kept during 1000 min at 70 °C or 250 min at 110 °C. The subsequent heatings showed only the endothermic peak at 172 °C.

From these experiments and the kind of diffractograms, representative of a 2-dimensional state, it follows that the only structure obtained for PDTMB is probably a smectic liquid-crystalline phase, stable at any temperature below its isotropization point. We were unable to generate any other structure with a higher degree of order, although other similar systems[6-9] have been reported to be able to undergo a transformation from the mesophase to a more ordered crystal structure. The results from this work show, however, that the only transformations of the liquid-crystalline phase of PDTMB, at least in the time scale of our experiments, are either to the isotropic melt or to the glassy state.

The texture of PDTMB was analyzed by using a polarizing microscope. Only very small "spheres", although birefringent, were observed below the isotropization temperature. No other texture was detected even at the maximum resolution of the microscope (×400). More revealing textures have been reported, however, for other similar systems,[8] although there seems to be a tendency to observe them only for lower molecular weights.

The type of mesophase of PDTMB can be inferred from the comparison with other poly(bibenzoates), particularly poly(heptamethylene *p,p'*-bibenzoate) (P7MB) with a structure very similar to PDTMB: the only difference is the change of the central methylene of that polymer by an ether group. P7MB has been reported to give rise to a smectic mesophase with a characteristic length[6,9] of 1.74-1.72 nm, showing an X-ray diffractogram for the mesophase almost identical with PDTMB. In fact, the change of a methylene by an oxygen is expected to produce minor differences in the length of the repeating unit and hence the smectic layer spacing. Curiously, the clearing temperature of the mesophase of P7MB[9] is about 10 deg lower than that for PDTMB, when one might expect a lowering of that temperature by the effect of the oxygen. However, there may be differences in the molecular weight, having the opposite influence (although the intrinsic viscosity of the PDTMB sample studied here is very similar to the value of 1.03 dL/g found for P7MB[9]).

The really important effect of the ether group, compared to the all-methylene spacer is the suppression of the crystalline state, and its seems that the flexibility introduced by the ether group does not affect the formation and characteristics of the mesophase, considering the similarities of the X-ray diffractograms. That the mesophase of PDTMB is not very different from the one of P7MB is also confirmed by the similarities of the enthalpies of isotropization (19 J g^{-1} for the former polymer and 18.5 J g^{-1} for the latter one[9]), and by the corresponding entropies, even closer (0.043 J g^{-1} K^{-1} for both polymers).

In conclusion, the substitution of the central methylene of poly(heptamethylene *p,p'*-bibenzoate) by an ether group leads to a polymer, PDTMB, with similar characteristics concerning the liquid-crystalline state of the two polymers. However, the presence of the oxygen atom precludes the formation of a 3-dimensional crystal structure in PDTMB, presumably as a consequence of the increase in flexibility introduced by the ether group. Thus, the properties of the liquid-crystalline phase of PDTMB can be studied at room temperature. Experiments are now in progress in order to study the mechanical properties and the kinetics of the formation of the mesophase of this polymer, as well as to synthesize new poly(bibenzoates) derived from the dimers of other substituted trimethylene glycols and to investigate the effect of different substituents on the properties of the resulting polyesters.

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References and Notes

(1) Mark, J. E. *J. Chem. Phys.* **1977**, *67*, 3300.
(2) Saiz, E.; Riande, E.; Guzmán, J.; de Abajo, J. *J. Chem. Phys.* **1980**, *73*, 958.
(3) Conjeevaram, S. V.; Benson, R. S.; Lyman, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 429.
(4) Wojtania, M.; Kubisa, P.; Penczek, S. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 201.
(5) González, C. C.; Bello, A.; Pereña, J. M. *Makromol. Chem.* **1989**, *190*, 1217.
(6) Watanabe, J.; Hayashi, M. *Macromolecules* **1988**, *21*, 278.
(7) Meurisse, P.; Noel, C.; Monnerie, L.; Fayolle, B. *Br. Polym. J.* **1981**, *13*, 55.
(8) Krigbaum, W. R.; Watanabe, J. *Polymer* **1983**, *24*, 1299.
(9) Pérez, E.; Bello, A.; Marugán, M. M.; Pereña, J. M., submitted for publication.

