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Coarse grain modeling of polyimide copolymers

Arnab Chakrabarty, Tahir Cagin*

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, USA

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ABSTRACT

Addressing the wide span of timescales, where various important phenomena takes place in a polymer system, is inconceivable through a typical molecular dynamics simulation. Coarsening of simpler polymer systems has demonstrated significant potential in computationally characterizing and simulating systems at larger timescales. Addressing the need to extend existing coarsening methodologies on multifunctional materials to help design future generation materials is both promising and challenging. In this paper we present development of an atomistically informed coarse grain bead model of piezoelectric polyimide copolymers for large-scale simulations of thermal, mechanical and especially electrical properties. The coarsening approach generated a gain of two and a half orders of magnitude in terms of computational time and an order of magnitude gain in system size (equivalent to ~ 360,000 atomistic model) while retaining the physical characteristics specific to the piezoelectric polymer. Reasonable agreement was observed between simulation results of the coarse grained and the atomistic model. Specifically mechanical moduli, density, dielectric constant, yield behavior, work hardening, response under dynamic loading and glass transition behavior were analyzed and compared.

1. Introduction

The long timescales required to appropriately sample the dynamics of a polymer system, owing to its long relaxation time, is prohibitively expensive for a typical Molecular Dynamics (MD) simulation. Furthermore, realistic estimates and convincing conclusions especially for amorphous polymers require simulation of a relatively larger system than what a typical atomistic MD simulation can address. Demanding the physics of polymeric systems at different time-scales and length-scales to mimic the thermodynamic limit with the effective use of resources through a multi-scale modelling approach (Fig. 1) spanning over a wide range has become a key problem in present day computational materials research. Transferring the particle-particle interaction information with appropriate tailoring for the next level of modelling hierarchy is non-trivial. Depending on the balance of specificity and efficiency desired, the existing computational models for polymeric materials range from a very fine grain approach like quantum mechanics (incorporating the elecronic degrees freedom) [1]; to a chemically sound approach through proper force fields in classical (MD) simulations; to atomistically infromed coarse grained models [2]; to conventional finite element based model [3] and to field-theoretic models [4,5] which describe the system in terms of composition parameters.

The stiffness of the equations of motions (second order differential equations) are mainly determined by the time scales corresponding to the high frequency modes in models described with atomistic detail; especially for polymeric systems the highest frequency modes arise from the vibrations of the molecular bonds and the periods of these oscillations are in the order of tens of femtoseconds (10^{-15} s).

This limits the integration time step of equation of motion pertaining to the system and restricts the exploration to a smaller domain in the phase space. In hierarchical multiscale modelling (Fig. 1) the next level to MD approach, the Coarse Grain (CG) models can eliminate these fast modes systematically in a non-unique fashion. So far this route has been employed earlier [6–13] on simple systems where the finer details are averaged out in order to simulate larger size models for longer periods of time through development of a lower-resolution model.

Use of coarse grain model in accessing the larger timescale and length scale phenomena [2,14–16] in polymer physics has been demonstrated through various works. One of the important usages is being to accelerate constructing of an equilibrated polymer structure through mapping and reverse mapping from atomistic to CG model [6,17,18]. Studies have been performed on critical issues like mapping techniques [17,18] and systematic approach in building a CG model [9,19,20]. Various approaches such as dissipative particle dynamics [21,22], Boltzmann inversion technique

* Corresponding author. Tel.: +1 9798621449; fax: +1 9798456446.
E-mail address: cagin@che.tamu.edu (T. Cagin).

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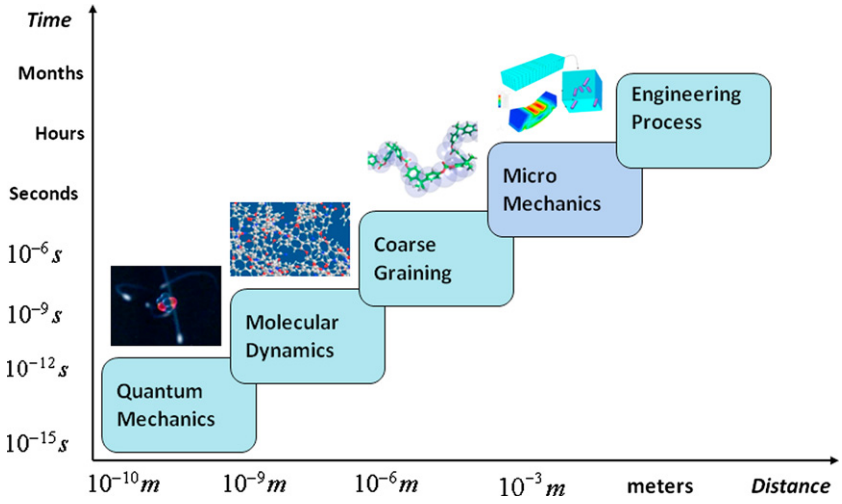

Fig. 1. Multiscale modeling hierarchy.

