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STRUCTURE OF THE LOWEST TRIPLET STATES OF POLY-α-METHYLSTYRYL SODIUM. *Ab initio* CALCULATIONS

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Ab initio optimization of a poly-α-methylstyryl sodium (PMSNa) fragment consisting of two cis units yields a triplet state energy which is close to the ground state energy. A new mechanism is proposed for depolymerization of "living" polymers, which implies that an elementary step involves excitation to the low-lying triplet state with a charge transfer and with further bond cleavage. In the reaction structure, electronic excitation occurs with a minor (~0.5 Å) displacement of the Na^+ cation between the last and the last but one monomer units. The reversible polymerization/depolymerization reaction of PMSNa in THF was studied experimentally. The experimental (5.6 kcal/mole) and calculated (7.3 kcal/mole) polymerization enthalpies are in reasonable agreement.

It is known [1, 2] that the "living" poly-α-methylstyrene (PMSNa) undergoes a reversible polymerization/depolymerization reaction

$$M_i^* + M \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} M_{i+1}^*, \qquad (1)$$

where M_i^* and M_{i+1}^* are the "living" polymer chains; K_1 and K_{-1} are the rate constants of propagation and depolymerization [1, 2]. The thermodynamic and kinetic characteristics of the depolymerization reaction are given in [1-3]. However, data on elementary stages are not available in the literature. Reaction (1) was primarily studied with the aim of determining the equilibrium constants K_e, polymerization heats, and equilibrium concentrations M_e of the monomer [1, 4-8].

Obviously, the depolymerization (degradation) mechanisms differ between the "dead" and "living" polymer chains. In the former case, a free monomer is released through a chain radical process [9, 10] occurring with a high activation energy (about 50 kcal/mole [11]). Depolymerization of "living" chains occurs reversibly giving a monomer, indicating that the active end of the "living" polymer retains its structure during the process.

The best-investigated case [1, 4-6] is the system "living" polymer+α-methylstyrene (α-MS) in THF, exhibiting high M_e for which

$$K_e = K_1 / K_{-1} \to 1/M_e \qquad (2)$$

for $M_0 / M_i^* > 10$, where M_0 is the initial concentration of the monomer [1, Fig. III.8]. For this system, the propagation activation energies are 5-7 kcal/mole [1, p. 427], the polymerization heat and entropy variations being $-\Delta H = 7$ kcal/mole and $-\Delta S = 24.8$ entropy units [1, p. 147; 3].

In the "living" polymer, as opposed to α-methylstyrene, the equilibrium concentration of styrene is negligibly small (10^{-7} M at 0°C [7]) and hence the polymer is stable under normal conditions. For other "living" polymers, the polymerization/depolymerization reactions are much less understood.

Styrene addition to the anion end of the "living" polymer was considered [13-15] in terms of electronic excitation (transfer); the reaction complex is a pair of ions separated by a monomer. The role of the cation lying close to the monomer molecule is to enhance its electron-accepting ability and promote the electron transfer giving rise to radical species. The

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reverse process of monomer release in the elementary step is obviously similar to the direct addition process and can be considered in terms of the general concept of thermal electronic excitation in chemical reactions [15].

Monomolecular thermochromic reactions of spiropyrans were also considered [16] in terms of electronic excitation. It was shown that the PM3 calculated triplet energies of spiropyrans are close to the experimental activation energies of opening of the six-membered pyran ring.

In this work, we present the results of a quantum chemical *ab initio* calculation (STO-3G basis) for two end units of "living" PMSNa and polystyryl sodium (PSNa) and analyze the results of kinetic studies of PMSNa polymerization/depolymerization. Apart from giving a more adequate representation, the *ab initio* methods allow the investigation of ion pairs with the Na^+ cation in the excited state, which are of critical importance to our study. In this respect, the semi-empirical AM1 method yields less reliable data because of the inadequate parametrization of the Li atom.

