl group have been extended to isotactic polystyrene.

(a) Rotation in Ideal Backbones. Starting with the isotactic structures already determined,[3] the activation energies have been calculated in the same way as for syndiotactic polystyrene. The following results have been obtained:

$$\text{gt sequence: } \Delta H = 10.3 \text{ kcal/mol}$$

$$\text{tt sequence: } \Delta H > 30 \text{ kcal/mol}$$

$$\text{gg sequence: } \Delta H = 13.7 \text{ kcal/mol}$$

In the case of the tt sequence, the value $\Delta H > 30$ kcal/mol is caused by strong phenyl–phenyl interactions and is obtained only under the restriction that the tt conformation of the backbone is preserved. Without restrictions, the tt conformation is destroyed in the neighborhood of the rotating phenyl group (two adjacent dihedral angles change from t to g), and so the activation energy is decreased to ca. 17 kcal/mol, and the energy difference between the two minima is increased from 0 to 7.5 kcal/mol.

(b) Rotation in Backbones with Defects (Kinks). Using already determined conformations of two kinks in the isotactic polystyrene chain,[3] the activation energies of phenyl groups near the defects have been investigated. The results for a $\bar{g}$ kink are given in Figure 2.

The corresponding values for a t kink (the same C–C bond rotated from g to t instead of from g to $\bar{g}$) are: (1) kink is annihilated, (2) $\Delta H = 12.2$ kcal/mol, and (3) kink is annihilated. In cases (1) and (3) the strong coupling between the phenyl group and the backbone causes an annihilation of the kink, as the activation energy (rotation in the backbone) $\Delta H_{t\rightarrow g}$ is smaller than $\Delta H_{\bar{g}\rightarrow g}$.[3]

We expected that the phenyl group rotation would be favored near defects, as there is no regular steric arrangement of the side groups, which were assumed to restrict the rotation to a higher degree.

The results given in Figure 2, however, show the opposite behavior; the activation energies increase in the neighborhood of the defect.

The calculations reported above may be summarized as follows: Activation energies of phenyl group rotation are in the range between ca. 10 and 20 kcal/mol, if the backbone is flexible. For low activation energies the phenyl–backbone interaction dominates, while for increasing activation energies the phenyl–phenyl interaction becomes more important.

As these values of activation energies are found in probable chain segments, energetic considerations cannot rule out phenyl group rotation as a mechanism for mechanically activated relaxation processes.[11]

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(10) For simplicity the phenyl ring was taken rigid and therefore interactions within the ring have also been omitted.
(11) Note added in proof: A recent carbon-13 NMR study of molecular motion of polystyrene in solution by Y. Inoue and T. Konno (*Polym. J.*, **8(5)**, 457 (1976)) reports 10.5 and 13.6 kcal/mol for the activation energies of phenyl ring rotation in isotactic and syndiotactic polystyrene, respectively. These experimental data confirm our calculations. A detailed discussion will be given elsewhere.

Notes

Inter- and Intramolecular Interactions of Polymers as Studied by Fluorescence Spectroscopy. 3. Oligo(isobutylene terephthalate)'s Having Pendant ω-Carbazolylalkyl Groups

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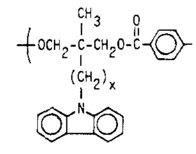
In the preceding articles, we have discussed the specificities of molecular interactions in polymeric systems in comparison with the monomeric model systems.[1–4] It was shown that the interactions between the polymer side chains depend on the distance between side chains if the side chain structures are identical.[4] The solvent effects on exciplex formation between carbazolyl and terephthalate groups, both bound to a polymer, were found to be different from those observed in the corresponding monomer model systems, which were attributed to the specific solvation of polymer chains.[3] This exciplex formation should also be affected by the structure of side chains at least in two ways. First, the encounter probability of the excited carbazolyl groups on the side chain forming an exciplex with the ground state terephthalate groups on the main chain should be a function of the structure of the side chain. Second, the solvation of polymer chains should be influenced by the structure of the side chain.

This note describes the side chain effects on exciplex formation of a pendant carbazolyl group with a terephthalate group in the main chain of an oligoester.



