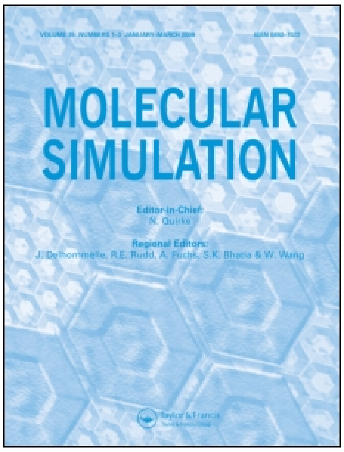
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular dynamics simulations on polythiophenes for chemical sensing applications

V. D. Ghule[a]; S. Radhakrishnan[b]; P. M. Jadhav[b]; T. Soman[b]
[a] ACRHEM, University of Hyderabad, Hyderabad, India [b] High Energy Materials Research Laboratory, Pune, India

First published on: 20 August 2009

To cite this Article Ghule, V. D. , Radhakrishnan, S. , Jadhav, P. M. and Soman, T.(2010) 'Molecular dynamics simulations on polythiophenes for chemical sensing applications', Molecular Simulation, 36: 1, 63 — 68, First published on: 20 August 2009 (iFirst)

To link to this Article: DOI: 10.1080/08927020903115245

URL: http://dx.doi.org/10.1080/08927020903115245

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation
Vol. 36, No. 1, January 2010, 63–68

Molecular dynamics simulations on polythiophenes for chemical sensing applications

V.D. Ghule[a], S. Radhakrishnan[b]*, P.M. Jadhav[b] and T. Soman[b]

[a]*ACRHEM, University of Hyderabad, Hyderabad, India;* [b]*High Energy Materials Research Laboratory, Pune 411 021, India*

(*Received 29 December 2008; final version received 13 June 2009*)

Molecular dynamics calculations have been performed on thiophene polymers bearing heterocyclic substituents at the third position in order to study the interaction of analyte with these heterocyclic substituents. Analysis of parameters like total energy, density, radial distribution function, end-to-end distance in polymer chains and radius of gyration of polymer–analyte system shows the variation in these properties with respect to nature of analytes and side chain on the polymer. Overall, the study aims to bring out the role of side chain in designing chemical sensory material.

Keywords: polymer modelling; molecular dynamics; polythiophenes; chemical sensors; pair-correlation functions

1. Introduction

Conjugated polymers [1] are of substantial interest due to their luminescent, electronic (such as light-emitting diodes, organic transistors, solar cells, batteries, photoresists and magnetic shielding materials), optical and optoelectronic properties. The development of chemical and biological sensors based on conducting polymers (CP) has gained considerable momentum in the past decade [2,3]. Among the conjugated polymers, polythiophenes (PT) and its derivatives are widely investigated due to their environmental and thermal stability [4]. Conjugated PT are versatile materials in which analyte recognition can be achieved in different ways including the selective interactions between polymers and analyte wherein the side groups in the thiophene play an important role. Detection relies on both electronic and structural interactions between the sensing material and the analyte [5]. Different polymers have varying degrees of response and this could lead to the development of a multisensor.

An important property of organic-based sensors is the chemical flexibility of the active layer that can be used to attain a selective device. An interesting approach demonstrated on a set of polysiloxanes uses side-chain functional groups to confer broad selectivity to a chemical sensor [6]. Recently, alkyl-substituted conjugated polymers have been employed in a chemiresistor-type configuration to promote the detection of non-polar vapours, normally a weak point of CP sensors [7], because such conductive layers are generally much more sensitive to polar substances. As an analyte approaches the polymer surface, the tendency to interact with that surface will depend on the inducement of H-bonding or non-bonded interactions. The interaction of analyte molecule with the polymer, whether by hydrogen bonding, van der Waals forces or even covalent interaction, will modulate electronic, optical or magnetic properties of the material so they become chemical transducers [8]. The versatile molecular recognition capabilities of CP, coupled with their ability to communicate electronically with input controlling and output monitoring systems, provide the basis for a powerful new sensing technology [9].

