ones. Quantitative measurements at different temperatures of the NOE effects in blends having different compositions, ionic group concentrations, solution concentrations, and molecular weights are in progress.

Conclusions

Poly(MMA) and poly(S) can be compatibilized by introducing groups that form ion pairs upon mixing. In Me$_2$SO solution at 85 °C, the proton transfer from an SSA group to a 4VP group is very rapid, but the subsequent forming of ion pairs and the alignment of the two chains is a slower process, which takes about 2 h for an 11% ionic group content. This process can be monitored by the upfield shift of most of the signals of poly(MMA-*co*-4VP). The signals shift upfield due to the screening effect of the neighboring aromatic S rings. A ca. 0.1 ppm shift suggests that most of the poly(MMA-*co*-4VP) chains are at a distance of maximum 6 Å from the poly(S-*co*-SSA) chains. One- and two-dimensional NOE-correlated spectra indicate that at least the methoxy protons of MMA are situated at a distance of ca. 4 Å from the aromatic protons of S units.

Studies of the kinetics of this coil overlap process and its dependence on temperature, ionic group concentration, and molecular weight are in progress.

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Registry No. (MMA)(4VP) (copolymer), 26100-41-4.

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Photophysics of Polystyrene. 2. Pariser-Parr-Pople Studies of Excimer Structure

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ABSTRACT: Calculations of the energies of the two lowest electronic transitions in various conformations of meso and racemic diads in polystyrene, based upon a modified Pariser-Parr-Pople method, have been performed. It is shown that the interactions between phenyl groups in the ground state do not result in dimer formation in polystyrene. In the case of electronic excitation, excimer formation is possible in a meso tt diad only.

Introduction

Excimer fluorescence, first observed by Förster and Kasper[1] in concentrated solutions of pyrene, was later studied both experimentally[2-5] and theoretically[2,4,6-11] for various organic and inorganic molecules. According to the mechanism of formation, excimers can be classified into inter- and intramolecular ones. In the case of small organic molecules in solution, excimer formation is a diffusion-controlled process.[4] On the other hand, intramolecular excimers are formed even in arbitrarily diluted solutions.[12] Studies of intramolecular excimers in dichromophore systems and vinyl macromolecules have been a subject of numerous experimental works.[13-18] It has been shown that for dichromophore systems, excimer formation depends

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on the conformation of the chromophores and, in the case of macromolecules, also on migration of the electronic excitation energy.[16-18]

In connection with studies of luminescence of macromolecules, conformations of diads capable of forming an excimer have been thoroughly analyzed theoretically[19-22] as well as experimentally.[13-15] Theoretical studies were based on the analysis of the energy of conformations in the ground state and were performed for diphenylpentanes[19,21] and dinaphthylalkanes.[22] The analysis of conformations of 2,4-diphenylpentane shows[21] that conformations t$\bar{g}$ and $\bar{g}$t (notation of Yoon et al.[23]) are the most stable ones for a meso isomer and that the excimer-forming conformation tt is about 1.8 kcal/mol higher. In the case of a racemic isomer conformation tt is the most stable one, and conformations t$\bar{g}$ and $\bar{g}$t capable of forming an excimer lie about 3 kcal/mol above the tt state. The theoretical expectations[19,21] are in agreement with experimental results which show that for diphenyl systems the probability of forming an excimer in a meso diad is much greater compared with that for a racemic diad.[24,25]

