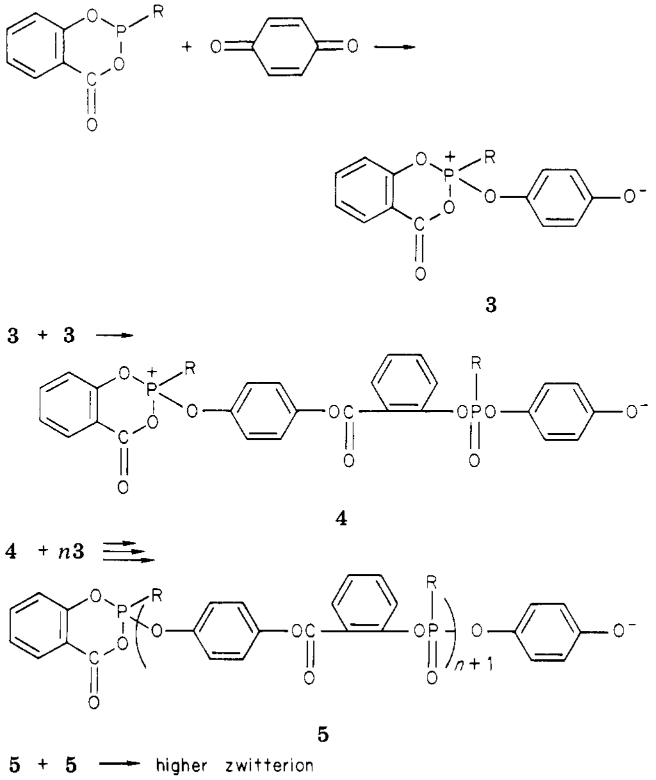
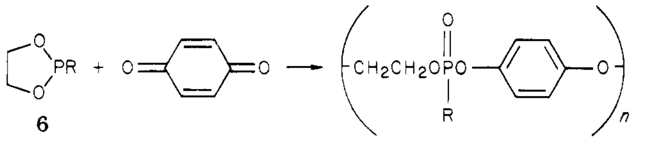


The first step is the reaction of SPO or SPI with *p*-benzoquinone to give a genetic zwitterion **3** of the phosphonium and phenoxide groups, which is an important key intermediate in both the initiation and propagation. Then, the reaction between two molecules of **3** occurs, in which the phosphonium ring of the one molecule is opened by nucleophilic attack of the phenoxide group of the other molecule, and the propagating species **4** is formed. **4** grows to **5** by the successive reaction with **3** to give the 1:1 alternating copolymer **2**. The reaction between two propagating zwitterions **5** is also possible, which increases sharply the molecular weight.

In relation to the copolymerizations of the present study, a Japanese patent[6] is to be mentioned, which describes the alternating copolymerizations of cyclic phosphorus compound **6** with *p*-benzoquinones at higher temperatures (e.g., 100 °C). The systems of SPO in the present study



could give the alternating copolymers at room temperature. From these results SPO has increased reactivities with the combination of *p*-benzoquinones.

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Fluorescence of Model Compounds with Two Groups Forming Intramolecular Excimers[1]

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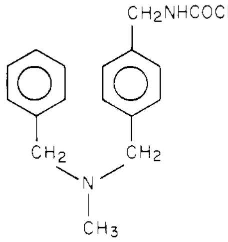
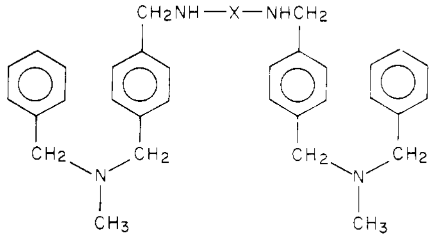
A number of investigators have found that intramolecular excimers can form in copolymers of monomers such as styrene, vinylnaphthalene, or *N*-vinylcarbazole only from nearest neighbor monomer residues carrying the aromatic chromophore.[2-5] On the other hand, it is well established that the excimer yield is increased by energy migration from the primary site of energy absorption to a site at which the conformation is particularly favorable for excimer formation.[2,6,7] This is the reason why the ratio of the fluorescence intensities at the excimer and the "monomer" band, I_D/I_M, is higher in polystyrene than in 2,4-diphenylpentane, the analogue containing only two chromophore groups.[8,9]

Recently, Reid and Soutar[10] have suggested that I_D/I_M in copolymers of monomers such as styrene or vinylnaphthalene should be proportional to $f_{aa}\bar{l}_a$, where f_{aa} is the fraction of linkages between the aromatic monomer residues and $\bar{l}_a$ is the mean sequence length of aromatic monomer residues. At nearly the same time, a study was published from Monnerie's laboratory[11] in which I_D/I_M was determined for the meso and the racemic 2,4-diphenylpentanes as well as for the isotactic and the syndiotactic 2,4,6-triphenylheptanes and 2,4,6,8-tetraphenylnonanes. Results of this study show that (1) the syndiotactic oligomers are characterized by much lower I_D/I_M ratios than the isotactic species and (2) that I_D/I_M increases sharply