The discovery of new electronic polymeric materials could be facilitated, accelerated and made more cost effective with the use of computer modelling and simulations for the identification of compounds with significant advantages over materials currently in use. The intrinsic electronic and optical properties of a material are governed by the electronic structure of molecules and therefore it is essential to successfully design such polymers to understand the evolution of the electronic properties of conjugated polymers in connection with their chemical structure [10,11]. Accurate simulation of atomic and molecular systems generally involves the application of quantum mechanical theory. However, quantum mechanical techniques are computationally expensive and are usually applied only to small systems containing between 10 and 100 atoms or small molecules. It is not practical to model large systems such as a condensed polymer containing many thousands of monomers in this way. Hence classical simulation tools are widely exploited and they incorporate a broad spectrum of molecular mechanics (MM) and dynamics (MD) methodologies that have demonstrated applicability to molecular design. Using a carefully derived empirical force field as the foundation, minimum energy conformations, as well as families of structures and dynamics trajectories of molecular systems, can be computed with confidence.

---

*Corresponding author. Email: sradha78@yahoo.com

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020903115245
http://www.informaworld.com

The present theoretical study investigates the role of chemically different side chains used as substituents of PT in conferring chemical selectivity towards the analytes. In order to understand the interaction between the polymer and analyte, the 3-substituted PT derivatives have been chosen as model compounds. Influence of analyte on the various properties such as energy and conformational changes are discussed.

2. Theoretical methodology

Molecular simulations were performed on Accelrys' Materials Studio Suite [12] on various structures of model polymers and analytes shown in Figure 1. MM and MD calculations have been executed using DISCOVER module using PCFF force field which handles electron delocalisation in aromatic rings by means of a charge library rather than bond increments. Periodic boundary conditions have been adapted for the simulation of structures consisting of a periodic lattice of identical subunits. Implementation of periodic boundaries to simulations provides improvement in the rigour and realism of a structure. Monomers and the analytes have been optimised at semi-empirical level: AM1 calculations using Gaussian 03 Package [13].

2.1 Construction of models

The polymer model is constructed from its optimised monomer structures in its isotactic form with inter-ring random torsions. The connectivity of these homo polymers are head-to-tail and the polymer chain is built with ten monomer units along 2, 5 position of parent thiophene. The charges of isolated polymer chains are based on the charge equilibrium method [14]. Simulation cell is an initial configuration to define polymer system for computer simulation. In the present study, a cell consisting of three chains has been constructed with periodic boundary conditions, the complete molecular models including monomer, analyte and cell have been energy minimised by MM calculations before going for MD simulations. The number of polymer chains and analyte in each model system has been kept constant.

Various electron-rich and -deficient analytes (Figure 1(a)) have been chosen to study their effect on polymer conformations (Figure 1(b)). An AM1 optimised analyte molecule has been included in simulation cell while its construction in order to study the influence of analyte on the polymer.

2.2 Simulation protocol

In order to bring the polymer model system to the most probable configuration consistent with target temperature and pressure, cell relaxations have been performed for the energy minimised cells of pure polymer and polymer with analytes using NVT-MD simulations. The relaxation protocol employed is similar to the Hoffmann's relaxation protocol [15]. Karayiannis et al. [16] modified the above to perform NPT dynamics at the end of the NVT cycles and the simulation protocol is shown in Table 1. The final structure has been taken from the relaxation simulation and it was equilibrated by NPT-MD simulations for 1000 ps (production run). Density of the cell is recorded

