



REGIOSELECTIVITY OF THE RADICAL CATION RECOMBINATION IN THE ANILINE POLYMERIZATION

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Abstract

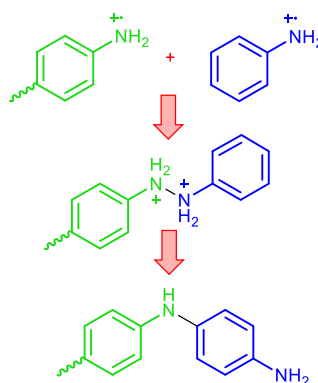
The regioselectivity of the fast stages of the aniline polymerization mechanism is considered. Using the AM1 method, the approaching of the radical cation of an aniline trimer to the aniline radical cation with chloride counterions, as well as the radical cations of the monomer to each other is simulated. It is shown that on passing from the recombination of the aniline radical cations with each other to the recombination of the aniline radical cations with the radical cations of an aniline trimer, the main approaching direction changes from C/N to N/N, which is followed by the semidine rearrangement. The high *para*-selectivity of the aniline polymerization is explained and the ratio of the rate constants of various recombination routes of the radical cations is evaluated.

Key words: polyaniline, aniline polymerization, polymerization mechanism, quantum chemical methods.

Introduction

The polymerization of aromatic amines is an independent class of reactions that underlies the production of nitrogen-containing polyconjugated systems, which has no analogs among the classical methods of polymer synthesis [1]. Under conditions of oxidative polymerization, the derivatives of aniline [2] and α -naphthylamine [3] bearing electron donating groups form a number of conducting polymers which are used in the creation of amperometric sensors, membranes, materials for biomedical applications, as well as coatings that prevent accumulation of static electricity and development of metal corrosion and improve the matrix adhesion to the filler [4–6]. The copolymerization of aromatic amines expands the range of available polymers with conjugated systems and is an effective way to control their properties [7].

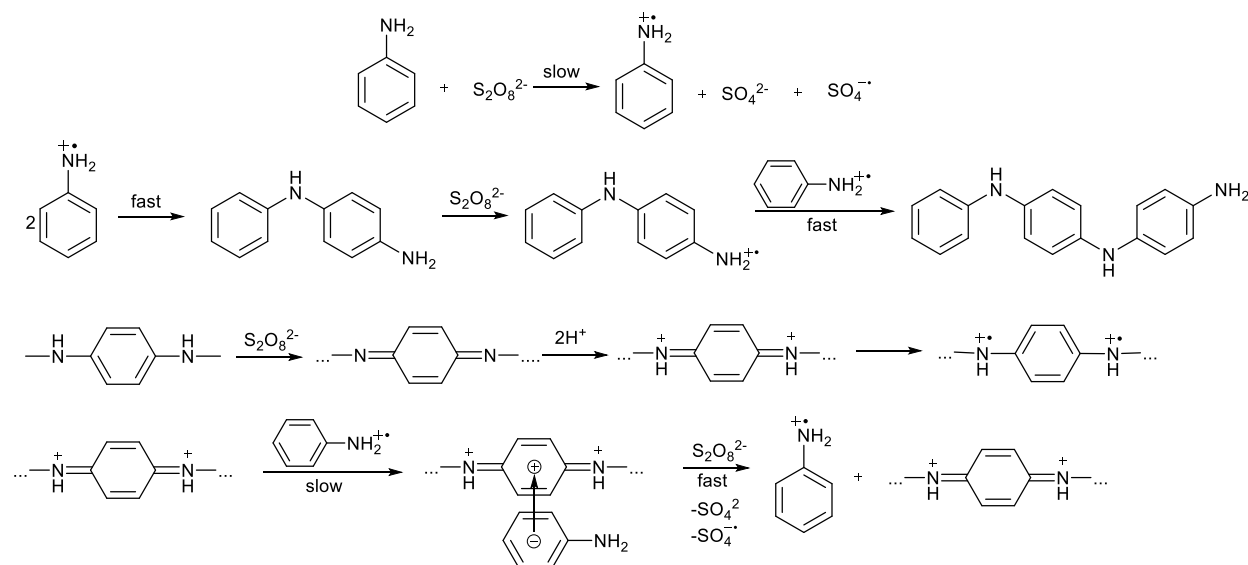
The rapid development of concepts about the mechanism of polymerization of aromatic amines in the last three decades has not resulted in the appearance of a unified and consistent approach that could become a reliable theoretical basis for describing the regularities of the synthesis of conjugated aromatic polyamines [8]. In contrast, even the nature of the active centers of oxidative polymerization remains controversial, although this role is most likely to belong to the radical cations of monomers and *x*-mers (oligomers) of aromatic amines [9–12]. Recent advances in establishing the kinetic regularities of polymerization of aromatic amines and predicting the molecular weight characteristics of the resulting polymers suggest that the mechanism presented in Scheme 1 matches the sum of currently available experimental data [8, 13, 14].