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Copolymerization of Alkenes with Sulfur Dioxide: A Semiempirical Molecular Orbital Study

Alkane- and arenesulfonyl radicals ($RSO_2^{\bullet}$) are reactive electrophilic intermediates that have been detected in a number of chemical reactions,[1] e.g., during the addition of alkane- and arenesulfonyl halides to unsaturated C-C bonds[2] and the alternating copolymerization of alkenes with liquid SO_2.[3] Because of the strongly electrophilic character of sulfonyl radicals, structural factors that affect the electron density distribution in the double bond manifest themselves in the relative reactivities of unsaturated compounds toward these radicals.[2g] Also, the alkene/SO_2 copolymerization systems exhibit low ceiling temperatures, T_c, reflecting the importance of depropagation reactions in such systems and the relative weakness of the C-S bond.[3]

Computational studies of reactions involving sulfonyl radicals should help to identify the various electronic and steric factors responsible for the observed reactivity order of alkenes and the observed low T_c values, but no such studies have been reported. Surveys of the literature indicate that computational studies of SO_2-containing compounds by both ab initio[5] and semiempirical[6] molecular

Table I
Heats of Formation for the Addition of $CH_3^\bullet$ to SO_2 and of $CH_3SO_2^\bullet$ to Ethene Calculated by Several Semiempirical MO Methods

	MINDO/3		MNDO		AM1		PM3		
compd	HE	UHF	HE	UHF	HE	UHF	HE	UHF	exp
$CH_3^\bullet$	42.3	41.0	25.8	24.6	31.3	30.0	29.8	28.0	34.8
$CH_2{=}CH_2$	19.2		15.4		16.5		16.6		12.4
SO_2	-70.7		4.5		27.0		-50.8		-71.0
$CH_3SO_2^\bullet$	-52.4	-58.9	34.8	29.9	46.4	37.1	-52.3	-54.4	-55.0[b]
$[CH_3{\cdots}SO_2]^\bullet$	-27.8		46.6	37.5	(≈63.8)		-13.0	-21.3	
R_{C-S} (TS), Å	(3.153)		(2.246)	(2.090)	(≈2.6)		(2.674)	(2.823)	
$CH_3^\bullet + SO_2$	-28.4	-29.7	29.9	29.1	58.3	57.0	-21.0	-22.8	-36.2[b]
$CH_3SO_2CH_2CH_2^\bullet$	-18.1[c]	-27.6[c]	84.0[c]	74.7[c]	87.1[c]	78.9[c]	-40.4	-46.1	
$[CH_3SO_2{\cdots}CH_2{\cdots}CH_2]^\bullet$							-25.6	-31.2	
R_{C-S} (TS), Å							(2.309)	(2.362)	
$CH_3SO_2^\bullet + CH_2{=}CH_2$	-33.2	-39.7	50.2	45.3	62.9	53.6	-35.7	-37.8	-42.6

[a] The lack of data indicates that no stable transition structure could be located; the data in parentheses are the forming bond lengths in the activated complex (in Å). [b] See refs 11c and 15. [c] Adduct unstable; the C–S distance was fixed at 1.831 Å.

orbital (MO) methods are beset by difficulties[4] related to the quantum mechanical treatment of hypervalent sulfur compounds.