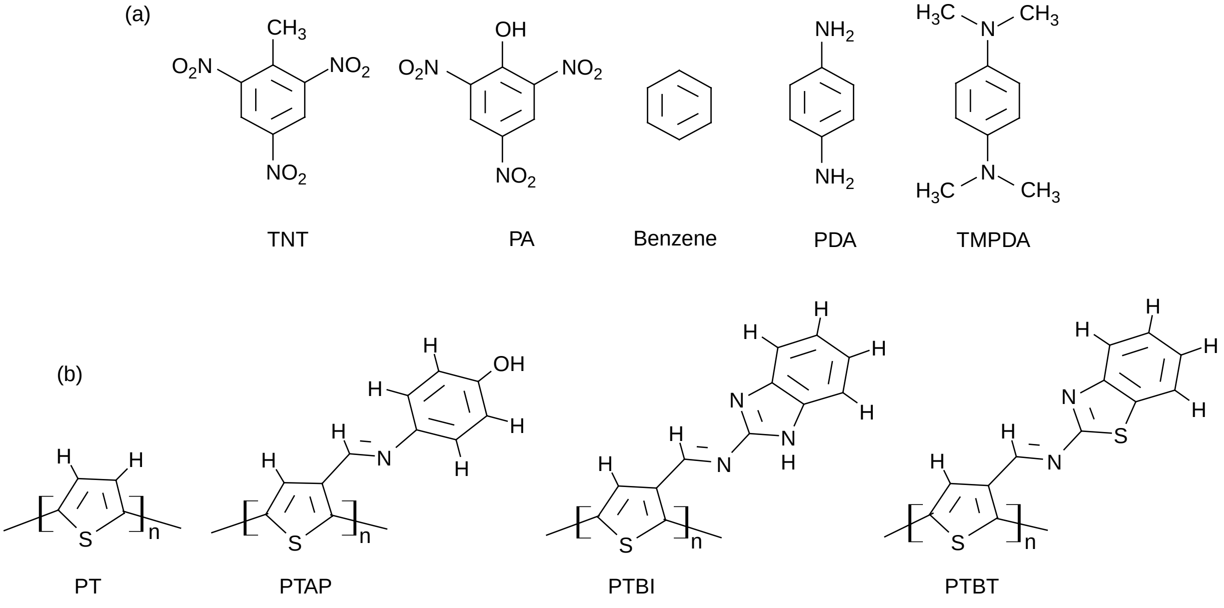


Figure 1. Polymer and analyte systems considered in the study (a) analytes; (b) polymers.

Table 1. Relaxation protocol.

Stage of equilibration	Ensemble	Temperature (K)	Time (ps)
1	NVT-MD	750	30
2	NVT-MD	600	20
3	NVT-MD	450	20
4	NVT-MD	303	100
5	NPT-MD	303	100

NVT, constant number of moles/constant-volume/constant temperature dynamics; NPT, constant number of moles/constant-pressure/constant temperature dynamics.

in equilibrium process and a constant density is ensured at the end of production run.

2.3 Analysis methodology

2.3.1 Energy expression

The total energy of a system is the sum of its potential and kinetic energies. While the kinetic energy depends on temperature, the potential energy (PE) of a system can be expressed as a sum of valence (or bond), crossterm, and non-bond interactions:

$$\mathrm{PE} = E_{\text{valence}} + E_{\text{crossterm}} + E_{\text{non-bond}}. \qquad (1)$$

The energy of valence interactions is generally accounted by diagonal terms like bond stretching (bond), valence angle bending (angle), dihedral angle torsion (torsion), inversion, out-of-plane (oop) interactions and Urey–Bradley (UB) may be used to account interactions between atom pairs involved in 1-3 configurations (i.e. atoms bound to a common atom).

$$E_{\text{valence}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{oop}} + E_{\text{UB}}. \qquad (2)$$

Cross terms can include the following: stretch–stretch, stretch–bend–stretch, bend–bend, torsion–stretch, torsion–bend–bend, bend–torsion–bend and stretch–torsion–stretch. The energy of interactions between non-bonded atoms is accounted for by van der Waals (vdW), electrostatic (Coulomb) and hydrogen bond (H-bond),

$$E_{\text{non-bond}} = E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{H-bond}}, \qquad (3)$$

where vdW accounts for intermolecular interactions between atoms that are separated by three or more bonds within a chain and their interaction potential is relatively short-range. While the coulombic interactions decrease at a much slower rate with distance, variation in interaction energy depends on the structure. Many force fields contain no special arrangement for hydrogen bonding and rely on vdW and electrostatic terms to produce the hydrogen bonding. Length distribution and radius distribution profile analysis has been performed for the polymer model having different analytes.

