Quantum chemical study of the reactivity in anionic polymerization. III. Study on initiation reactions

S. MIERTUŠ, O. KYSEĽ, and P. MÁJEK

Polymer Institute, Slovak Academy of Sciences,
809 34 Bratislava

The possible course of initiation reactions of anionic polymerization for radical anions of benzophenone and 2,2'-bipyridyl as initiators and for acrylonitrile, styrene, and 4-vinylpyridine as polymerizing monomers were discussed by quantum chemical calculation in the π approximation. Calculations showed that the equilibrium of these reactions is greatly affected by solvation. Calculations indicate that the initiation can proceed only in the case of acrylonitrile (and partially in the case of 4-vinylpyridine) and 2,2'-bipyridyl ought to be the more effective initiator than benzophenone.

На основе квантовохимического расчета в π-приближении были обсуждены возможности хода инициирующих реакций анионной полимеризации в случае анион-радикалов бензофенона и 2,2'-бипиридила как инициаторов и акрилонитрила, стирола и 4-винилпиридина как полимеризующихся мономеров. Расчеты показали, что значительное влияние на равновесие этих реакций оказывает сольватация. Обнаружено, что инициирование имело бы место только в случае акрилонитрила (и частично 4-винилпиридина), причем более эффективным инициатором должен быть 2,2'-бипиридил.

Anionic polymerization is one of the processes intensively investigated experimentally and applied recently [1—3]. It was shown that initiation reactions which are the first step towards successful polymerization may proceed in various ways [3]. The participation of individual reactions in the initiation process was in most cases estimated intuitively with regard to difficulties of experimental determination.

We aimed at evaluating the course of reactions when the initiator (I) is generated by reduction of the conjugated molecules and the radical anion is formed. During initiation, the transfer of an electron from an initiator (I) to a monomer (M) [1] is significant.
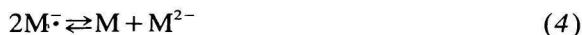
$$I^{\overline{\cdot}} + M \rightleftarrows I + M^{\overline{\cdot}} \qquad (1)$$

The radical anion of the initiator can disproportionate according to the scheme

$$2I^{\bar{}} \rightleftarrows I + I^{2-} \qquad (2)$$

Dianion I^{2-} formed by disproportionation reaction can also give rise to radical anion of monomer [1]

$$I^{2-} + M \rightleftarrows I^{\bar{}} + M^{\bar{}} \qquad (3)$$
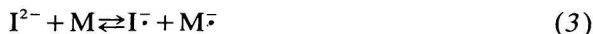
The radical anion of monomer can disproportionate according to the scheme

$$2M^{\bar{}} \rightleftarrows M + M^{2-} \qquad (4)$$

From the view-point of the polymerization the following reactions are interesting

$$M^{\bar{}} + M^{\bar{}} \rightleftarrows {}^{-}M{-}M^{-} \qquad (5)$$

$$M^{\bar{}} + M \rightleftarrows {}^{-}M{-}M\cdot \qquad (6)$$

since they are the initial stage [1] of propagation reactions

$$^{-}M{-}M^{-} + M \rightleftarrows {}^{-}M{-}M{-}M^{-} \qquad (7)$$

$$\cdot M{-}M^{-} + M \rightleftarrows \cdot M{-}M{-}M^{-} \qquad (8)$$

Since the calculation of the rate constant for the above-mentioned reactions is not feasible we restrict to determination of the relative stability of individual components in the mentioned reactions considering only changes in π-electron and solvation energies. On this basis one may estimate relative reactivity. It should be kept in mind that such a procedure involves several approximations. Thus *e.g.*, neither the effect of the change in entropy, nor the possibility of the formation of ion pairs with the present alkali metal cations is considered. With regard to this fact the calculations are only of qualitative character.