RESULTS AND DISCUSSION

The equilibrium polymerization of α-MS was studied in a wide temperature range, from −60 to +15°C in the system PMSNa+α-MS in THF. Figures 1 and 2 show that the experimental K_e values are in satisfactory agreement with the literature data [1, 4] and the polymerization heats (5.63 and 7 kcal/mole) calculated from the dependences presented in Figs. 1 and 2 are also close [4]. Our data together with the available literature values suggest that the equilibrium constants and the thermodynamic characteristics of the PMSNa+α-MS+THF system are not markedly affected by the initial concentration of the monomer.

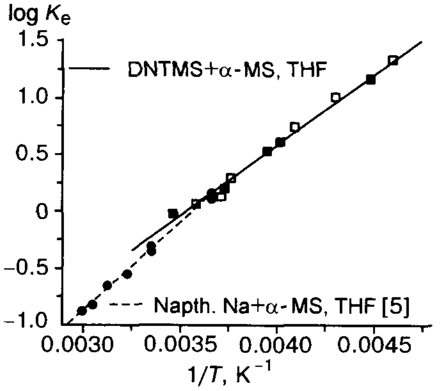

Fig. 1. Plot of the logarithm of the equilibrium constant K_e vs reciprocal temperature. Solid line — this work (M_0 = 1.1 M); empty squares — polymerization; filled squares — depolymerization; dashed line — [5] (M_0 = 0.75-7.5 M).

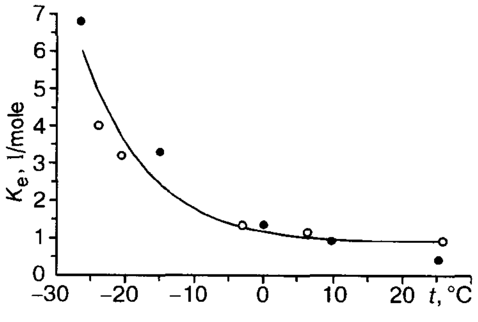

Fig. 2. Plot of the equilibrium constant K_e vs polymerization temperature for PMSNa+α-MS+THF. Empty circles — data of this work, filled circles — data of [1, Table III.4].

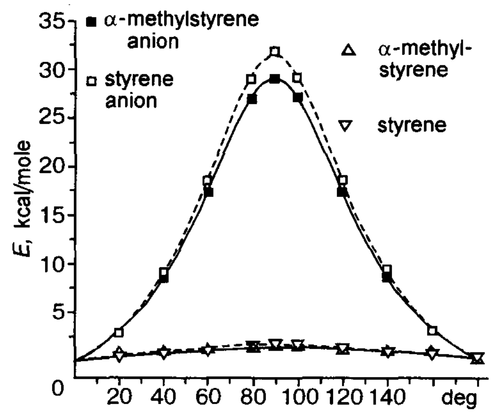

Fig. 3. Potential curves of rotation around the C_{arom}–C_{α} axis.

The unusual properties of poly-α-methylstyryl sodium as compared to polystyryl sodium may be attributed to the presence of the methyl group, whose steric interaction with the *ortho* hydrogen atom of the aromatic ring destabilizes the planar structure of the end anion unit, thus decreasing the energy of the lowest triplet state, which is active in the depolymerization reaction. Indeed, as shown by semi-empirical quantum chemical calculations, the lowest triplet of PMSNa, which is essentially a charge transfer state, is rather sensitive to rotation around the C_{arom}–C_{α} bond and lowers to thermal values at large rotation angles. However, a simple calculation shows that both styrene and α-methylstyryl anions have planar structures, the differences in the formation heats between the planar and perpendicular forms being large for both anions: 31.7 and 29.2 kcal/mole, respectively (Fig. 3). For the starting α-methylstyrene and styrene, the rotation barriers are relatively small: 1.47 and 1.18 kcal/mole, respectively. Hence this parameter may not be responsible for the fast depolymerization of PMSNa.