3. Results and discussion

Appropriate molecular design of polymer side chains and intelligent engineering of surfaces and interfaces will lead to polymers with specific physico-chemical properties for the chemical sensing applications. Recent literature shows alkyl- and alkoxy-substituted PT regioregular thin films show very promising properties for employment as chemical sensors [17,18]. Molecular design of materials for deemed application requires the detailed investigation of the process involved. This study explores bringing out the weak interaction associated with the chemical sensing phenomena. Interaction of analyte with polymer can produce a conformational change in the side chain/backbone. These changes can be better realised by analysing the orientational/structural changes of the polymer system through length and radial distribution profiles. In addition, any structural change will lead to a change in the energy of a system.

3.1 Energy contributions

The total energy content of the polymer–analyte composite depends not only on polymer and analyte, but also on the interaction between them. The nature and the extent of interaction are decided by the molecular features of the analyte. Comparison of total energies of various polymer systems without analytes is shown in Figure 2. No significant change in total energy is observed in polymers PT, poly[4-((thiophen-3-yl)methyleneamino)phenol]-2,5-diyl (PTAP) and poly[*N*-((thiophen-3-yl)methylene)-1H-benzo[d]imidazol-2-amine]2,5-diyl (PTBI) while poly[*N*-((thiophen-3-yl)methylene)benzo[d]thiazol-2-amine]-2,5diyl (PTBT) exhibits high energy of about 3300 kcal/mol. This deviation in PTBT may be attributed to the presence of sulphur atom unlike nitrogen in PTBI. Sulphur-containing molecular systems possess very high energy of non-bonded

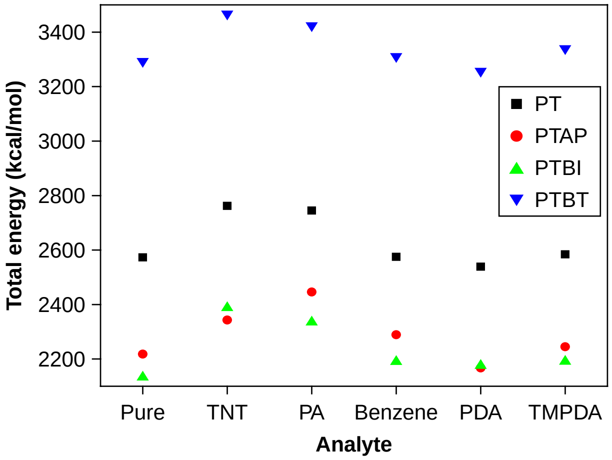


Figure 2. Total energy distribution profile.

interactions, which is in turn due to the electrostatic interaction component.

A plot of total energies of the polymer systems with different analytes is shown in Figure 2. A polymer model without analyte has been taken as reference and is depicted as pure in the graph. All the polymer models behave similarly towards different analytes. Substitution of the electron-withdrawing nitro groups on the aromatic ring lowers the energy of the empty π^* orbitals, thereby making nitro aromatic compounds good electron acceptors [19]. Conjugated polymers are promising candidates for redox sensing because they are electron donors [20] and their donor ability is further enhanced due to delocalisation of π electrons in the backbone chain. Total energy of the polymer models having TNT and picric acid (PA) as analytes show high energy compared to other analytes. As these nitro compounds (TNT and PA) are electron deficient in nature, they interact well with electron donating conjugated polymers and hence the overall energy of these polymer model systems becomes relatively high. In contrast to electron-deficient analytes, electron-rich analytes (p-phenylene diamine (PDA), N,N,N′,N′-tetramethyl-p-phenylene diamine (TMPDA)) will have poor interaction with conjugated polymers. The present study confirms the same and in the similar lines, benzene behaves moderately.