1, 2, 3

	x	n
1	0	2-4
2	4	3-5
3	10	3-5

Figure 1. The structure and the degree of oligomerization of carbazole derivatives.

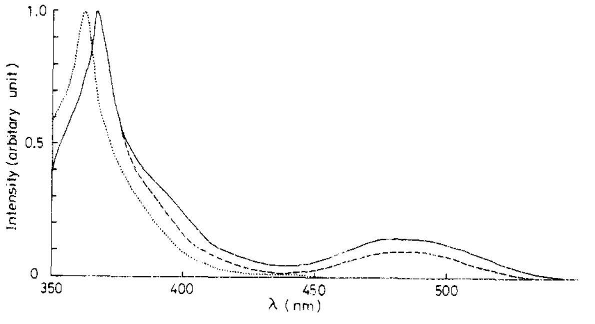


Figure 2. Fluorescence spectra of carbazole derivatives: [fluorescer] = 1 × 10^{-3} M; solvent = dioxane; temperature = 20.0 ± 0.5 °C; (···) 1; (—) 2; (- - -) 3.

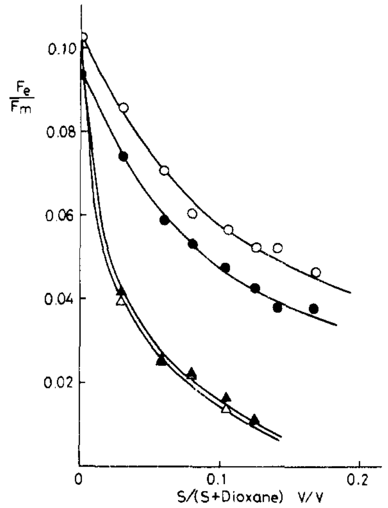


Figure 3. Effects of mixed solvent on exciplex emission: temperature = 20.0 ± 0.5 °C; (○) [2] = 1 × 10^{-3} M, S = lauryl alcohol; (●) [3] = 1 × 10^{-3} M, S = lauryl alcohol; (△) [2] = 1 × 10^{-3} M, S = ethanol; (▲) [3] = 1 × 10^{-3} M, S = ethanol.

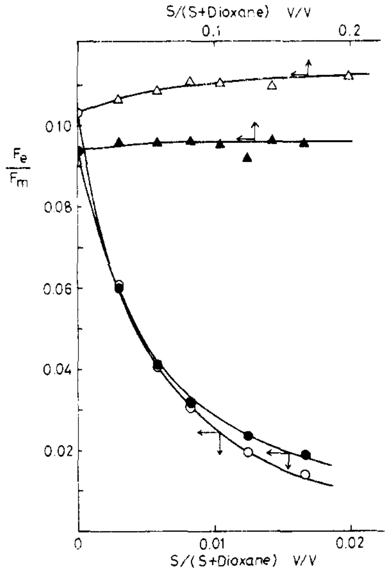


Figure 4. Effects of mixed solvent on exciplex emission; temperature, 20.0 ± 0.5 °C: (○) [2] = 1 × 10^{-3} M, S = H_2O; (●) [3] = 1 × 10^{-3} M, S = H_2O; (△) [2] = 1 × 10^{-3} M, S = *n*-dodecane; (▲) [3] = 1 × 10^{-3} M, S = *n*-dodecane.

Experimental Section

The preparation of oligo(2-carbazolylisobutylene terephthalate) (1) and oligo[2-(ω-carbazolylbutyl)isobutylene terephthalate] (2) has been reported previously.[1] Oligo[2-(ω-carbazolyldecyl)isobutylene terephthalate] (3) was prepared from *N*-(ω-bromodecyl)carbazole by the same method used for preparing **2**. GPC analysis indicated that the oligomers consisted of two to five repeating units. The structure and the degree of oligomerization are shown in Figure 1.

Fluorescence spectra were measured by a Hitachi MPF-4 fluorescence spectrometer.