The experimental basis for the mechanism depicted in Scheme 1 is numerous data on the kinetics of oxidative polymerization [10–14]. At the same time, the kinetic data enable characterization of the nature of only slow stages of oxidative polymerization, while structures of the polymer products is largely determined by the nature of the fast ones. In particular, of note is the unprecedentedly high selectivity of the *para*-coupling of a polyaniline chain formed during the aniline polymerization [15, 16]. An explanation of the high *para*-selectivity of the aniline polymerization requires consideration of the details of the fast stages of recombination of the aniline radical cations with each other, as well as recombination of the aniline radical cations and the radical cations of aniline oligomers included in the particles insoluble in the reaction medium (acidic aqueous solutions) [10–14]. Since the possibilities to establish experimentally the regularities of the fast processes of recombination of radical cations are limited, this article provides a theoretical consideration of the problem of regioselectivity during recombination of the radical cations of aniline *x*-mers using the semi-empirical quantum chemical method AM1.

Results and discussion

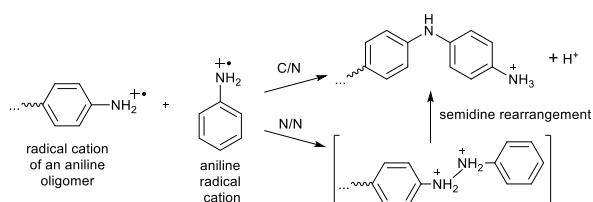
It was previously found that the chain growth in oxidative polymerization occurs exclusively as a result of recombination of the aniline radical cations with the radical cations of aniline oligomers [10–14]. The latter circumstance is associated with the low solubility of aniline oligomers, starting already from its trimers, in acidic aqueous solutions and is confirmed by a linear



Scheme 1. Proposed mechanism of the aniline polymerization.

increase in the molecular weight of polyaniline with the monomer conversion [17]. Thus, the recombination with the aniline radical cations (mainly during the induction period) or with the radical cations of aniline oligomers (mainly after the completion of the induction period) is possible for the aniline radical cations. The recombination of the radical cations of aniline x -mers with an arbitrary x value is thus impossible [18].

For chain growth processes occurring after the completion of the induction period, both C/N recombination, leading to the formation of a new C–N bond and the involvement of an aniline residue in the chain, and N/N recombination with subsequent semidine rearrangement are considered as alternatives (Scheme 2) [15].



Scheme 2. Possible mechanisms of the recombination of the radical cations of aniline oligomers with the aniline radical cations.

To estimate the main direction of the recombination of the radical cations of aniline x -mers with the aniline radical cations, the radical cations of aniline oligomers were modeled with an aniline trimer, and the calculations took into account the presence of counterions. Chloride ions were chosen as the counterions to the nitrogen cation radical centers in the quantum chemical calculations. First, the oxidative polymerization of aniline with the formation of an emeraldine salt is possible in the presence of only chloride counterions, for example, when FeCl_3 is used as an oxidizing agent [19, 20]. Second, chloride anions are believed to have a minimal coordinating effect when bringing the radical cations of aniline x -mers closer. This allows us to consider the most general case, when the role of counterions is reduced to creating an electrostatic field without any specific or cooperative interactions noted in a number of

studies [21, 22]. The structures of the supermolecules and the molecular electrostatic potential obtained as a result of modeling the approach of the above-mentioned radical cations in the presence of chloride counterions using the AM1 method are shown in Fig. 1.