In this paper, we report the results of semiempirical MO calculations of the individual addition steps during the alternating free-radical copolymerization of ethene with SO_2. We have investigated the addition of the methanesulfonyl radical to ethene and the reaction of methyl and methanesulfonylethyl ($CH_3SO_2CH_2CH_2^\bullet$) radicals to sulfur dioxide by several semiempirical molecular orbital methods including MNDO-PM3 recently developed by Stewart.[7] Although its performance in modeling molecular properties and bonding situations not included in the original parametrization set is unknown, the results of calculations for the addition of $CH_3^\bullet$ and $O(^3P)$ to $CH_2{=}CH_2$, for which extensive experimental and theoretical data are available,[8,9] showed good agreement with both experiment and higher level ab initio calculations (see Table SI in the supplementary material).[10]

The results of single-determinant (HE and UHF) calculations for the addition of $CH_3^\bullet$ to SO_2 and $CH_3SO_2^\bullet$ to ethene are summarized in Table I.

Since even high-level single-determinant ab initio calculations of ΔH_f° and $\Delta H_a^{\ddagger}$ for free-radical reactions can result in errors on the order of 10 kcal/mol in the values,[8f,9] the calculated enthalpies for the reaction of a methyl radical with SO_2 using MINDO/3, AM1, and PM3 methods are satisfactory (see Table I; experimental $\Delta H_r^\circ = -23.3$ kcal/mol).[10] With the exception of MNDO, all three methods predict very low values of $\Delta H_a^{\ddagger}$ and very loose transition states (Table I). Such low $\Delta H_a^{\ddagger}$ values appear to be in agreement with kinetic measurements for the reaction of $CH_3^\bullet$ with SO_2 in the gas phase, which indicate a rate close to the diffusion-controlled limit ($k = 5 \times 10^{-8}$ M^{-1} s^{-1}).[12] The PM3/UHF ΔH_f° value appears to be more reliable, since the transition-state structure is less contaminated with higher spin states ($\langle S^2 \rangle = 0.78$) than the UHF values calculated by other methods. The $\langle S^2 \rangle$ values obtained by MINDO/3, MNDO, and AM1 were 1.13, 1.09, and 1.31, respectively.

It is generally believed that multiple-determinant wave functions are often necessary to describe various bond-breaking and bond-forming reactions.[5] Therefore, we have also performed limited configuration interaction (CI) calculations for some species.[10b] As expected, the PM3/CI ΔH_f° results for the majority of the studied species were lower by 1.5–3 kcal/mol than the corresponding PM3/UHF results. Notable exceptions were ΔH_f° values for ethene and SO_2. While the PM3 value for ethene (16.6 kcal/mol) *overestimates* the experimental result by 4.2 kcal/mol, the PM3/CI value (7.2 kcal/mol) *underestimates* it by 5.2 kcal/mol. However, the largest CI effect by far was observed for SO_2, for which the PM3 ΔH_f° value (−50.8 kcal/mol) differs from the experimental result (−71.0 kcal/mol) by 20.2 kcal/mol, while the PM3/CI result (−70.3 kcal/mol) is essentially equal to the experimental one. The inclusion of electron correlation in MNDO led to a similar decrease in ΔH_f° of SO_2 (+4.45 vs −17.9 kcal/mol), but the effect was much less pronounced in the case of the MINDO/3 method (−70.7 vs −75.8 kcal/mol). Since such a large CI effect was limited only to the free SO_2 molecule with the exclusion of SO_2-containing radicals, the resulting $\Delta H_a^{\ddagger}$ values for sulfonyl radical addition reactions were seriously overestimated. Interestingly, a similar, although smaller, correlation effect resulting in the activation energy barrier that was too high was reported in the case of ab initio studies of the addition of the methyl radical to ethene.[8f]

The PM3/UHF-optimized geometry of $CH_3SO_2^\bullet$ is in good agreement with ESR data and with INDO[6] and STO-3G*[5] calculations that predict a pyramidal structure for the whole class of σ-type $RSO_2^\bullet$ radicals. The optimized O–S–O angle is 117°, and the C–S bond forms a 134° angle with the O–S–O plane. The S=O and C–S bond lengths are 1.468 and 1.782 Å.