Calculations

The course of the mentioned reactions was discussed for the systems:

Initiators   benzophenone (BPh); 2,2'-bipyridyl (BPy)
Monomers: acrylonitrile (AN); styrene (ST); 4-vinylpyridine (VP)

For individual forms of the respective molecules the total π-electron energy E_T was calculated; for closed-shell systems (neutral molecules and dianions) the PPP method was used in the π approximation [4] and for open-shell systems (radical anions) the LHP method in the π (PPP-like) approximation [5] was employed. The original parametrization [6] was used in both methods. Resonance integrals $\beta_{\mu\nu}$ were expressed as a function of bond lengths [7]. Bicentric repulsion integrals $\gamma_{\mu\nu}$ were computed according to *Mataga* and *Nishimoto* [8]. The experimental or standard geometry of neutral molecules [9] was considered for all

systems, simply assuming the same geometry for the neutral form, radical anion or dianion of a molecule.

Since in the systems studied we consider charged molecules in medium or strongly polar solvents (tetrahydrofuran, dimethylformamide, *etc.*), we may expect that the equilibrium in reactions is influenced not only by the total π-electron energy for individual components E_T, but also by their solvation energy calculated as follows [10]
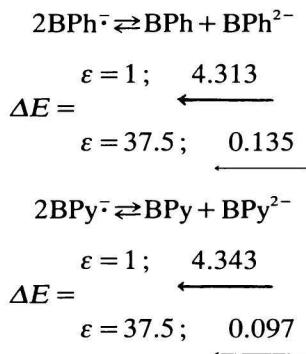
$$E_{solv} = -\frac{1}{2}\left(1 - \frac{1}{\varepsilon}\right) \sum_\mu \sum_\nu Q_\mu Q_\nu \gamma_{\mu\nu} \qquad (9)$$

where Q_μ and Q_ν are the net charges on atoms μ and ν, $\gamma_{\mu\nu}$ is the electron repulsion integral, and ε is the dielectric constant for solvent.

In calculations we considered $\varepsilon = 37.5$ (value for dimethylformamide). From the calculated π-electron energies and solvation energies for individual reactants, the energetic difference ΔE was computed for each reaction considered.

Results and discussion

The first problem to be studied is the equilibrium of disproportionation reaction of radical anions of an initiator since it controls concentration of the individual forms of initiator ($I^{\cdot-}$ and I^{2-}). For BPh and BPy, the following values were obtained (all values are given in eV)

$$2BPh^{\cdot-} \rightleftarrows BPh + BPh^{2-}$$

$$\Delta E = \begin{array}{l} \varepsilon = 1; \quad 4.313 \quad \overleftarrow{\hspace{2cm}} \\ \\ \varepsilon = 37.5; \quad 0.135 \quad \underleftarrow{\hspace{2cm}} \end{array}$$

$$2BPy^{\cdot-} \rightleftarrows BPy + BPy^{2-}$$

$$\Delta E = \begin{array}{l} \varepsilon = 1; \quad 4.343 \quad \overleftarrow{\hspace{2cm}} \\ \\ \varepsilon = 37.5; \quad 0.097 \quad \underleftarrow{\hspace{2cm}} \end{array}$$

These values show that solvation plays a significant role. Without considering solvation (*i.e.* in the gas phase), the disproportionation should not proceed at all. Since E_{solv} is for products (dianion and neutral molecules) considerably larger (about twice) than E_{solv} for two radical anions, the values obtained for strongly polar media indicate that disproportionation might be here significant. $BPy^{\cdot-}$ ought to disproportionate a little more than $BPh^{\cdot-}$.