Figure 4 shows the calculated structures of two end units in PMSNa (dim-α^-Na^+), whose size permits an *ab initio* calculation and at the same time bears all basic characteristics of the reaction structure of the end unit. Similar *ab initio* calculations were performed for the PSNa dimer (dim$^-Na^+$). To simplify the calculations, the polymer radical was replaced by the hydrogen atom.

The dimer model can have a *cis* or *trans* arrangement of aromatic rings. The former configuration is 5 kcal/mole more stable for the anion, while the *cis* structure is stable for the ion pair. Semi-empirical and *ab initio* calculations were performed for both structures in order to determine the energy states of the system. We also considered PMSLi oligomers with chains consisting of 2 to 5 units.

It is well known that the intra- and intermolecular charge transfer states are chemically active. Therefore our aim was to find low-energy states of this kind which would thus be accessible for thermal occupation under normal conditions. The potential energy surfaces of the ground and excited triplet states were tested by the semi-empirical AM1 method, which was parametrized for the Li atom thus allowing the calculation of the M^-Li^+ ion pairs.

The semi-empirical calculations have revealed two positions of the Li^+ cation: one is at the α-carbon atom of the anion fragment bearing the maximum negative charge (I), and the other is over the neighboring uncharged aromatic ring (II). In *trans* dim-α^-, the two centers are separated by 5 Å (Fig. 4), while in the *cis* configuration they almost coincide in space (Fig. 4). The latter structure is of particular interest and was studied by *ab initio* methods using the dim-α^-Na^+ and dim$^-Na^+$ models.

Structure I, which is generally used to represent the ion pair of the "living" polystyrene, is the most stable one in the ground state; it is also chemically stable and exhibits a low dipole moment, 5.7 D (AM1 method). The polar excited triplet state (μ = 8.5 D) is a state of charge transfer from the anion unit to the adjacent uncharged ring. Because of its high energy (24.1 kcal/mole), it cannot be occupied at ambient temperature and is therefore chemically inert.

Optimization of dim-α^-Li^+ in the triplet excited state has revealed another position of the Li^+ cation — over the center of the adjacent uncharged ring to which the entire negative charge is transferred. In the S_0(II) as well as in the S_0(I) ground state, the negative charge is localized on the end unit. Figure 5 shows the energy diagram as well as the charge

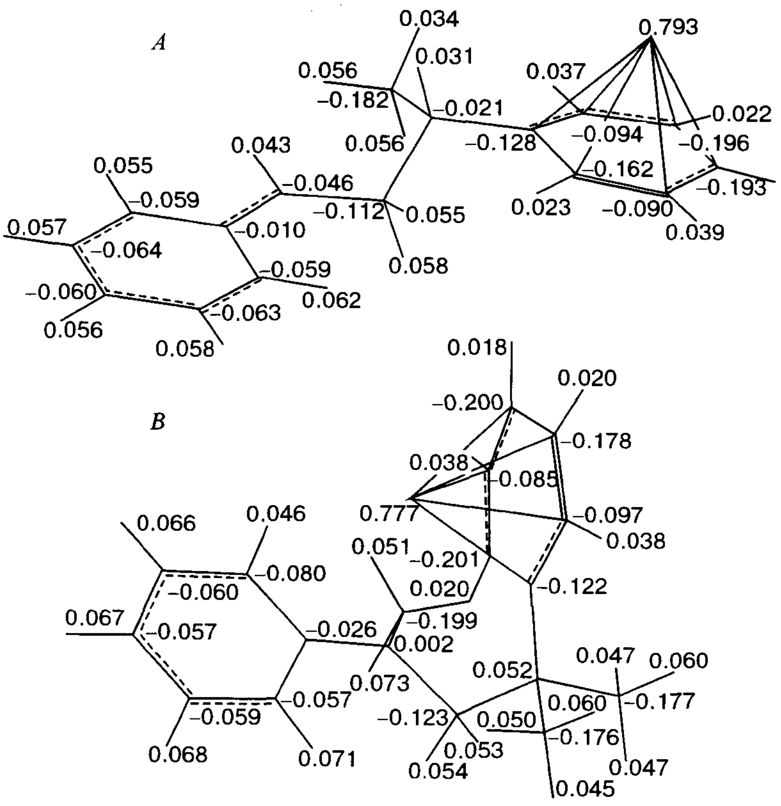

Fig. 4. Charge distribution in the triplet state of the *trans* (*A*) and *cis* (*B*) configurations of dim-$\alpha^{-}Na^{+}$.

and spin density localizations for the *cis* configuration (*ab initio* data). It is important that the charge transfer states T_1 are radical states and hence exhibit a high chemical activity.