Side Chain Effects on Exciplex Formation

Fluorescence spectra of the oligomers showed a broad emission at about 480–500 nm due to exciplex formation of the excited carbazolyl–terephthalate pair[3] as well as a monomer emission peaking at 360–370 nm. The exciplex emission was clearly observed for **2** and **3**, whereas the spectrum of oligomer **1** showed no characteristic band in the region of 430–600 nm. Intermolecular interactions of the present oligoesters at a concentration of 10^{-4} M are negligible as judged by the previous results on the dependence of intermolecular exciplex formation on the degree of polycondensation.[2] Consequently, the exciplex emission shown in Figure 2 is ascribed to intramolecular interaction.

Comparing the present results with the reported results of exciplex formation in the dimer systems of the $D-(CH_2)-A$ structure, it is apparent that the mobility of carbazolyl groups in **1** is restricted. For $D-(CH_2)_n-A$ in which the D–A combinations are 4-*N*,*N*-dimethylanilino–anthryl or -pyrenyl,[5] dimethylamino-1-naphthyl,[6] diethylamino-9,10-dicyanoanthryl,[7] and diethylamino–1-naphthyl or 9-anthryl,[8] it seems that the length of the polymethylene chain does not influence exciplex intensity as strongly as in the case of excimer formation. Excimer emission from $X-(CH_2)_n-X$ systems is known to be strongly dependent on *n* and reaches a maximum when *n* is 3.[9] The absence of exciplex emission in **1** should therefore be interpreted as being caused by conformational factors such as a lack of mobility of carbazolyl groups, the rigid terephthalate main chain, and others. Favorable conditions for efficient intramolecular exciplex formation would include an appropriate length of a flexible polymethylene chain linking the fluorophores and the main chain. In the case of **2** and **3** the intensities of exciplex emission are almost equal, indicating that the carbazolyl groups are free enough to interact with the terephthalate main chain when the length of the side chain is within the range of $-(CH_2)_4-$ to $-(CH_2)_{10}-$.

Solvent Effects on Exciplex Intensities

Although the exciplex intensity is nearly identical for **2** and **3** in dioxane, solvent effects on F_e/F_m (i.e., the ratio of exciplex intensity to monomer intensity) of **2** and **3** are different as shown in Figures 3 and 4. The value of F_e/F_m was corrected for the reabsorption of fluorescence as described previously.[3] As the kinetic equation derived previously shows,[3] the value of F_e/F_m is a complex function of several elementary rate constants and we cannot decide which processes are solvent dependent. The solvent effects, however, should be identical for **2** and **3** whose functional groups participating in exciplex formation are identical, unless the difference in specific solvation and the subsequent change in a micro solvation sphere

Table I
Solvent Effect on the Relative Intensity of the Exciplex[a]

Additive (vol) %)	$(F_e/F_m)_{dioxane}/(F_e/F_m)_{dioxane+add.}$ **2**	**3**	Ratio[b]
Ethanol (3.4)	2.60	2.34	1.11
Lauryl alcohol (14.0)	2.03	2.34	0.87
Water (0.6)	2.66	2.34	1.14
n-Dodecane (15.0)	0.92	0.97	0.95

[a] [Fluorescer] = 1×10^{-3} M, 20.0 ± 0.5 °C. [b] $[(F_e/F_m)_{dioxane}/(F_e/F_m)_{dioxane+add.}$ for **2**$]/[(F_e/F_m)_{dioxane}/(F_eF_m)_{dioxane+add.}$ for **3**].

are considered. In the preceding paper,[3] we compared solvent effects on exciplex formation in monomeric and polymeric systems and interpreted the results as due to specific solvation of polymer chain resulting in changes in the composition of a micro solvent sphere around polymer molecules. In addition to the problem of specific solvation, a comparison of **2** and **3** should take into account hydrophobic interaction as a function of solvent composition. Since the magnitude of hydrophobic interactions between long polymethylene chains increases gradually with an increasing number of methylene units up to 15–16,[10] the contribution of hydrophobic interactions in exciplex formation is certainly more important in **3** than in **2**. From the viewpoint of both solvent polarity and hydrophobic interactions, the effect of solvent in reducing F_e/F_m should be in the order water ≫ ethyl alcohol > lauryl alcohol. This order agrees well with the experimental results. To achieve an arbitrary standard of solvent effects, the concentrations of additives were chosen so that F_e/F_m of **3** was constant at 0.04, and the relative effectiveness of these three protic solvents was compared for **2** and **3**. A 15 vol % was chosen for *n*-dodecane which is nonpolar and affords slight enhancement of F_e/F_m. The results are tabulated in Table I.

