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Theoretical investigation of block copolymerization of tetrahydrofuran and pyrrole

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Abstract

In this work, semi-empirical quantum mechanical techniques were employed in order to discuss the feasibility of the copolymerization reaction between tetrahydrofuran and pyrrole starting from two different macromonomers in which polytetrahydrofuran has a pyrrole moiety at one or both ends. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Conducting polymers have attracted great interest owing to their electrical properties, though they have limited practical use because of their poor mechanical and physical properties. Chemical and electrochemical blending have been considered in improving the processability of these materials [1–3]. In addition, insulating polymer backbones containing pyrrole moieties as pendant and/or end groups have also been studied in forming graft or copolymers of conducting polymers with better mechanical properties [4,5]. A theoretical work supporting the possibility of having such conducting copolymers has also been presented [6]. Use of living ionic polymerization in the synthesis of polytetrahydrofuran (PTHF) allows the preparation of polymers with pyrrole end groups [7,8]. The chain length of PTHF segments can be changed with reaction conditions. Further polymerization of the macromonomers with pyrrole yields polymer chains containing polpyrrole chains on either or both ends [9,10]. In this work we present the discussion on the feasibility of such a copolymerization between PTHF and pyrrole studied by semi-empirical quantum mechanical techniques [11]. Effect of chain length of PTHF on the possibility of adding a second pyrrole group on an existing pyrrole moiety was discussed.

2. Results and discussion

Monomers which were exposed to polymerization are given in Fig. 1 where n represents the number of soft segments or chain length. In the calculations, n is changed from 1 to 7 to analyze the effect of chain length on polymerization. For each n, the number of pyrrole units added to the monomer was also changed until satisfactory information was obtained on the polymerization mechanism. In Tables 1 and 2, formation enthalpies of monomer-1 and monomer-2 for different n values are given. Formation enthalpies of pyrrole-added monomer-1 are given in Table 3. As it can be seen from these tables, pyrrole addition to the monomer-1 does not depend on n. Addition of pyrrole increases the formation enthalpies by approximately 40.5 kcal/mol whatever the number of n is and the reaction enthalpy of pyrrole addition is about −4.6 kcal/mol except for $n = 3$. Starting geometries and the optimized geometries of the molecules are similar. For some n values, one molecule may be different from the others if there exist more than one local energy minima close to each other. For $n = 3$ case, the energy difference is insignificant.

$$(\text{monomer-1})_n + \text{pyrrole} \rightarrow (\text{pyrrole-added monomer-1})_n + H_2$$

Pyrrole addition to monomer-1 is feasible irrespective of the n values. In systems with two pyrrole moieties, there are always four possible ways of bonding the second pyrrole ring to the first one. In our calculations we considered all

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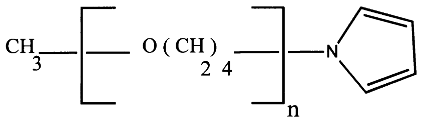
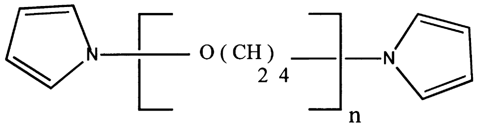


monomer-1



monomer-2

Fig. 1. Monomer-1, PTHF with one pyrrole ring at one end; monomer-2, PTHF with pyrrole rings at both ends.