In the case of PTBT, PE of pure polymer and polymer–analyte composite is very high (nearly ≈ 1000 kcal/mol). Energy difference in the PE as compared with PT, PTAP, PTBI polymers composite and this energy contribution may be due to bond stretching, bond angle bending, out-of-plane bending, torsion and steric interaction between side chains.

3.2 *Polymer packing behaviour*

Packing calculations may reveal how effectively polymer chains can pack together in the presence of an analyte and this efficiency depends on the molecular potentials and the nature of polymer–polymer interaction as well as polymer–analyte interactions. In the present study, packing effects in terms of density for the relaxed polymer cells have been compared to understand the conformational changes and intensity of interaction.

Comparison of densities of pure polymers Figure 3 show the following order,

PT > PTAP > PTBI > PTBT.

In the case of 3-substituted PT the presence of side chain affects the free rotation of polymer chain and offers steric hindrance to the overall system in a cell while these constraints are not found in PT. Hence better packing is possible in PT and higher the density.

Figure 4 presents various densities of different polymer–analyte systems. Overall the trend of the unsubstituted PT is different from 3-substituted polymers (PTBI, PTAP and PTBT). In general, 3-substituted polymers have the highest density for the electron-deficient analyte system (TNT), while it is low for electron-rich systems like PDA, TMPDA. Functional side chains of these 3-substituted polymers make the polymer system interact with the electron-accepting analytes. Presence of —OH and NH in PTAP and PTBI can bring more negative charge on these systems unlike PTBT and hence there is a deviation in PTBT. In the case of PA as analyte, the partial negative charge on OH group may create repulsive force towards polymer system and hence it results in poor packing behaviour. This may be the reason for lower density of polymer–PA system compared to TNT. On the other hand, electron-rich analytes may not interact well with 3-substituted polymers as they are already rich in electron and hence, overall, all 3-substituted polymer–PDA/TMPDA systems have similar density. Polymer–benzene system behaves moderately in contrast to other systems.

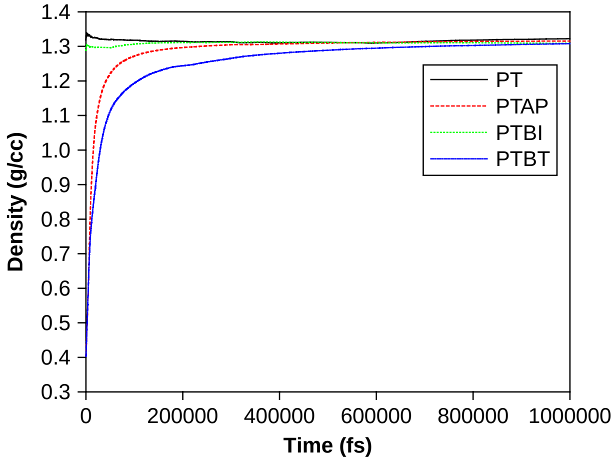


Figure 3. Plot of density versus time of polymer models (without analyte) from NPT-MD simulations.

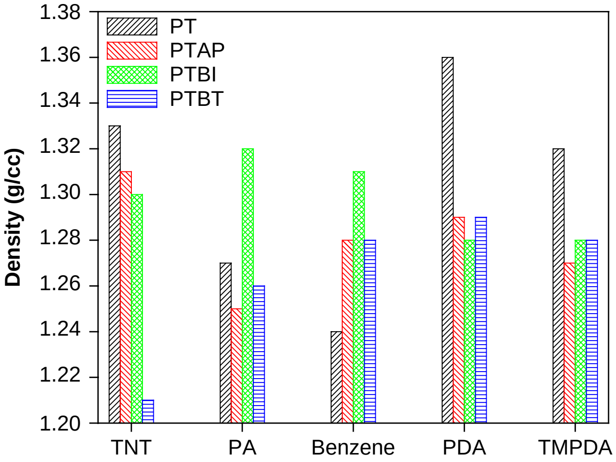


Figure 4. Cell density of various polymer–analyte systems.