It is interesting to compare the relative effectiveness of solvents on exciplex intensity of **2** and **3** as given by the ratio of solvent effect on **2** to that on **3** (the rightmost column of Table I). Very polar solvents (water and ethanol) influence **2** more than **3** whereas lauryl alcohol has a stronger influence on **3** than on **2**. Apparently, the hydrophobic environment resulting from pendant ω-carbazolyldecyl groups would be a barrier separating water or ethanol from **3**. On the other hand, approach of lauryl alcohol to **3** seems to be facilitated by hydrophobic interactions between long polymethylene chains. The role of lauryl alcohol is disruption of the hydrophobic sphere around the polymer chain and/or to bring about a polar environment at the site of exciplex formation. Both effects would reduce the intensity of exciplex emission, particularly of **3**. When *n*-dodecene is added, the F_e/F_m value increases slightly. The interaction of *n*-dodecane, a nonpolar higher alkane, with **3** should be preferred to that with **2**, while the enhancing effect of *n*-dodecane on F_e/F_m is slightly weaker for **3** than for **2**. Disorganization of hydrophobic interactions between pendant decamethylene chains would in part offset the positive effect on *n*-dodecane on F_e/F_m caused by the reduction in polarity around the exciplex.

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Cryoscopy of Polyethylene Oxide Irradiated in Air

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It has been shown that the depression of the melting point caused by irradiation can be used to provide a convenient estimate of overall chemical changes in some crystalline polymers.[1-4] In order to formulate rules which will allow a more informed interpretation of such results, it is desirable to extend studies to all those polymers for which independent analyses of total chemical changes are known. Detailed analytical results of this kind are available for poly(ethylene oxide) (PEO) irradiated in vacuum,[5] and an investigation is in progress on corresponding cryoscopic changes.[6] A sidelight of this work stems from King's report that the radiolysis of PEO is remarkably sensitive to the presence of oxygen in air, giving G values of several hundred for scission of the macromolecules.[7] The limited objective of the present note is to report experiments designed to investigate whether or not a similar sensitivity can be detected by cryoscopy.

The sample studied was Polyox WSRN-750 (Union Carbide Corp.), a PEO having a weight average molecular weight of ca. 3×10^5 ($[\eta] = 253$ g^{-1} ml using an aqueous solution at 30 °C where $K = 12.5 \times 10^{-5}$ g^{-1} dl and $a = 0.78$[8]). The polymer was obtained in powdered form with a particle size such that 98% passed through a No. 20 USBS sieve.[9] Dry powder was exposed to γ rays from a Cs^{137} source at a dose rate of 0.85 Mrad/h and at an ambient temperature of 30 °C. To avoid depletion of oxygen at the particulate surfaces, the powder (ca. 100 mg) was spread over ca. 200 mm^2. Differential thermal analysis (DTA) scans were made on thoroughly mixed samples (10–20 mg) under nitrogen at a heating rate of 20 °C/min in a Dupont Model 990 apparatus. Irradiated samples were examined ¼–½ h after removal from the source to minimize contributions from relatively slow postirradiation reactions. Ten hours after a dose of 20 Mrad, the melting point of each run increased ca. 4 °C over its initial postirradiation value. A similar increase was observed over the same period after a dose of 35 Mrad. Further smaller postirradiation effects (<1 °C) occurred over the interval from 10 to 100 h.

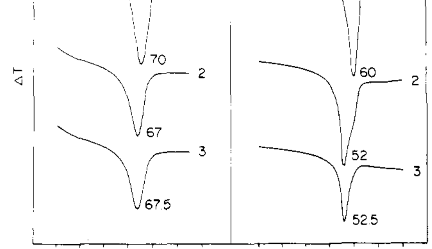

Figure 1. Thermograms for PEO irradiated in air: left set, 0 Mrad; right set, 14.1 Mrad. Consecutive runs numbered 1, 2, and 3.