We proceed now to the evaluation of the reaction (*1*), *i.e.* to the electron transfer from an initiator to a monomer. It is obvious from the results of calculations in Table 1 that the electron transfer reaction does not proceed unless

Table 1

Energy changes in the reaction of the electron transfer from initiator to monomer; ΔE (eV)

I	M	$I^{\overline{\cdot}} + M \rightleftarrows I + M^{\overline{\cdot}}$		
BPh	AN	$\Delta E =$	$\varepsilon = 1$	0.611 ←
			$\varepsilon = 37.5$	-0.129 →
BPh	VP	$\Delta E =$	$\varepsilon = 1$	0.304 ←
			$\varepsilon = 37.5$	0.137
BPh	ST	$\Delta E =$	$\varepsilon = 1$	0.899 ←
			$\varepsilon = 37.5$	0.882 ←
BPy	AN	$\Delta E =$	$\varepsilon = 1$	0.620 ←
			$\varepsilon = 37.5$	-0.184 →
BPy	VP	$\Delta E =$	$\varepsilon = 1$	0.313 ←
			$\varepsilon = 37.5$	0.042
BPy	ST	$\Delta E =$	$\varepsilon = 1$	0.908 ←
			$\varepsilon = 37.5$	0.827 ←

E_{solv} is considered. However, the effect of E_{solv} is in these reactions different. A comparison of various monomers shows that the effect of solvation is the greatest for AN, smaller for VP, and the smallest for ST. Consequently the initiation with radical anion ought to proceed only with AN and to a small extent with VP. As far as the electron transfer reactions are concerned the calculations indicate that BPy$^{\overline{\cdot}}$ should be more reactive than BPh$^{\overline{\cdot}}$.

In a similar way we may discuss electron transfer reactions with dianions (Table 2). Here, in contrast to the case with radical anions, without considering solvation all equilibria should be shifted to the right. Solvation shifts all equilibria to a reverse direction. Thus for VP and AN we obtain negative values of ΔE not exceeding the value -0.3 eV and for ST the equilibrium is shifted completely to the left. This indicates that dianions BPy^{2-} and BPh^{2-} could be effective initiators only with respect to AN (BPy^{2-} being the more effective); their initiation ability is considerably smaller in regard to VP and for ST the initiation should not occur at all.

156

Table 2

Energy changes in the reaction of the electron transfer from dianion to monomer; ΔE (eV)

I^{2-}	M	$I^{2-} + M \rightleftarrows I^{\overline{\cdot}} + M^{\overline{\cdot}}$		
BPh	AN	$\Delta E =$	$\varepsilon = 1$	$-3.701 \longrightarrow$
			$\varepsilon = 37.5$	$-0.264 \longrightarrow$
BPh	VP	$\Delta E =$	$\varepsilon = 1$	$-4.009 \longrightarrow$
			$\varepsilon = 37.5$	$0.003 \dashrightarrow$
BPh	ST	$\Delta E =$	$\varepsilon = 1$	$-3.405 \longrightarrow$
			$\varepsilon = 37.5$	$0.747 \longleftarrow$
BPy	AN	$\Delta E =$	$\varepsilon = 1$	$-3.723 \longrightarrow$
			$\varepsilon = 37.5$	$-0.282 \longrightarrow$
BPy	VP	$\Delta E =$	$\varepsilon = 1$	$-4.030 \longrightarrow$
			$\varepsilon = 37.5$	$-0.055 \dashrightarrow$
BPy	ST	$\Delta E =$	$\varepsilon = 1$	$-3.435 \longrightarrow$
			$\varepsilon = 37.5$	$0.730 \longleftarrow$

The next stage of the initiation process which precedes the propagation are different reactions of the radical anion of monomer. In the first place the disproportionation reaction will be considered [4]. The values ΔE are listed in Table 3.

Similarly to disproportionation reaction of radical anions of initiators, solvation energy exerts also here considerable effect. The disproportionation would not practically proceed without solvation; however, in strongly solvating medium some disproportionation should occur, the degree of this disproportionation being almost the same in all three monomers considered.