3.3 *End-to-end distance (r) and radius of gyration (S)*

In general, polymer molecules assume an enormous number of spatial arrangements given as statistical

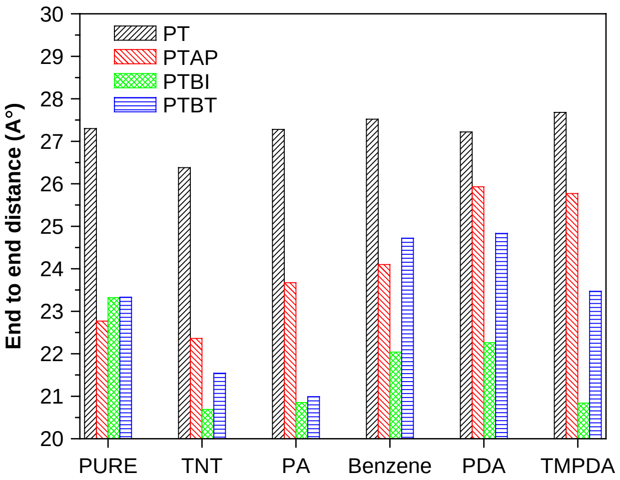


Figure 5. End-to-end distribution analysis of polymer-analyte systems.

(ensemble) averages of some characteristic property. The parameters to specify average global configuration are the distribution and moments of the end-to-end distance and the radius of gyration. End-to-end distribution for the different polymer–analyte systems are shown in Figure 5. In the case of unsubstituted PT, there is no significant change in distance, which may be attributed to the absence of side chain. Comparison of end-to-end distance of various polymer systems without analyte (depicted as ‘pure’ in figures) reveals unsubstituted PT has a high value of about 27 Å while other systems exhibit 23 Å. Presence of side chain offers strain on the polymer backbone and forces the molecule to fold and hence there is reduction in the end-to-end distance value of 3-substituted polymer systems. Electron-deficient analytes (TNT, PA) have less distance distribution than electron-rich ones (PDA, TMPDA) and this trend is similar in all the polymer–analyte systems. It shows that electron-deficient analytes affect the free orientation of polymer in a cell, while this may not be significant in the case of electron-rich analytes since both polymer and analyte are electron rich.

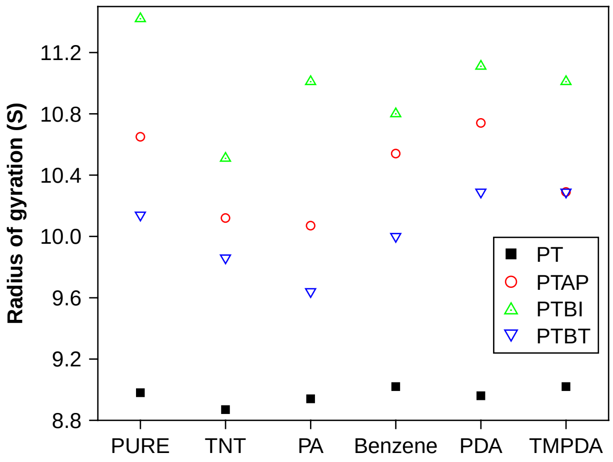


Figure 6. Radius of gyration of different polymer–analyte systems.

Radius of gyration is the root mean square distance of the atoms in the molecule from their common centre of mass. Local chain geometry is frequently characterised by measurements of valence and dihedral angle distributions whose values are essentially determined by a combination of packing effects and local intramolecular interactions that are strongly correlated with global dimensions. Figure 6 compares the radius of gyration values of polymers for the different systems following the reverse trend of end-to-end distance. It is observed that for electron-rich analytes (PDA, TMPDA and benzene), *S* is found to be less as compared to electron-deficient analytes (TNT and PA).