Table 1
Heats of formation of the monomers-1 with increasing *n* values

n	Heat of formation of monomer-1 (kcal/mol)
1	− 16.55311
2	− 76.27985
3	− 137.47134
4	− 197.92178
5	− 258.38551
6	− 318.83618
7	− 379.25960

Table 2
Heats of formation of monomers-2 with increasing *n* values

n	Heat of formation of monomer-2 (kcal/mol)
1	86.57775
2	27.61269
3	− 34.49685
4	− 94.57837
5	− 154.15774
6	− 214.51084
7	− 275.59787

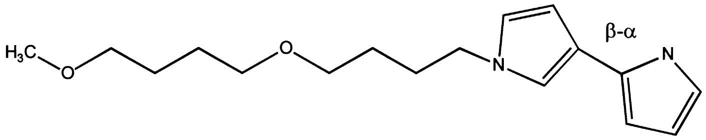
types of bondings and we observed that the energy differences found by semi-empirical calculations are very small and the one with lowest energy is $\beta-\alpha$ type bonding as previously noted in the literature [12]. Therefore, we bonded the second pyrrole to the first one through $\beta-\alpha$ linkages. For further oligomers, we bonded the pyrroles through $\alpha-\alpha$ linkages. In Fig. 2, we give the schematic picture of pyrrole-added monomers. For the second type of monomers, pyrrole addition can take place in both sides or either side of the molecules as there are two pyrrole units at the end of the chain. We define the beginning of the chain as an O-end, meaning oxygen-end and the end of the chain as C-end, meaning carbon-end. Before adding one pyrrole unit to both ends of the chain, we added only one pyrrole unit from each end separately to see whether chain extension was preferential. Formation enthalpies of pyrrole-added monomer-2 are given in Tables 4 and 5 where it can be noted that the pyrrole-added monomer-2 are energetically similar and when the reaction enthalpies are concerned, pyrrole-addition through the C-end is only less than 1.0 kcal/mol more favorable than pyrrole-addition through the O-end. Such a small energy difference is not significant in electrochemical reactions which are run in nonaqueous media. This shows that pyrrole polymerization from either end has equal probability. Polypyrrole can be formed at either side or both sides of the soft segment. Thus, two units of pyrrole were added to both sides of the monomer-2 and the formation enthalpies of two pyrrole-added monomer-2 are given in Table 6.

$$(\text{monomer-2})_n + 2\text{pyrrole} \longrightarrow (\text{pyrrole-added monomer-2})_n + 2\text{H}_2$$

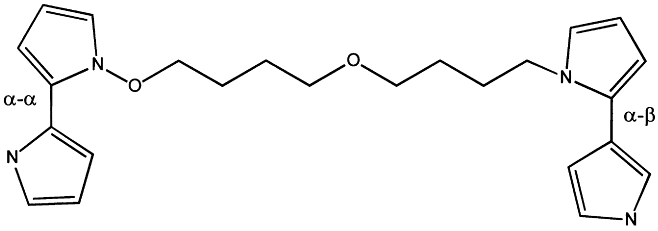
It is clear from the tables that energy differences between the pyrrole added and unadded systems is about 40.5–41.0 kcal/mol/pyrrole irrespective of the monomer type. This means that both monomers are equally open to polymerization without being affected by the chain length. Pyrrole addition can take place at both sides of monomer-2. Finally, two pyrrole units are added to monomers-1 in two different ways. In the first case, the third pyrrole is added directly to the second pyrrole through $\alpha-\alpha$ type bonding. In the second case, the third pyrrole is also added to the first

Table 3
Heats of formation of pyrrole added monomers-1 (PAM1), energy differences between PAM1 and monomers-1 (M1) and heats of reaction with increasing *n* values

n	Heat of formation of PAM1 (kcal/mol)	ΔE (PAM1 − M1) (kcal/mol)	Reaction enthalpy (kcal/mol)
1	23.84449	40.40	− 4.66
2	− 35.76899	40.51	− 4.55
3	− 95.06679	42.40	− 2.65
4	− 157.33926	40.58	− 4.48
5	− 217.92271	40.46	− 4.60
6	− 278.45948	40.38	− 4.68
7	− 338.90988	40.35	− 4.71



PAM1



TPAM2

Fig. 2. Pyrrole-added monomer-1 and two pyrrole-added monomer-2, where $n = 2$. As an example, different types of bondings between pyrroles were shown.