The electronic energy of the supermolecule formed during the N/N recombination of the aniline radical cation and the radical cation of an aniline trimer is -24247.25 kJ/mol. The electronic energy of the supermolecule which is a product of the C/N approaching of the radical cations is -24241 kJ/mol. Hence, it can be expected that the activation energy of the N/N recombination of the aniline radical cation and the radical cation of an aniline trimer is at least 6.25 kJ/mol less than that for the C/N recombination.

Consequently, the rate of N/N recombination of the aniline radical cation and the radical cation of an aniline trimer is at least 12.5 times higher than that of C/N recombination at 298 K. Therefore, the chain growth during aniline polymerization is a consequence of the N/N approaching of the radical cations of aniline x -mers with the aniline radical cations and subsequent semidine rearrangement. The latter circumstance explains the high *para*-selectivity of polyaniline synthesis, but raises the question about the regioselectivity of recombination of the aniline radical cations with each other at the early stages (induction period). In addition, the results of quantum chemical calculations predict that the cleavage of the H–N bond precedes the formation of covalent bonds in the main chain during chain growth (Fig. 1). This result is consistent with a rapid decrease in the basicity of aniline oligomers with an increase in their molecular weight.

If we extend the results of modeling the approach of the radical cations of aniline oligomers with the aniline radical cation to the recombination of two radical cations of a monomer, then we can assume that the main result will be N/N recombination followed by the benzidine rearrangement. The formation of benzidine as the main intermediate at the early stages of aniline polymerization contradicts the literature data, which indicate the predominant formation of *para*-semidine [16]. In particular, the AM1 method previously predicted the

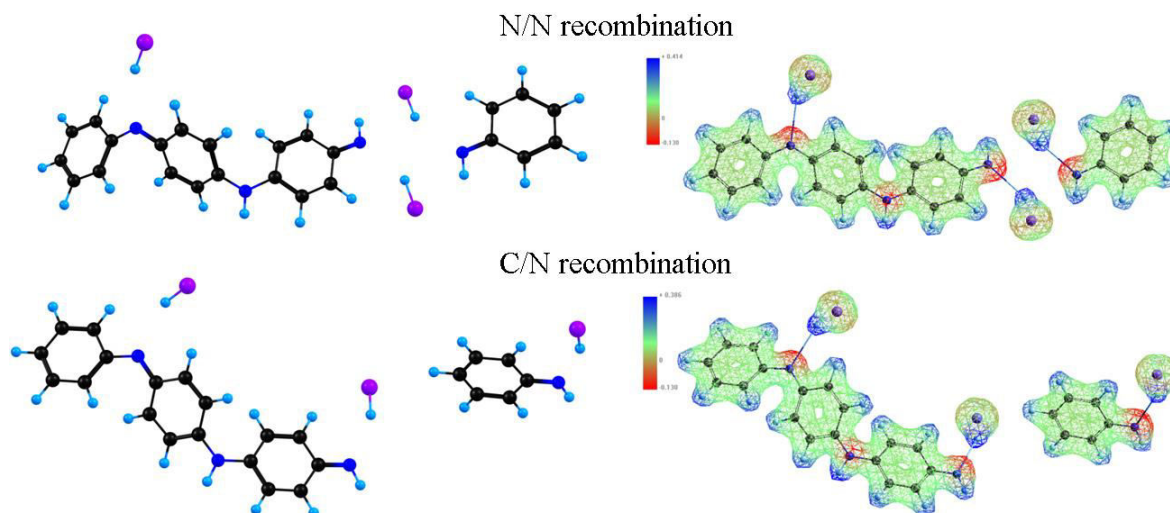
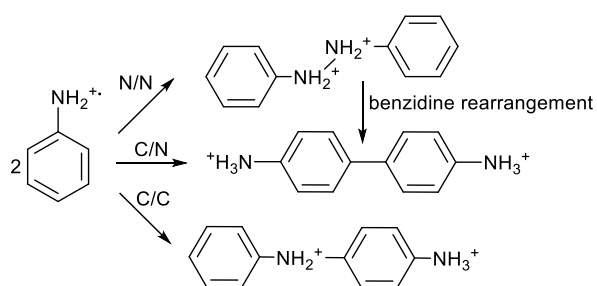