3.4 Pair correlation function

In order to study the changes in the local packing of polymer, which occur during physical processes, polymer–analyte microstructure can be evaluated by calculating the radial distribution function, $g(r)$, from the trajectories [21]. The pair correlation function (the radial distribution function) gives a measure of the probability that, given the presence of an atom at the origin of an arbitrary reference frame, it gives the idea of the distribution of the polymer and analyte in a cell and there will be an atom with its centre located in a periodic cell with different periodic boundary conditions at a distance, r, from the reference atom. It gives the number of atoms found at a given distance in all the directions seen from an atom of interest [22]. The radial distribution function is useful not only because it provides insight into the polymer–analyte microstructure, but also the ensemble average of any pair function may be expressed in the form number of different approaches, which give partial descriptions of orientation ordering developed. Table 2 presents the minimum distance at which interaction starts between the polymer and analyte sets obtained from radial distribution analysis. It can be seen that in general, electron-deficient analytes exhibit interactions even at shorter distances than electron-rich analytes. Table 1 shows the maximum possible $g(r)$ for polymer–analyte system obtained from MD simulations followed by radial distribution analysis. Maximum interaction $g(r)$ is observed in PTBT and PTBI polymers. In case of unsubstituted PT, electron-rich analytes interact better than deficient analytes.

4. Conclusions

This paper reports the interaction of thiophene-based conducting polymer with analyte by the analysis of various parameters obtained from MD simulations. Analysis of parameters like total energy, density, radial distribution function, end-to-end distance in polymer chains and radius of gyration of polymer–analyte system shows the

Table 2. Results of the pair-correlation analysis.

	PT		PTAP		PTBI		PTBT	
System	d[a]	$g(r)_{\max}$[b]	d	$g(r)_{\max}$	d	$g(r)_{\max}$	d	$g(r)_{\max}$
TNT	2.35	0.968	2.05	1.006	2.15	0.990	2.35	0.998
PA	1.95	0.969	2.25	1.001	1.85	1.002	2.55	1.040
Benzene	2.25	1.000	2.35	0.984	2.35	1.006	2.25	1.006
PDA	2.25	1.003	2.05	0.992	2.35	1.003	2.25	1.059
TMPDA	1.95	1.003	1.95	0.958	2.35	0.970	2.35	0.969

[a] The minimum distance at which the interaction starts.
[b] Maximum possible $g(r)$.

variation in these properties with respect to the nature of analytes and side chain on the polymer. PTAP and PTBI show better interaction with analytes like PA and TNT. Hence the study brings out the role of side chain in designing chemical sensory material for the specific analyte. Presently, experimental studies are being carried out to support the simulation results.

Acknowledgements

The authors are thankful to Dr A. Subhananda Rao, Director and Mr V. L. Narasimhan, Associate Director, HEMRL, for their approval to publish this work. The authors thank Professor M Durgaprasad, University of Hyderabad for his valuable suggestions. V. D. Ghule thanks ACRHEM, University of Hyderabad for the financial support.

References

[1] T.A. Stotheim, *Handbook of Conducting Polymers*, Vol. I, II, Marcel Dekker, New York, 1986.

[2] J.V. Hatfield and P.I. Neaves, *A new generation of integrated electronic noses*, Sens Actuators 27 (1995), pp. 223–231.

[3] T.M. Aminabhavi and S.S. Jawalkar, *Molecular dynamics simulations to compute diffusion coefficients of gases into polydimethylsiloxane and poly{(1,5-napthalene)-co-[1,4-durene-2,2′-bis(3,4-dicarboxylphenyl) hexafluoropropanediimide]}*, Polym. Int. 56 (2007), pp. 928–934.

[4] D. Fichou (ed.), *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, New York, 1999.

[5] M.L. Homer, K.S. Manatt, A.M. Manfreda, M.A. Ryan, A.V. Shevade, and H. Zhou, *Molecular modeling of polymer composite-analyte interactions in electronic nose sensors*, Sens. Actuators B 93 (2003), pp. 84–91.