pyrrole of the monomer-1, i.e., two pyrroles are bonded to the first pyrrole again through $\alpha - \alpha$ type bonding. Here, we only give (Table 7) the formation enthalpies of two pyrrole added monomer-1 systems where the pyrroles are linearly bonded to each other as the energies of the second type of systems are almost the same. From the values given in Table 7, one can again conclude that addition of one pyrrole unit increases the formation enthalpy of a molecule by 40.6 kcal/mol. This almost constant increase in the energy of the systems with different n values can also be seen in Fig. 3 where monomer energies and pyrrole-added monomer energies versus n were drawn. The perfect linear correlation between energies and n stresses once again the constant increase in energy due to pyrrole addition and n independency of polymerization mechanism. Extension of pyrrole units can be in any direction. As we have noted before bonding between pyrrole rings can be $\alpha - \alpha$, $\alpha - \beta$, $\beta - \alpha$, or $\beta - \beta$ as the energy differences calculated by

Table 4
Heats of formation of pyrrole added monomers-2 (PAM2), energy differences between PAM2 and monomers-2 (M2), and heats of reaction of pyrrole addition through C-end to M2 with increasing n values

n	Heat of formation of PAM2 (kcal/mol)	ΔE (PAM2 − M2) (kcal/mol)	Reaction enthalpy (kcal/mol)
1	127.03131	40.45	− 4.61
2	67.40360	39.79	-5.27
3	5.82751	40.32	-4.73
4	-52.95583	41.62	-3.44
5	-114.18632	39.97	-5.09
6	-175.49130	39.02	-6.04
7	-234.37270	41.23	-3.83

Table 5
Heats of formation of PAM2, energy differences between PAM2 and M2, and heats of reaction of pyrrole addition through O-end to monomers-2 with increasing n values

n	Heat of formation of PAM2 (kcal/mol)	ΔE (PAM2 − M2) (kcal/mol)	Reaction enthalpy (kcal/mol)
1	127.73695	41.16	− 3.90
2	68.65252	41.04	− 4.02
3	6.40455	40.90	− 4.16
4	− 52.65856	41.92	− 3.14
5	− 114.28537	39.87	− 5.19
6	− 174.37869	40.13	− 4.93
7	− 233.0005	42.60	− 2.46

Table 6

Heats of formation of two pyrrole added monomers-2 (TPAM2), energy differences between TPAM2 and PAM2, and reaction enthalpies of pyrrole addition to PAM2 with increasing *n* values

n	Heat of formation of TPAM2 (kcal/mol)	ΔE (TPAM2 − PAM2) (kcal/mol)	Reaction enthalpy (kcal/mol)
1	168.14054	41.11	− 8.56
2	108.42237	41.02	− 9.31
3	46.90235	41.07	− 8.72
4	− 11.89777	41.06	− 7.44
5	− 73.00396	41.18	− 8.96
6	− 134.24286	41.25	− 9.85
7	− 193.58295	40.78	− 8.10

Table 7

Heats of formation of two pyrrole added monomers-1 (TPAM1), energy differences between TPAM1 and PAM1, and reaction enthalpies of pyrrole addition to PAM1 with increasing *n* values

n	Heat of formation of TPAM1 (kcal/mol)	ΔE (TPAM1 − PAM1) (kcal/mol)	Reaction enthalpy (kcal/mol)
1	64.57862	40.73	− 4.32
2	4.85138	40.62	− 4.44
3	− 56.13315	38.93	− 6.13
4	− 116.29114	41.05	− 4.01
5	− 177.09593	40.83	− 4.23
6	− 237.73772	40.72	− 4.34
7	− 297.51357	41.40	− 3.66