Thus the semi-empirical quantum chemical calculations have shown that in anion systems $M_n^{-}Li^{+}$ and M_n^{-} the lowest electron transition is an (electron) charge transfer between the last (charged) and the last but one (neutral) monomer units. In the trimers M_3^{-}, the electron excitation results in an electron transfer to the last but one monomer unit. In the free tetramer M_4^{-} and pentamer M_5^{-} anions, the triplet excitation is localized on the end unit. Hence in the free M_n^{-} anions, the lowest triplet state is excitation in the end unit or charge-transfer excitation depending on the structure and electron-accepting abilities of the uncharged units of the polymer anion. Excitation of the second type is reactive in depolymerization. However, since these states are thermally unattainable due to the high energy, in the dark conditions the free anions must be inactive.

Structures I and II obtained from semi-empirical calculations were studied by the *ab initio* method (Fig. 5). The *ab initio* calculations of dim-$\alpha^{-}Na^{+}$ and dim$^{-}Na^{+}$ with geometry optimization support the results obtained by the semi-empirical AM1 method. Structures I and II found in previous calculations were used as an initial approximation. In the triplet state T_1, the electron is actually transferred from the end unit, which becomes neutral ($\Sigma q = -0.05$), to the adjacent uncharged aromatic ring (Fig. 4). The charge transfer takes place for both the ion pair dim-$\alpha^{-}Na^{+}$ and the free anion dim-α^{-}. Minor differences between the semi-empirical and the *ab initio* results are observed in charge distributions and electron transfer energies. As in the AM1 method, the maximum charge is on the α-carbon atom but is approximately half of the AM1 calculated value, and the total negative charge is distributed between the end unit atoms more uniformly.

The calculations were performed for dim-$\alpha^{-}Na^{+}$ and for the dim$^{-}Na^{+}$ analog. As mentioned above, the two "living" polymers PMSNa and PSNa are similar in chemical structure but show essentially different thermodynamic characteristics. Structural differences must affect the reaction heats, which control equilibrium (1), as well as the triplet state energies, defining the activation energy of the reaction.

For the *cis* dimer, the energies of the vertical electron transitions $T_1 \leftarrow S_0$ (Table 1) calculated as the differences between state energies $E(T_1)_I - E(S_0)_I$ are of the order of magnitude of the triplet energy (45.4 kcal/mole) expected for the

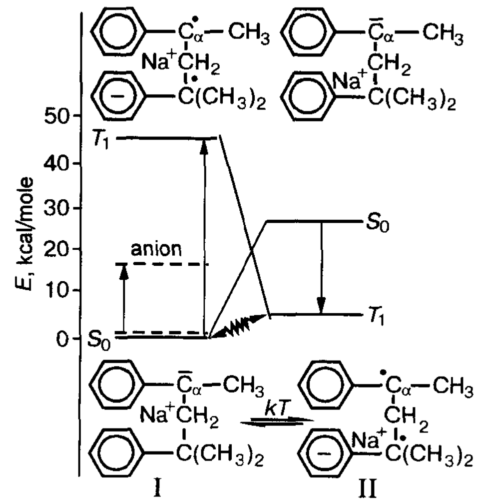

Fig. 5. Energy diagram of the electronic states of *cis* dim-α^-Na$^+$ (*ab initio* optimization).

experimentally observed lowest singlet-singlet transition in the absorption spectrum of PMSNa 29,400 cm^{-1} (84.3 kcal/mole). For the *trans* configuration, the corresponding triplet energies are higher (>80 kcal/mole).