MINDO/3, MNDO, and AM1 calculations for the addition of the $CH_3SO_2^\bullet$ radical to ethene predict that the radical adduct is unstable with respect to the reactants by 12–30 kcal/mol, clearly in contradiction with the experimental data.[12] However, PM3/HE and PM3/UHF results predict that the $CH_3SO_2CH_2CH_2^\bullet$ radical is stabilized by 4.7 and 8.3 kcal/mol, respectively. The corresponding $\Delta H_a^{\ddagger}$ values obtained by these methods are 10.1 and 6.6 kcal/mol.

The copolymerization of alkenes with SO_2 consists of three elemental steps: an initial propagating reaction ($CH_3^\bullet + SO_2$, step 0) and two alternating addition steps ($CH_3SO_2^\bullet + CH_2{=}CH_2$ (step 1) and $CH_3SO_2CH_2CH_2^\bullet + SO_2$ (step 2). The reaction energy profile for all three steps calculated by PM3/UHF is shown in Figure 1. The sum of ΔH_r° for step 1 (−8.3 kcal/mol) and step 2 (−19.8 kcal/mol) equals −28.1 kcal/mol per one repeat unit of poly(ethene sulfone), which is equal to the heat of reaction for the formation of 1 base mol of the copolymer from the monomers. This value is larger by ca. 8 kcal/mol than the experimental value of −20 ± 1 kcal/mol reported for the liquid-phase copolymerization of but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, or hexadec-1-ene with

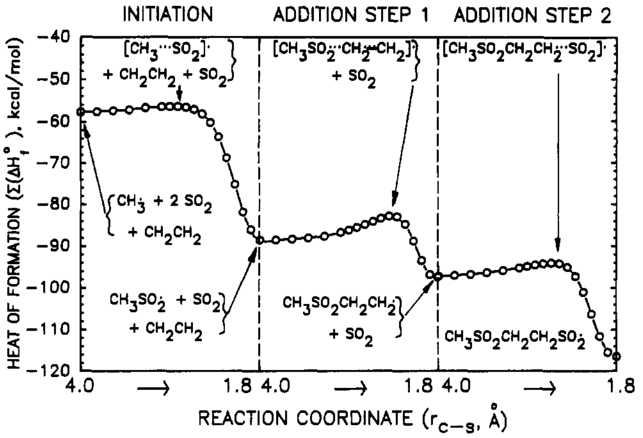

Figure 1. Reaction profile for the consecutive additions of $CH_3^{\bullet}$ to SO_2, $CH_3SO_2^{\bullet}$ to ethene, and $CH_3SO_2CH_2CH_2^{\bullet}$ to SO_2, calculated by the PM3/UHF method. The length of the developing C–S bond is the reaction coordinate. $\sum(\Delta H_f^\circ)$ calculated at each point is the sum of ΔH_f° for all shown components.

SO_2.[15] The observed difference may have two sources: (i) the calculations are carried out for isolated, gas-phase molecules while the experimental data have been obtained in the liquid phase where the reactant–polar solvent interactions may be considerable; (ii) the heat of reaction of the methyl radical with SO_2 calculated by PM3 is overestimated by ca. 8 kcal/mol.

The calculated activation energies for steps 1 and 2 are 6.6 and 2.7 kcal/mol. Thus, a comparison of the ΔH_a^* and ΔH_r° values for both steps (see Figure 1) indicates that step 1 is the rate-determining step of the reaction. Further, the temperature dependence of the reversibility of step 1 should be greater than for step 2 as was observed in numerous alkene/SO_2 copolymerization systems.[3]

In conclusion, the recently published semiempirical MNDO-PM3 method[7] appears to be the only semiempirical MO procedure providing approximately correct descriptions of such difficult electronic systems as sulfonyl radicals and their addition reactions to unsaturated C–C bonds. Studies of such systems by high-level ab initio calculations are either impractical or impossible. Experimental and calculational studies of the copolymerization of higher alkenes and alkenylsilanes with SO_2 are in progress.