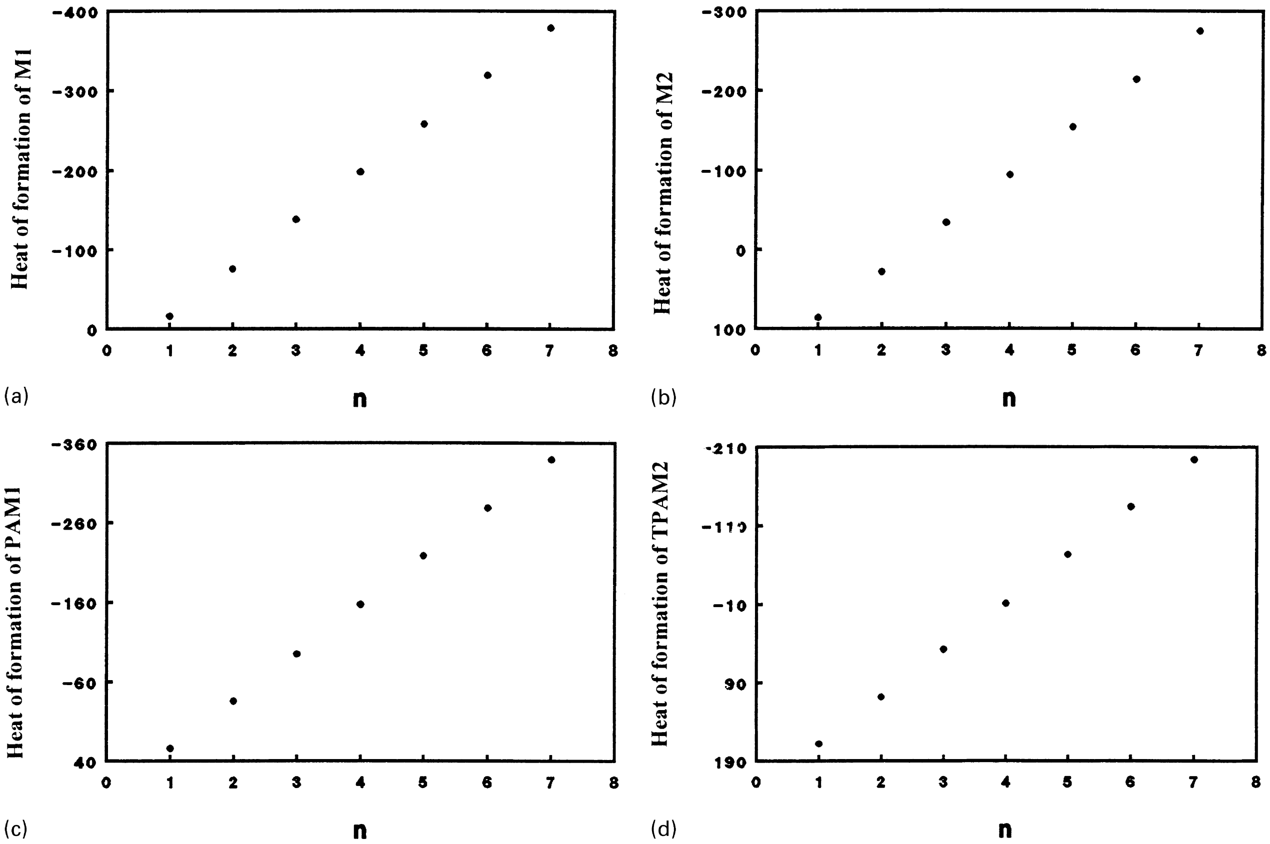


Fig. 3. Heats of formations versus monomer units: (a) monomer-1; (b) monomer-2; (c) PAM1; (d) TPAM2.

semi-empirical quantum mechanical calculations between these bonding types are negligible.

3. Conclusions

After carrying out a number of semi-empirical quantum chemical calculations on the behavior of the different monomers in electrochemical copolymerization reactions, we conclude that the monomers having pyrrole moiety at one or both ends are equally open to pyrrole polymerization. The length of the soft segment, *n*, however, does not play a significant role on this type of polymerization reactions.

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