The $(T_1 \leftarrow S_0)_{\mathrm{I}}$ and $(S_0 \leftarrow T_1)_{\mathrm{II}}$ transitions (Table 1) were obtained without optimization of the highest states (T_1 or S_0) and thus belong to the class of vertical transitions, while in the case of $E(T_1)_{\mathrm{II}} - E(S_0)_{\mathrm{I}}$, both combined states were optimized. The aim of this calculation, however, was to establish the nature of electron transitions which are essentially intramolecular charge transfer states (as indicated by the charge distribution (Fig. 4) and dipole moments (Table 1) for the two positions of Na$^+$) rather than to achieve the spectroscopic accuracy, which is very hard to attain without considering configuration interaction.

In the excited state T_1(I), during the vertical transition the electron is transferred from the end unit to the adjacent aromatic ring, leading to increased μ. The relatively small dipole moment in the T_1(II) state is also due to the electron transfer; however, in this case, the cation is located at the second unit. The values of dipole moments of the singlet ground state are explained in the same way. A certain difference in triplet energies between the free dim-α^- and dim$^-$ anions and the corresponding ion pairs (Table 1) may be attributed to the effect of the cation, which hinders electron transfer (increases the ionization potential) when involved in the contact pair.

Of particular interest for understanding the mechanism of depolymerization is the *cis* configuration of the dimer, whose energy diagram is shown in Fig. 5. An important result of our *ab initio* calculations of dim-α^-Na$^+$ and dim$^-$Na$^+$ are the low triplet state energies which we found for structure II (Fig. 5, Table 1). This means that for dim-α^-Na$^+$ ion pairs there exists an electronic state T_1(II) whose energy is close to that of the singlet state S_0(I), the only difference between the structures of these two states lying in a minor shift of the Na$^+$ cation (~0.5 Å) toward the neighboring uncharged ring. Transitions of this kind are classified with indirect transitions involving both electron transfer and migration of heavy particles (in this case, Na$^+$).

TABLE 1. *Ab initio* Calculations of Electron Transition Energies for the *cis*-Configuration (structures I and II, Fig. 5) (AM1 data given in parentheses)

Molecule	$E(T_1)_i - E(S_0)_i$, kcal/mole		μ, D				$E(T_1)_{\mathrm{II}} - E(S_0)_{\mathrm{I}}$, kcal/mole
	i = I	i = II	S_0(I)	T_i(I)	S_0(II)	T_i(II)	
dim-α^-Na$^+$	47.6(24.1)	−34.7	7.0	9.7	10.6	6.9	1.5(8.6)
dim$^-$Na$^+$	38.6(30.4)	−30.8	7.2	9.3	10.8	7.0	6.9(11.7)
dim-α^-	16.0(21.0)						
dim$^-$	22.6(20.4)						

The electronic state of the free anions depends strongly on the configuration of the two last units of the "living" polymer. In the *cis* configuration, the negatively charged end unit is in the vicinity of the last but one neutral aromatic ring. This circumstance significantly decreases (to 16 kcal/mole) the energy of the excitation involving electron transfer between the two units. On the contrary, the *trans* configuration is unfavorable for the electron transfer between units, in which case the excitation energy is high (46 kcal/mole).

The *cis* configuration of the end fragment considered in this work is supported experimentally by the ^{1}H and ^{13}C NMR studies [17] of the isomerization of the "living" polymers during chain propagation.

The reactivity of the triplet states T_1(II) in depolymerization is dictated by their biradical nature. The radical centers are localized on the last and last but one monomer units of the polymer, as indicated by the spin density distribution in the triplet state T_1(II) (Fig. 6). A similar distribution is observed in the T_1(I) state with the cation localized at the α-carbon atom of the end unit. This suggests that the electronic states in the two cases differing in cation position are identical. Both the T_1(I) and T_1(II) states as well as the triplet state of the free anion are dissociative with respect to the bond between the last and last but one monomer units. Thus these states are active in depolymerization. The difference between them lies in the fact that the thermally attainable state is T_1(II) and, to a lesser degree, T_1^{anion}, while T_1(I) relates to photoprocesses.