[6] K. Bodenhofer, A. Dominik, W. Gopel, A. Heirleman, and A.J. Ricco, *Conferring selectivity to chemical sensors via polymer side-chain selection: Thermodynamics of vapor sorption by a set of polysiloxanes on thickness-shear mode resonators*, Anal. Chem. 72 (2000), pp. 3696–3708.

[7] N. Guernion, B.P.J. de Lacy Costello, and N.M. Ratcliffe, *The synthesis of 3-octadecyl- and 3-docosylpyrrole, their polymerisation and incorporation into novel composite gas sensitive resistors*, Synthetic Metals 128 (2002), pp. 139–147.

[8] K.C. Persaud, *Polymers for chemical sensing*, Materials Today 8 (2005), pp. 38–44.

[9] P.R. Teasdale and G.G. Wallace, *Molecular recognition using conducting polymers: Basis of an electrochemical sensing technology – Plenary lecture*, Analyst 118 (1993), pp. 329–334.

[10] R. Parthasarathi, S. Radhakrishnan, N. Somanathan, and V. Subramanian, *Quantum chemical studies on polythiophenes containing heterocyclic substituents: Effect of structure on the band gap*, J. Chem. Phys. 123 (2005), pp. 164905–164915.

[11] R. Parthasarathi, S. Radhakrishnan, N. Somanathan, and V. Subramanian, *Structure and properties of polythiophene containing hetero aromatic side chains*, Comput. Mater. Sci. 37 (2006), pp. 318–322.

[12] Materials Studio 4.3, Accelrys Inc., San Diego, CA, 2008.

[13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03 Package*, Gaussian, Inc., Pittsburgh, PA, 2003.

[14] W.A. Goddard and A.K. Rappe, *Charge equilibrium for molecular-dynamics simulations*, J. Phys. Chem. 95 (1991), pp. 3358–3363.

[15] M. Entrilgo-Castano, M. Heuchel, D. Hofmann, A. Lerbret, and Y. Yampolskii, *Molecular modeling investigation of free volume distributions in stiff chain polymers with conventional and ultrahigh free volume: comparison between molecular modeling and positron lifetime studies*, Macromolecules 36 (2003), pp. 8528–8538.

[16] N.Ch. Karayiannis, V. Mavrantzas, and D.N. Theodorou, *Detailed atomistic simulation of the segmental dynamics and barrier properties of amorphous poly(ethylene terephthalate) and poly (ethylene isophthalate)*, Macromolecules 37 (2004), pp. 2978–2995.

[17] N. Cioffi, M.C. Gallazzi, M.M. Giangregorio, S.V. Meille, G. Raos, L. Sabbatini, M.C. Tanese, L. Torsi, and P.G. Zambonin, *Side-chain role in chemically sensing conducting polymer field-effect transistors*, J. Phys. Chem. B 107 (2003), pp. 7589–7594.

[18] H. Gu, T.M. Swager, and F. Wang, *Carbon nanotube/polythiophene chemiresistive sensors for chemical warfare agents*, J. Am. Chem. Soc. 130 (2008), pp. 5392–5393.

[19] R.M. Calhoun, M.J. Sailor, H. Sohn, and W.C. Trogler, *Detection of TNT and picric acid on surfaces and in seawater by using photoluminescent polysiloles*, Angew. Chem. Int. Ed. 40 (2001), pp. 2104–2105.

[20] D.T. McQuade, A.E. Pullen, and T.M. Swager, *Conjugated polymer-based chemical sensors*, Chem. Rev. 100 (2000), pp. 2537–2574.

[21] P.N. Bartlett, N. Blair, S. Friel, J.W. Gardner, and T.C. Pearce, *Electronic nose for monitoring the flavour of beers*, Analyst 118 (1993), pp. 371–377.

[22] M.P. Allen and D.J. Tildesley, *Computer Simulations of Liquid*, Clarendon Press, Oxford, 1987.