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Supplementary Material Available: Table SI giving calculated heats of formation for the reactants, activated complexes, and products of addition of the methyl radical and triplet oxygen atom to ethene (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) For reviews on sulfonyl radicals, see: (a) Kice, J. L. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Part 2, p 711. (b) Lunazzi, L.; Pedulli, F. In *Organic Sulfur Chemistry. Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; p 484. (c) Freeman, F.; Keindl, M. C. *Sulfur Rep.* **1985**, *4*, 231. (d) Chatgilialoglu, C. In *Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C., Eds.; Wiley: Chichester, 1988; p 1089.

(2) Some examples of addition reactions of $RSO_2^{\bullet}$: (a) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**, 4962. (b) da Silva Correa, C. M. M.; Waters, W. A. *J. Chem. Soc. C* **1968**, 1874. (c) Orochov, A.; Asscher, M.; Vofsi, D. *J. Chem. Soc. B* **1969**, 255. (d) Zakharkin, L. I.; Zhigareva, G. G. *J. Gen. Chem. USSR* **1973**, *9*, 891. (e) Or, A.; Asscher, A.; Vofsi, D. *J. Chem. Soc., Perkin. Trans. 2* **1973**, 1000. (f) Kao, L. K.; Jen, K.-Y. *J. Org. Chem.* **1980**, *45*, 406. (g) Takahara, Y.; Iino, M.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2268.

(3) For a comprehensive review, see: Ivin, K. J.; Rose, J. B. *Adv. Macromol. Chem.* **1968**, *1*, 336.

(4) An ab initio STO-3G* study: (a) Boyd, R. J.; Gupta, A.; Langler, R. F.; Lownie, S. P.; Pincock, J. A. *Can. J. Chem.* **1980**, *58*, 331. ESR and INDO (Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970) studies: (b) Alberti, A.; Chatgilialoglu, C.; Guerra, M. *J. Chem. Soc., Perkin. Trans. 2* **1986**, 1179. (c) Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1429. (d) Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 770.

(5) Polarization basis sets, such as 3-21G* and 6-31G* are quite successful in predicting the geometries of simple hypervalent S compounds: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 181. However, high-level calculations of thermochemical quantities requiring the inclusion of electron correlation (*Ibid.*, p 288) are not yet feasible for molecules containing more than three or four heavy atoms.

(6) Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985; p 151.

(7) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209 and 221. The PM3 method uses an AM1-like Hamiltonian and has been parametrized using an extensive set of compounds (~650), including 63 hypervalent sulfur and 13 SO_2-containing species. All calculations have been performed with the MOPAC 5.0 package: Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10. All molecules and activated complexes were constrained within a C_s symmetry; the stationary nature of the latter has been confirmed by vibrational analysis.

(8) (a) Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Part 2, p 63. (b) O'Neal, H. E.; Benson, S. W. *Ibid.* p 275. (c) Houk, K. N. In *Frontier of Free Radical Chemistry*; Pryor, W. A., Ed.; Academic Press: New York, 1980. (d) Bonacic-Koutecky, V.; Koutecky, J.; Salem, L. *J. Am. Chem. Soc.* **1977**, *99*, 842. (e) Delbecq, F.; Ilavsky, D.; Anh, N. T.; Lefour, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 1623. (f) Clark, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1774.

(9) For an ab initio study of the $O(^3P) + CH_2{=}CH_2$ system, see: Dupuis, M.; Wendoloski, J. J.; Takada, T.; Lester, W. A., Jr. *J. Chem. Phys.* **1982**, *76*, 481 and references cited therein.