Although dichromophore systems are often regarded as satisfactory models of vinyl macromolecules, their conformational analysis is not fully applicable to macromolecules. This follows from a justified assumption[26] that in the case of a macromolecule the $\bar{g}$ state may be neglected because of spatial interactions. This assumption was taken into account by Yoon, Sundararajan, and Flory[23] in their conformational analysis of polystyrene (PS) statistics. On the basis of the results of Yoon et al.[23] other authors studying fluorescence of PS in films[27] and solutions[28] assumed that excimers were formed when migrating energy was trapped in meso tt diads. An analytical calculation of the population of meso tt diads is possible for the isotactic PS of infinite molecular weight yielding 13.4% at 300 K.[27] For the atactic PS, the population of meso tt diads has been evaluated by Monte Carlo simulation giving the values 2.6%[27] and 3.6 ± 0.4%[28] at 300 K. Luminescence studies of PS in poly(vinyl methyl ether) blends[27] have shown that the population of meso tt diads capable of excimer formation, estimated from Monte Carlo simulation, is sufficient for the explanation of the experimental results, provided a one-dimensional model of a random energy walk is assumed. However, in the case of PS solutions, it has been suggested that the population of meso tt diads estimated from Monte Carlo is too small to give a satisfactory description of the excitation energy trapping.[28] The conclusions are similar in the case of solutions of poly(2-vinylnaphthalene).[29]

As we have already mentioned, conformational analysis of PS was performed for the ground state under the assumption of classical Lennard-Jones potential, and the conclusions concerning excimer formation were based only on the condition of parallel or almost parallel position of the phenyl groups. It is well established from studies of small organic molecules that this sandwich structure is only a sufficient condition for the formation of a singlet excimer.[2-11]

For the above reasons as well as because of the fundamental importance of intramolecular excimers in PS luminescence, it is useful to determine by means of quantum mechanical calculations which diads may form excimers in PS. This paper deals with this problem through an application of a simple yet general and well-tested method for π electron systems, namely, the Pariser–Parr–Pople (PPP) method.[30-32]

Calculation Procedure

Calculations have been performed by using a modified version of the PPP method,[30-32] neglecting the σ electrons of the main chain of PS. The π electron approximation is so far the most common approach in the theoretical treatment of excimers.[2,4,6-11] However, its limitations should be remembered,[33] among them the fact that the minimum of the excited-state potential energy cannot be evaluated. In the following, a simple model based on the standard PPP theory[32] is described, including the transannular through-space effects.

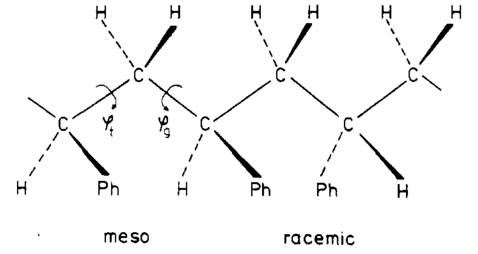

Figure 1. Portion of the PS chain with meso and racemic diads.

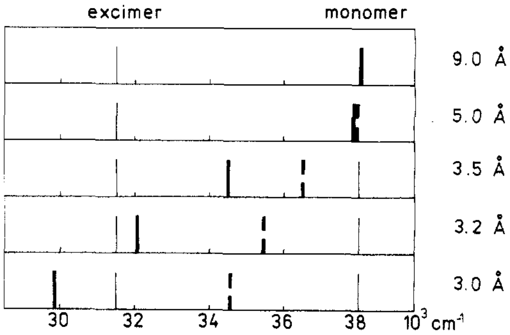

Figure 2. Electronic transitions calculated for the eclipsed benzene rings with interdeck distances given in the figure: (full lines) first transition; (broken lines) second transition; (thin lines) observed transitions.[4,32]

The benzene rings are taken to be regular hexagons located in space according to the diad conformations considered by Yoon et al.[23] In generating diads, only states t and g are considered, excluding the state $\bar{g}$, which as we have already pointed out is insignificant for conformations of PS.[23] Rotational states are taken at $\varphi_t = 10°$ and $\varphi_g = 110°$ (see Figure 1). Rotations of phenyl groups are ignored.