The calculation of ΔE of the reactions leading to the beginning of the polymer chain formation (reactions (5) and (6)) is rather problematic since the σ bond is formed in dimer and the dimer system thus loses conjugation. *Zahradník* and *Čársky* [9] proposed for such reactions a method for calculating dimerization energy within the π method and we employed the method here. The energy for
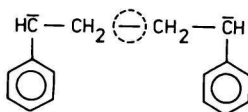
Table 3

Energy changes in the disproportionation reaction of monomer radical anions; ΔE (eV)

M	$2M^{\cdot-} \rightleftarrows M + M^{2-}$		
AN	$\Delta E =$	$\varepsilon = 1$	6.357 $\leftarrow$
		$\varepsilon = 37.5$	-0.044 $\dashrightarrow$
VP	$\Delta E =$	$\varepsilon = 1$	5.000 $\leftarrow$
		$\varepsilon = 37.5$	-0.061 $\dashrightarrow$
ST	$\Delta E =$	$\varepsilon = 1$	4.973 $\leftarrow$
		$\varepsilon = 37.5$	-0.022 $\dashrightarrow$

dimer was calculated as follows (we present the computation of the dimer energy for ST$^{\cdot-}$).

The following structure of the dimer is assumed

The energy of this system is in the π approximation expressed as

$$E_{\text{dimer}} = 2E_{\text{T, benzyl anion}} + 2I_{2p_{\pi}} + E_{\sigma}$$

The ionization potential of electrons (with negative sign) on π orbitals of carbon in —CH_2— group ($I = -11.16$ eV) is added to the π-electron energy of the two benzyl anions. E_{σ} represents the energy for the σ bond formed and according to *Zahradník* and *Čársky* [9] is equal to 3.562 eV. The energy for ST is then $\Delta E = 0.257$ eV in favour of monomer radical anions of ST$^{\cdot-}$. For AN$^{\cdot-}$ and VP$^{\cdot-}$, extremely high values were obtained in favour of the stabilization of dimer ($\Delta E \sim 30$ eV). Considering the level of approximation of the method, these values have to be taken with caution; despite this one may expect greater activity of AN$^{\cdot-}$ and VP$^{\cdot-}$ to dimerization than in the case of ST$^{\cdot-}$. Analysis of the reaction (6) provided an analogous picture.

158

Conclusion

In the introduction to this article we mentioned approximation considered in discussing initiation reactions of anionic polymerization. In spite of these approximations, useful information was acquired, especially the information concerning the initiation processes. The effect of electronic structure of the initiators and monomers as well as the solvent effect on equilibria in different reactions involved in these processes was discussed. Of special significance is the inclusion of solvation which, in most cases, entirely changes the equilibria. It is encouraging that the theoretical conclusions agree with experimental findings [3, 11]. This explains why our experimental attempt to initiate polymerization of 4-vinylpyridine and especially styrene by radical anions of 2,2'-bipyridyl and benzophenone failed [11].

References

1. Szwarc, M., *Carbanions, Living Polymers and Electron Transfer Processes*. Wiley—Intersience, New York, 1970.
2. Szwarc, M., *Ions and Ion Pairs in Organic Reactions*, Vol. *1, 2*. Wiley—Interscience, New York, 1974.
3. Gaylord, N. G. and Dixit, S. S., *J. Polym. Sci. (Macromol. Rev.) 8,* 51 (1974).
4. Pople, J. A., *Trans. Faraday Soc. 49,* 1375 (1953).
5. Longuet-Higgins, H. C. and Pople, J. A., *Proc. Roy Soc. 68A,* 591 (1955).
6. Hinze, J. and Jaffé, H. H., *J. Amer. Chem. Soc. 84,* 540 (1962).
7. Hochman, P., Zahradník, R., and Kvasnička, V., *Collect. Czech. Chem. Commun. 33,* 3478 (1968).
8. Mataga, N. and Nishimoto, K., *Z. Phys. Chem.* (Frankfurt) *13,* 140 (1957).
9. Zahradník, R. and Čársky, P., *Chem. Listy 67,* 113 (1973).
10. Jano, I., *C. R. Acad. Sci.* (Paris) *261,* 103 (1965).
11. Miertuš, S. and Kyseľ, O., *Chem. Zvesti 33,* 160 (1979).