Thermal degradation of poly-α-methylstyrene [9, 10], in which radicals were detected, is a well known example of chain radical depolymerization. The radicals are generated when the polymer is heated to high temperatures (~250°C) leading to fast depolymerization liberating a free monomer. Pronounced thermal activation is needed to achieve primary C–C bond cleavage between the monomer units, and subsequent elimination of other monomer molecules appears to occur quite easily.

The experimental activation energy E_a of thermal degradation of poly-α-methylstyrene (PMS) is 50 kcal/mole [11]. Optimization of the "dead" PMS trimer in the triplet state gives $E(T_1) = 47.3$ kcal/mole, which is in reasonable agreement with the experimental value of E_a. In this state, the spin density is localized on the central fragment of the "dead" trimer and on the neighboring C–C bonds. In the elementary process, the bond cleavage occurs in the low-lying electronically excited triplet state of the molecule [15].

The $E(T_1)_{\text{II}} - E(S_0)_{\text{I}}$ values characterize the activation energies E_a^{depol} of the thermal degradation and, as seen from Table 1, slightly differ between dim-α$^-$Na$^+$ and dim$^-$Na$^+$. For PMSNa, the experimental value of E_a^{depol} can be estimated as the sum of the activation energy of propagation E_a^{pol} (4.9 kcal/mole) and the heat of the reaction ΔH_r (5.63 kcal/mole): $E_a^{\text{depol}} = E_a^{\text{pol}} + \Delta H_r = 10.53$ kcal/mole. For PSNa, E_a^{depol} should be higher due to the high polymerization heat: $-\Delta H_r = 17.4$ kcal/mole [1, p. 128].

Thus the theoretical analysis of depolymerization of the "living" polymers showed that the triplet excited state

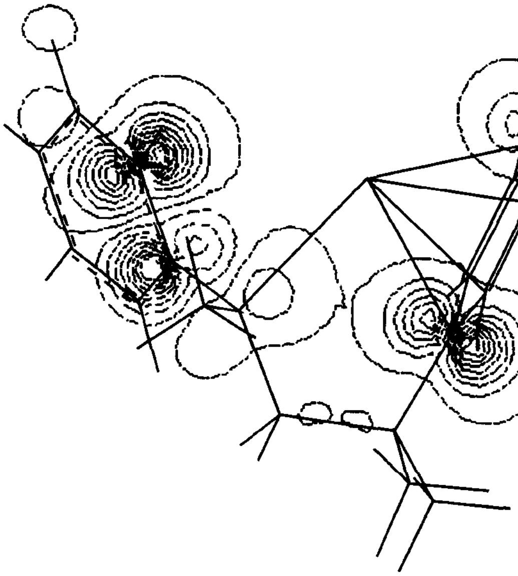

Fig. 6. Spin density distribution in the triplet state of the dim-α$^-$Na$^+$ (*cis*) dimer with the cation localized on the second monomer unit over the center of the aromatic ring.

of the end fragment of the polymer is responsible for the cleavage of the C–C bond between the end monomer unit and the unit lying next to it. This state has the following characteristic features. First, it is generated by the the cation shift from the end unit to the adjacent aromatic ring by ~0.5 Å for the *cis*, and by 5 Å for the *trans*, configuration. Second, the cation shift is accompanied by an electron transfer in the same direction, leading to a biradical structure which is active in bond cleavage steps. Third, the energies of these states are close to the ground state energy, providing high occupation and hence high reaction rate. Finally, the monomer elimination is followed by regeneration of the ground state of the end of the "living" polymer, which is capable of either chain propagation or further depolymerization.

An important result of this treatment is the conclusion about the lower depolymerization rate of isolated polymer anions compared to ion pairs due to the higher dissociation energies of the triplet states. This suggests that a direct chain propagation reaction on the free anion is also hindered.

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