(10) (a) Calculations have been carried out by MINDO/3, MNDO, AM1, and PM3 methods using half-electron (HE) method and unrestricted Hartree–Fock (UHF) formalism for open-shell systems. The PM3/UHF geometry of the activated complex $[CH_3{\cdots}CH_2{\cdots}CH_2]^{\bullet}$ is very close to that obtained by high-level (MP2/6-31G*) ab initio calculations.[8f] The PM3/UHF length of the developing C–C bond in the activated complex was 2.222 Å (the MP2/6-31G* value 2.246 Å), and the calculated activation energies (ΔH_a^*) are 4.0 (PM3/UHF), 10.3 (PM3/HE), and 14.4 (MP2/6-31G*) kcal/mol, which can be compared to the experimental value of 7.7 kcal/mol. In the case of the second test reaction, i.e., $O(^3P) + CH_2{=}CH_2$, the PM3/UHF activation energy (3.5 kcal/mol) is much closer to the experimental value (1 kcal/mol) than the 3-21G result (16.6 kcal/mol).[9] The length of the developing C–O bond (2.269 Å) and the $\angle(C_1C_2O)$ angle (94.0°) can be compared to the 3-21G values of 1.873 Å and 107.4°, respectively.[9] Stable transition-state structures for this reaction could not be located by the PM3/HE, MINDO/3/HE, and both AM1 methods. (b) Multielectron configuration interaction (CI) calculations have been carried out for the four highest occupied and four lowest unoccupied orbitals (CI = 7), which led to 1225 microstates.

(11) (a) Bushfield, W. K.; Ivin, K. J.; Mackle, H.; O'Hare, P. A. G. *Trans. Faraday Soc.* 1961, *57*, 1064. (b) Thoi, H. H.; Iino, M.; Matsuda, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *20*, 564. (c) The source of the difference of 4.5 kcal/mol between ΔH_f° of $CH_3SO_2^{\bullet}$ given in refs 10a and 10b and that obtained as a difference between $\sum(\Delta H_f^\circ)$ for $CH_3^{\bullet}$ and SO_2 and ΔH_f° for $CH_3SO_2^{\bullet}$ (ref 15) is unknown; an error

resulting from the indirect determination of $\Delta H_f°$ of the latter is one possibility.
(12) (a) Good, A.; Thynne, J. C. J. *Trans. Faraday Soc.* **1967**, *63*, 2708 and 2720. (b) Gilbert, R. C.; Norman, R. O. C.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 303 and 308. (c) James, F. C.; Kerr, J. A.; Simons, J. P. *J. Chem. Soc., Faraday Trans.* **1973**, *2*, 2124.
(13) Ethene exhibits the highest ceiling temperature of copolymerization with SO_2 among all alkenes ($T_c > 135$ °C; Cook, R. E.; Dainton, F. S.; Ivin, K. J. *J. Polym. Sci.* **1957**, *26*, 351), which indicates the relatively high stability of the growing sulfonylethenyl macroradical.
(14) Dainton, F. S.; Diaper, I.; Ivin, K. J.; Sheard, D. R. *Trans. Faraday Soc.* **1957**, *53*, 1269.
(15) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23 (an entry in Table X).

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Photoinduced Electron-Transfer Reactions To Probe the Structure of Starburst Dendrimers

The so-called *starburst dendrimers*, a new class of compounds possessing unique structural and topological features, have recently been introduced by Tomalia and coworkers.[1] Controlled branching reactions from an initiator core allow for the synthesis of particles with various types of surface groups that might be successfully compared to micellar structures (schematic two-dimensional cross sections of the 1.5, 2.5, 3.5, 6.5, and 9.5 generations are shown in Figure 1) without their dynamic structure. For example, an increase in the ionic strength of the medium will change the aggregation number and size of micelles but not of the starburst particles. The measured hydrodynamic diameter increases from 2.8 to 21.0 nm (e.g., Figure 1) as the dendrimer generation (number of synthetic steps, *G*) rises from 0.5 to 9.5.[2] Recent molecular dynamics calculations have pointed out that a shape transition from a starfishlike to a more congested structure is brought about the generation 3.[3] This paper describes the use of photoinduced electron-transfer reactions to probe the structure of the starburst dendrimers as a function of their generation and opens the exciting possibility of studying this kind of reaction in microenvironments of well-defined geometry.[4]