Figure 1. Structures (left) and molecular electrostatic potential (right) of the supermolecules obtained by modeling the approach of the radical cations of an aniline trimer to the aniline radical cations.

predominant formation of *para*-semidine [23], rather than the *ortho*-isomer, as the main product of aniline oxidation by peroxydisulfate anion in an acidic environment, although some studies suggest the opposite due to the presence of two *ortho*-positions as opposed to one *para*-position [15]. In this case, the formation of even small amounts of *ortho*-semidine, serving as a precursor of phenazine derivatives, can have a significant impact on the morphology of polymer products due to the realization of π - π stacking interactions. Although the regioselectivity issue of the recombination of aniline radical cations remains a subject of debate, most studies suggest the predominant formation of *para*-semidine as an intermediate product of the oxidative polymerization of aniline [16, 18, 24]. Therefore, the modeling by the AM1 method was performed separately for the aniline radical cations with chloride counterions (Fig. 2), taking into account possible N/N, C/C, and C/N approaching scenarios (Scheme 3).



Scheme 3. Possible directions of the interaction of aniline radical cations.

The energies of the resulting supermolecules for the N/N, C/C, and C/N approaching of the aniline radical cations are –12610.98 kJ/mol, –12638.56 kJ/mol, and –12641.48 kJ/mol, respectively.

Thus, it can be expected that the rate constants for the interaction of the aniline radical cations according to N/N, C/C, and C/N scenarios are no less than $1/6.87 \times 10^4 / 2.23 \times 10^5$. Consequently, the main scenario is C/N recombination of the aniline radical cations. Since the charge does not change during

the formation of a supermolecule from the aniline radical cations (Fig. 2) and the local dielectric constant is obviously much less than the dielectric constant of the continuum, the effects associated with hydration were neglected in the calculations. At the same time, the results obtained are qualitatively consistent with the analysis of the reactivity of aniline with respect to a peroxydisulfate anion in an acidic medium, taking into account the effects of solvation by the COSMO method, but within the framework of a static rather than dynamic consideration of the properties of multielectron systems by the AM1 method [23].

Calculations

The HyperChem program was used to carry out quantum chemical calculations. The analysis of the radical cation approaching was performed using the AM1 method without taking solvation into account. When interpreting the computation results, we proceeded from the assumption that the total electronic energy of supermolecules obtained by simulating the approach of the reagents reflects changes in the activation energy of transition states for various variants of recombination of the radical cations of aniline *x*-mers. Thus, it is assumed that the difference in activation energies for the formation of alternative transition states for different options of the reactants approaching is no less than the difference in the total electronic energy of supermolecules calculated by the AM1 method. Differences in frequency factors for different variants of recombination of the radical cations of aniline *x*-mers were neglected. The last assumption cannot introduce a significant error that could change the semi-quantitative result of assessing the regioselectivity of the approaching of the radical cations of aniline *x*-mers, since the positive charge and unpaired electron are largely delocalized. Thus, the ratio of the rate constants for various options of the reagents approaching can be estimated by the following equation:

$$\frac{k_2}{k_1} \geq e^{\frac{(E_1 - E_2)}{RT}}$$

where: E_1 , E_2 are the energies of the supermolecules obtained by

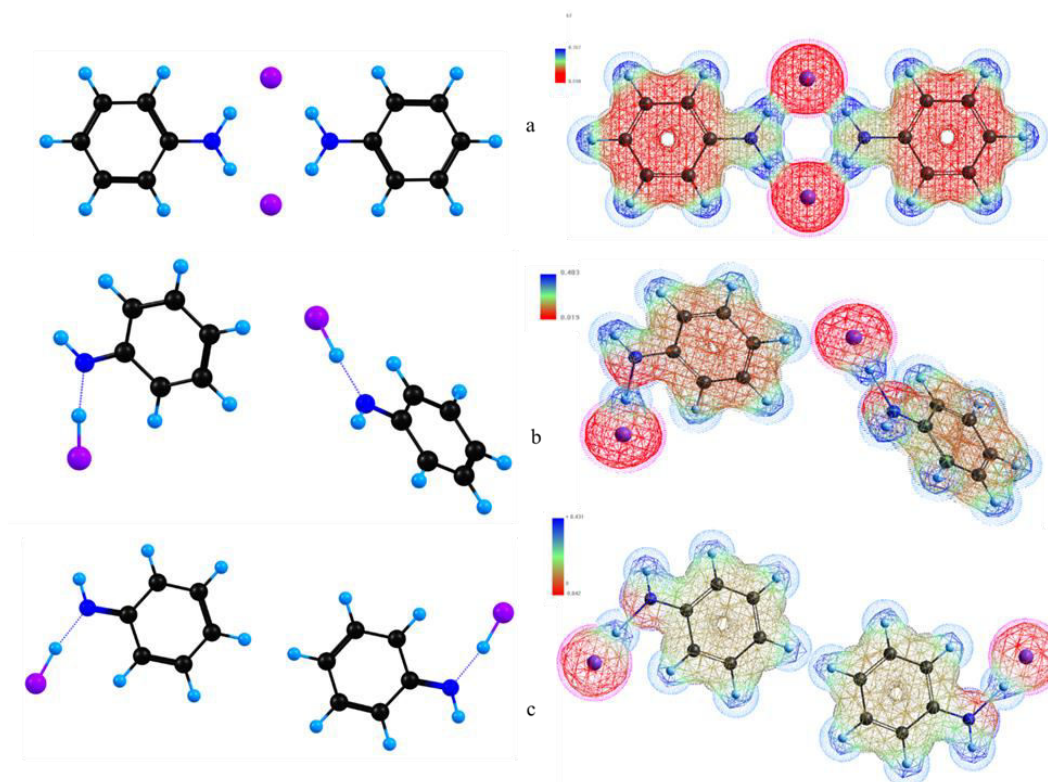


Figure 2. Structures (left) and molecular electrostatic potential (right) of the supermolecules obtained from modeling N/N, C/N, and C/C scenarios of the approach of the aniline radical cations to each other.

modeling the alternative options of the reagents approaching; k_1 , k_2 are the rate constants of the interaction of identical reagents for alternative options of their approaching; R is universal gas constant, T is the temperature.

The delocalization of electron density in the radical cations of aniline x -mers also suggests that hydration will contribute to a decrease in the energy of the system to approximately the same extent for different scenarios of the approaching of active centers and will not have a decisive impact on the value of energy differences for the supermolecules under consideration.

Conclusions

The calculations by the AM1 method showed that the main direction of the interaction of the aniline radical cations with each other is C/N recombination, while in the reaction of the radical cations of aniline trimers with the monomer radical cation, N/N recombination with subsequent semidine rearrangement predominates. Thus, the main product of the initiation stage of aniline polymerization is *para*-semidine. After the completion of the induction period, when the concentration of aniline oligomers is high, chain growth occurs primarily as a result of N/N recombination of the aniline radical cations with the radical cations of aniline oligomers and subsequent semidine rearrangement. The latter circumstance explains the high *para*-selectivity of polyaniline chain formation. The results presented were obtained by semi-empirical calculations without taking into account the effects associated with solvation and will be refined using *ab initio* quantum chemical methods as well as taking into account hydration in subsequent works.

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