Table II
Rate Constants for Propagation Reaction of Anionic Polymerization of Styrene at 25 °C

	k_{ap}, L mol^{-1} s^{-1}	
counterion	dioxane	tetrahydrofuran
Li^+	0.94[a]	160[c]
Na^+	3.4[a]	80[d]
Cs^+	15[b]	22[c,d]

[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] Reference 14.

the extremely simplified model postulated in the present paper one cannot expect quantitative accord between the dielectric constants of solvents used in experiment and the dielectric constant from the theoretical model.

Table II indicates that by transfer from dioxane to tetrahydrofuran at constant counterion (both for Li^+ and Na^+) the rate constant increases markedly and for Cs^+ it changes slightly. In order to explain this phenomenon and for more complex evaluation of the problem, account has to be taken of the fact that as the solvent polarity increases, dissociation of ion pairs into free ions increases (Figure 4); these free ions are more reactive. This means that the reactivities of free ions, ion pairs, and their dissociation equilibrium have to be considered as they are expressed by relation for the rate constant k_p[1].

$$k_p = k_\pm + (k_- - k_\pm)K_{diss}^{1/2}LP^{-1/2}$$

where $k_\pm$ is the rate constant for propagation reaction of ion pairs, k_- is the rate constant for propagation reaction of free anions, K_{diss} is the equilibrium constant for dissociation ion pairs, and LP is the concentration of living polymer.

By combining the effect of the solvent polarity on $k_\pm$ and K_{diss} the trends shown in Table II can be explained qualitatively also in our approximative model. Moreover the problem is complicated as is indicated by the fact that according to calculations another reaction path should exist in polar media where the structures forming ion pair in the initial state pass through the activated complex not containing any alkali metal.

When evaluating the theoretical results, it should be kept in mind that apart from the approximativeness of the method used for calculation and the model studied, changes in the activation entropy, which might in some cases affect considerably the total reactivity, were not considered. In spite of this, the calculations presented led to interesting findings which may be of some aid in explaining various effects on the rate and mechanism of anionic polymerization.

References and Notes

(1) M. Szwarc, "Carbanions Living Polymers and Electron Transfer Processes", Wiley-Interscience, New York, 1970.
(2) M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions", Vol. I, Wiley-Interscience, New York, 1972.
(3) M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions", Vol. II, Wiley-Interscience, New York, 1974.
(4) N. G. Gaylord and S. S. Dixit, *J. Polym. Sci., Macromol. Rev.*, 8, 51 (1974).
(5) N. L. Holy, *Chem. Rev.*, **74**, 243 (1974).
(6) T. A. Claxton and McWilliams, *Trans. Faraday Soc.*, **65**, 3129 (1969).
(7) S. Miertuš and O. Kysel', *Chem. Phys. Lett.*, **35**, 531 (1975).
(8) S. Miertuš, O. Kysel', and P. Mach, *Collect. Czech., Chem. Commun.*, in press.
(9) S. Miertuš, O. Kysel', and P. Mach, *Collect. Czech., Chem. Commun.*, in press.
(10) I. Jano, *C. R. Hebd. Seances Acad. Sci.*, **261**, 103 (1965).
(11) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).
(12) F. S. Dainton, G. C. East, G. A. Harpell, N. R. Hurworth, K. J. Ivin, R. T. LaFlair, R. H. Pallen, and K. M. Hui, *Makromol. Chem.*, **89**, 257 (1965).
(13) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).
(14) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 796 (1967).

Quantum-Chemical Study of the Reactivity in Anionic Polymerization. 2. The Effect of Electronic Structure of Monomer on the Rate of Propagation Reaction

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ABSTRACT: The effect of a change in the structure of monomer on the activation energy of the propagation reaction of variously substituted styrene monomers with living styrene polymer has been investigated by the semiempirical quantum-chemical method. The theoretical conclusions are in qualitative agreement with the experimental data available.

In part 1 of this series,[1] interesting theoretical knowledge was acquired on the effects of various counterions and solvent polarity upon the relative activation energy of the propagation reaction of styrene by semiempirical quantum-chemical calculations, by employing a simple model of activated complex. In addition to these effects, the activation energy and thus also the rate of propagation reaction depend evidently on the electronic structure of polymerizing particles. The effect of the structure was studied experimentally for styrene copolymerization with styrene derivatives,[2] where the following can be observed: (i) the effect of the change in the structure of polymer anion during reaction with the same monomer; and (ii) the change in the reactivity of variously substituted monomers with the same living anionic end of polymer.

In the present paper we theoretically investigated propagation reactions of living styrene polymer with para-substituted styrene monomers.

Calculations

The Pariser–Parr–Pople method in the π approximation[3] was used for calculating the energies of individual systems and the activation energy of the propagation reaction. The method has already been used

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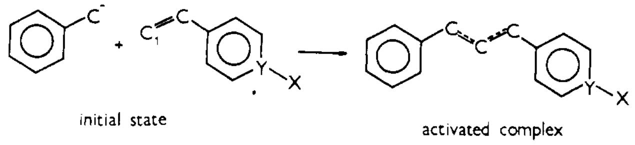

Figure 1. Model structures considered in calculation of the activation energy.