The luminescence from the triplet metal-to-ligand charge-transfer (MLCT) excited state of tris(2,2′-bipyridine)ruthenium(II) (abbreviated $Ru(bpy)_3^{2+}$) is quenched by electron transfer to the 1,1′-dimethyl-4,4′-bipyridinium ion (methyl viologen, MV^{2+}).[5] In homogeneous solution, the rate constant of this process is slightly below diffusion control (ca. 1×10^9 M^{-1} s^{-1}) and follows a normal Debye–Hückel behavior as a function of the ionic strength.[6] Several authors have also investigated this photoreaction (and related complex/viologen couples) in microheterogeneous media (micelles,[7] vesicles,[8] polyelectrolytes[9]), particularly in connection to light-induced water-splitting research.

In recent years, our interest has focused on the study of photoinduced electron-transfer quenching of ruthenium(II) polypyridyls to provide information about the structure of different microenvironments such as micelles,[10] anionic polyelectrolytes,[11] polynucleotides,[12] and clays.[13] The carboxylate-terminated starburst dendrimers are very suitable candidates for the employment of this type of cationic probes, and a systematic relationship between the external features of the former and the quenching constants of the latter is expected.

The decrease of the emission intensity of $^*Ru(bpy)_3^{2+}$ as a function of added MV^{2+} has been monitored with a Perkin-Elmer LS-5 spectrofluorometer at 25 °C in water, in the presence of different generation dendrimers (sodium carboxylate terminated). The I_0/I ratio initially follows a linear dependence with the concentration of MV^{2+}, but upward curvature of the plot is always observed above a certain amount of quencher. The slopes of the linear portion of the plots (Stern–Volmer constants, K_{SV}), as well as the linear ranges exhibited, are collected in Table I.

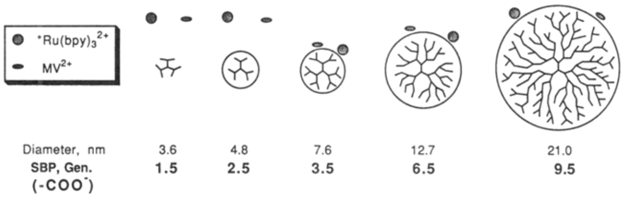

Figure 1. Schematic drawing of the carboxylate-terminated *starburst* dendrimers and the Ru(II)/quencher system selected to probe their structure. The hydrodynamic diameters have been determined by size-exclusion chromatography.

The lowest generation dendrimers (0.5 and 1.5) show K_{SV} values very similar to those obtained in homogeneous solution and are in agreement with previously reported values.[5] In the presence of the 2.5-G dendrimer a borderline behavior is observed: more efficient quenching occurs at low MV^{2+} concentration whereas a rate comparable to that for the aqueous phase occurs for high quencher conditions. A plateau is observed between both regimes. This fact indicates that the 2.5-G starburst already possesses certain polymeric features and is capable of attracting simultaneously some amount of probe and quencher into its electrostatic field. However, some of the probe is displaced from the dendrimer surface when the concentration of quencher is raised. The enhancement of the quenching rate due to a simple ionic strength effect has to be ruled out: control experiments in the presence of sodium chloride or sodium acetate (Table I) show only a 2.5-fold increase of K_{SV}.

Large values of K_{SV} (2 or 3 orders of magnitude when compared to the experiments in homogeneous media) are obtained for dendrimers of the 3.5 generation and higher (Table I; Figure 2). A strong interaction between the starburst dendrimers and the ruthenium complex is also evident from the enhanced luminescence of the latter as the dendrimer is added to the solution. Nevertheless, no changes in the intensity or position of the metal-to-ligand charge-transfer absorption band of the $Ru(bpy)_3^{2+}$ are detected. Time-resolved emission measurements (vide infra) also confirm this interaction and stress the polyelectrolyte behavior of the larger dendrimers (Figure 2). The highly efficient quenching observed should be related to the effect of the reaction occurring in a reduced space, namely, the polymer surface.[9] Additional observations corroborate the fact that the excited complex is quenched on the surface of the starburst: (a)

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