I



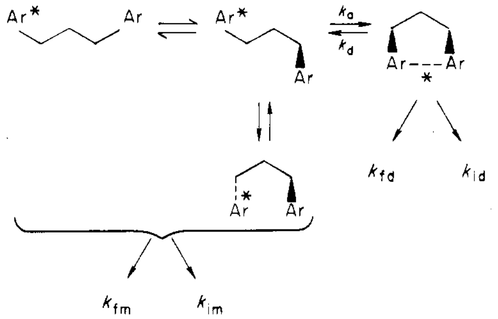
II

a, X = -C(=O)-
b, X = -C(=O)(CH$_2$)$_2$C(=O)-
c, X = -C(=O)(CH$_2$)$_3$C(=O)-
d, X = -C(=O)(CH$_2$)$_4$C(=O)-

from the compound containing two phenyl groups to that carrying three such groups (from 1.37 to 5.35 in the isotactic series and from 0.19 to 0.27 in the syndiotactic series) but does not increase further when the chain is extended to the tetraphenyl compound. These results contradict the treatment of Reid and Soutar. Their formulation would also lead to much higher I_D/I_M ratios in styrene homopolymers than have been observed.

In the present work, we compared the fluorescence behavior of compound I with that of a series of model compounds of type II in which two pairs of phenyl residues separated by a three-atom linkage are connected by a chain of varying length. The fluorescence of these compounds was measured in deoxygenated ethanol solution containing 0.1 M HCl, since the unprotonated form of dibenzylmethylamine does not fluoresce.[12]

In an earlier paper from this laboratory,[13] we used the following scheme for the fluorescence behavior of compounds in which two aromatic chromophores are separated by a three-atom linkage:



Here k_{fm} and k_{fd} are the rate constants for fluorescence from the monomer and excimer, k_{im} and k_{id} characterize the corresponding rate constants for internal quenching, and k_a and k_d are rate constants for the intramolecular excimer formation and for excimer dissociation.

The species in which one of the chromophores is excited while the other is in its ground state can exist in three conformations; only the *tg* form can lead to an excimer after a single hindered rotation while the *tt* and $g^{\pm}g^{\pm}$ conformations require two hindered rotations to arrive at the $g^{\pm}g^{\mp}$ conformation of the excimer.

At relatively low temperatures, k_d is negligible compared with k_a, and we may then distinguish two cases: (1) If the interconversion of the *tt*, *tg*, and $g^{\pm}g^{\pm}$ forms of the "monomer" is rapid compared with the $tg \rightarrow g^{\pm}g^{\mp}$ transitions, the excited monomer will exhibit simple exponential decay. (2) If the rate constants for the interconversion of the conformations of the excited monomer are not large compared to k_a, the time dependence of excimer formation will reflect the relative populations of the monomer conformations at the time of excitation, with the *tg* conformation transformed more rapidly into excimer that *tt* or $g^{\pm}g^{\mp}$. In that case, energy transfer in compounds of type II should increase the probability of excimer formation, since it could lead to a transfer from a chromophore pair in which the conformation is unfavorable to a chromophore pair with the *tg* conformation. Assuming an energy requirement of 600 cal/mol for the $tt \rightarrow tg$ and the $tg \rightarrow g^{\pm}g^{\pm}$ transitions and taking account of the multiplicity of the latter two conformations, we may estimate that approximately half of the monomer is in the *tg* form at equilibrium at 25 °C. Thus, the probability that at least one of the chromophore pairs in a compound of type II is in the favorable conformation should be about $^3/_4$, i.e., there should be a significant increase in the excimer yield of II relative to that of I if energy transfer is effective.

Table I

	I	IIa	IIb	IIc	IId
I_D/I_M	0.50	0.59	0.57	0.56	0.50

Table I lists the I_D/I_M ratios observed at 25 °C, a temperature at which excimer formation is kinetically controlled. It may be seen that compounds IIa, IIb, and IIc, in which the two dibenzylmethylamine residues are separated by 5, 7, and 8 atoms, have I_D/I_M only marginally higher than compound I. (We estimate that I_D/I_M can be determined with an accuracy of about ±2%.) This result can be interpreted either as implying that there is little energy transfer in these compounds or as being due to the fact that conformational equilibrium of the excited monomer is not perturbed by excimer formation, so that energy transfer would not affect I_D/I_M. The latter interpretation is supported by an observation in Nishijima's laboratory[14] that the monomer fluorescence in 1,3-di(2-naphthyl)propane exhibits simple exponential decay.

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