The repulsion integrals[30-32] $\gamma_{\mu,\nu}$ are computed according to the Mataga–Nishimoto formula[34] with $\gamma_{\mu,\mu} = 11.13$ eV. The $\beta_{\mu,\nu}$ integrals[30-32] over all centers are computed proportional to the overlap integrals of SCF-AO, expanded on the basis of Slater orbitals according to Mulliken et al.,[35] with the scaling coefficient ensuring the correct spacing interaction (CI) picture. Singlet states are generated by CI between monoexcited configurations involving excitations from the four highest occupied to the four lowest unoccupied molecular orbitals.

In order to test the procedure we have calculated the electronic structure of the eclipsed conformation of two benzene rings as a function of the distance between them. The resulting values of electronic transitions of the lowest energy are illustrated in Figure 2. A comparison of the results with experimental data concerning the excimer fluorescence of benzene solutions[36] shows that benzene excimers are formed at a distance of about 3.1 Å. Similar values were obtained by other authors.[37,38]

Results and Discussion

Figure 3 shows the results of the calculation of the energy of the two lowest electronic transitions in various conformations of meso and racemic diads in PS. The

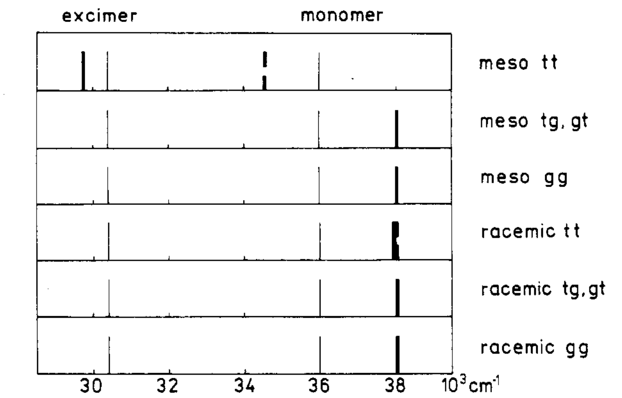

Figure 3. Electronic transitions calculated for various diad conformations in PS: (thin lines) observed fluorescence.[20]

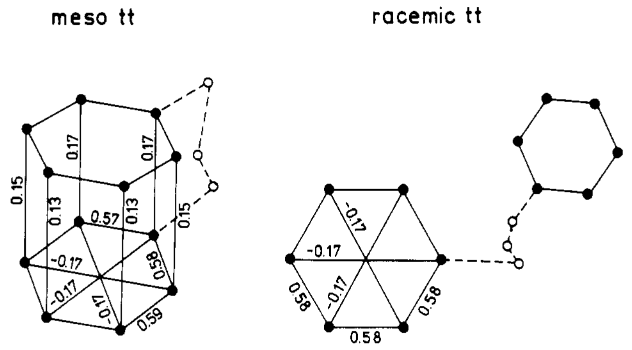

Figure 4. Example of electronic densities in the first excited state in PS diads. Only densities greater than 0.1 are depicted.

population analysis of the ground state of all studied conformations shows no substantial increase of electronic density between the phenyl groups, which suggests an absence of dimers in PS.

As shown in Figure 3, the only excimer-forming diad is the meso tt diad. For this conformation the characteristic red-shift of spectral lines is accompanied by an increase of electronic density between the phenyl groups. For other diads, calculated transitions correspond to the monomer fluorescence of PS, and the electronic densities between the phenyl groups may be ignored (Figure 4).

The presented results, limited to π electrons, show that the assumption concerning excimers in PS made by other authors[27,28] in fully justified. We believe that inclusion of the interactions of π orbitals with σ orbitals of the chain atoms does not lead to substantial changes in results. These conclusions seem to be in conflict with the results of studies of diphenyl systems, where excimer fluorescence has been observed also in racemic diads.[13,24,25] It is our opinion that the conformational analysis of diphenyl systems cannot be limited to the rotational states t and g only. A more free rotation of the chromophores should be allowed than in the case of macromolecules.[21,39]

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Registry No. PS, 9003-53-6.

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