Table I
The Effect of Substituents on the Relative Activation Energies of the Propagation Reaction and on the Electronic Density at the C_α Atom and Experimental Data

X	Y	E_a^{rel}, eV $\epsilon = 1$	E_a^{rel}, eV $\epsilon \to \infty$	q_{C_α}	$\log k_{exptl}$[a]
H	C	0.6961	1.5379	1.0319	2.9778
CH_3	C	0.7596	1.6148	1.0374	2.2552
OCH_3	C	0.8581	1.7034	1.0468	1.6990
C_6H_6	C	0.5715	1.6117	1.0347	3.2201
	N	0.3321	1.0859	1.0051	4.4771

[a] Reference 2.

with success.[1,4,5] Apart from the electronic energy, solvation energy calculated according to relation[6]

$$E_{solv} = -\tfrac{1}{2}\sum_{\mu}\sum_{\nu} Q_\mu Q_\nu \gamma_{\mu\nu}(1 - (1/\epsilon)) \qquad (1)$$

is also important in this system. Here Q_μ and Q_ν are the net charges on the atoms μ and ν of solute molecule (calculated quantum-chemically), $\gamma_{\mu\nu}$ is the electron repulsion integral, and ϵ is the dielectric constant of the medium.

In calculations, a simple model of propagation reaction (Figure 1) was taken into account, where, similar to part 1, the activated complex was considered as the plane and symmetrical system and where $r_{C_1-C_2} = r_{C_2-C_3} = 1.53 \times 10^{-10}$ m. The following styrene derivatives were considered: Y = C, X = H, CH_3, C_6H_5; and Y = N. For all derivatives the standard and experimentally found geometry was used.[7] To simplify matters, the effect of alkali metal cation was not investigated (it was studied in detail in part 1); the experimental results[2] were obtained in polar medium (tetrahydrofuran) assuming that only free ions take part in the reaction.

Results and Discussion

We calculated the total electron and solvation energies for individual substituted styrenes, benzyl anion, and activated complexes. Substracting the energy of substituted monomers and benzyl anion from the energy of the respective activated complexes we obtained activation energy. Table I contains the relative activation energies, E_a^{rel}, without considering solvation energy ($\epsilon = 1$) and for thoroughly solvating medium ($\epsilon \to \infty$). The charges at the reactive center of styrene monomer (q_C) and the logarithms of the experimentally found rate constants for corresponding reactions[2] are presented.

The results indicate that electron-accepting substituents ($-C_6H_5$, aza-) lower the values for activation energies compared with unsubstituted styrene; on the contrary, electron-donor substituents increase the activation energy for propagation reaction. Good linear correlation of the activation energy with the experimental data was found (Figure 2). We failed in finding the rate constant for 4-vinylpyridine; it is assumed that its value is greater than 30 000 L mol^{-1} s^{-1}. According to our correlation it should have the value of ~78 000 L mol^{-1} s^{-1}.

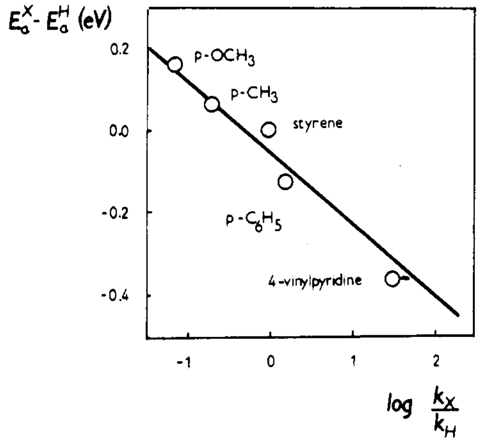

Figure 2. A plot of the calculated relative changes of activation energies of the propagation reaction of variously substituted monomers of styrene vs. the logarithm of the ratio of experimental rate constants.

The effect of substitution is manifested also by the change in electron density on the reactive center (carbon C_α in styrene derivatives, Table I). The electron density correlates well with the experimentally found values for the rate constants indicating qualitative agreement between the simple electrostatic model (model of isolated molecule) of propagation reaction and the experimental data.

On the basis of our calculations the effect of solvent polarity accompanying the change of the structure can be evaluated. Evidently, the increase of the polarity in general leads to a rise in the activation energy of the propagation reaction. For individual styrene derivatives this effect is greatest for *p*-vinylbiphenyl; hence in thoroughly solvating medium this derivative should become theoretically less reactive than the unsubstituted styrene.

We conclude that the model calculation described well the experimental reactivity of individual derivatives from the qualitative point of view in spite of several simplifications.

References and Notes

(1) S. Miertuš, O. Kysel', and P. Mâjek, *Macromolecules*, preceding paper in this issue.
(2) M. Shima, D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 1306 (1963).
(3) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
(4) S. Miertuš, O. Kysel', and P. Mach, *Collect. Czech., Chem. Commun.*, in press.
(5) S. Miertuš, O. Kysel', and P. Mach, *Collect. Czech., Chem. Commun.*, in press.
(6) I. Jano, *C. R. Hebd. Seances Acad. Sci.*, **261**, 103 (1965).
(7) *Chem. Soc. Spec. Publ.* **No.** 11 (1958).