[18,23], force matching method [24], fitting energy distribution [7,25] have been used to develop coarse grain models of several systems. Successes in CG modelling have been demonstrated through applications on biological systems [13,14,26–28], polymers [8,10,18,29,30] dendrimers [8,31] and complex liquid systems [32,33]. A few noteworthy reviews on existing coarse graining approaches at various levels of multi-scale modelling methodology have already appeared in literature [34–36].

Designing novel multifunctional materials and devices utilizing piezoelectric polymer has been very appealing to scientists and engineers over the last few years. As a result, the interest in piezoelectric polymers has grown substantially in recent years [37–51]. Very few works attempting to address the characteristics of a piezoelectric polymer through computation exist so far [46,52–54] due to time and length scale restrictions imposed by atomistic models. Hence, the extension and specific refinement of the existing CG approaches to model these polymeric systems is both scientifically and technologically important in order to assist the development of future generation materials and devices. Here, the main challenge is not only to represent the structure, thermal and mechanical properties but also the electrical properties such as dipoles and dielectric constants. In our present work, we aim to develop coarse grain model parameters for an amorphous, aromatic, piezoelectric polyimide exclusively based on our atomistic level simulation results and to describe the system without compromising the material specificity while accessing length and time scales of interest. As a result, we have developed an efficient coarse grain modelling approach targeted towards studying the piezoelectric polymers given their potential as future generation material with useful and complex electromechanical properties. The uniqueness of our work is that our work systematizes the coarse grain parameter development for a piezoelectric polymer system. With this parameterization, in addition to accessing larger length scales, we have gained access to time scales in two and half orders of magnitude (result in computational time gain of 2–3 orders of magnitude).

2. Coarse grain model and parameterization

2.1. Choice of polymer system

Piezoelectricity in ceramics and polymers has generated a great interest to researchers [37,46,55–60] owing to its numerous potential applications ranging from microelectronics to actuation and energy harvesting material systems and devices. Among the piezoelectric polymers, PVDF (Poly vinylidene fluoride) has attracted particular attention due to their large piezoelectric response [39,41,42,51,61]. Evidence [38,40,43] of piezoelectric behavior even in widely used Nylon11 has been reported [38]. PVDF's limitation in high temperature applications [49,56], has prompted researchers to look for thermally stable piezoelectric polymers suitable for high temperature applications. The piezoelectric polyimide studied in this work is such a polymer. It is an amorphous, aromatic polyimide substituted with nitrile dipole. Fig. 2 represents the (β − CN)APB/ODPA polyimide monomer. Experiments have shown that amorphous polyimide made from (β − CN)APB/ODPA monomer can generate substantial piezoelectric responses at elevated temperatures [45]. The glass transition temperature (T_g) of the polyimide is close to 500 K [44] ensuring a much larger temperature range for application.

Stimulated by (β − CN)APB/ODPA polyimide's high thermal stability and piezoelectric nature we have chosen this polymer as our model system to develop coarse grain parameters founded on atomistic information and furnish a path to address the challenges involved in understanding the piezoelectric polymer physics at a higher scale to help realize the viability of designing amorphous piezoelectric polyimide as future generation materials.

2.2. Defining a coarse grained system

Coarsening refers to lumping a set of atoms into a single super-atom. The reduction in resolution in the model portrait leads to loss of material detail. Although the term 'coarse graining' has been employed recently to demonstrate such model transformation in polymers; coarsening in the form of united atom model has been used by researchers much earlier [62,63]. In these works on alkanes, the authors treat $-CH_3$ and $-CH_2-$ groups as single atoms. Identifying the set representing the super-atom is a tricky step in its own right as the mapping partially contributes to the degree of sacrifice made in the material detail. It also, in addition, dictates the gain in computational

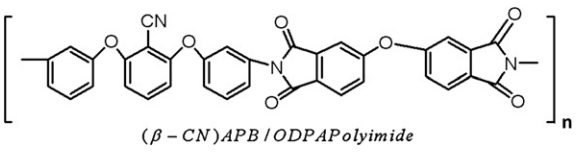

Fig. 2. Chemical structure of (β − CN) APB/ODPA Monomer.

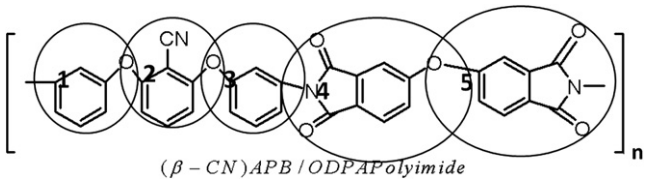

Fig. 3. Coarse grain model of the monomer used in this study.

resources as expected to be achieved through the process. An efficient balancing of the two effects, and retaining materials specificity to a high degree hence play crucial role in defining the super atoms. In our study, based on the structure and dielectric properties of the polymer, the system was coarsened from 62-atoms per monomer to a 5-interaction site per monomer polymer system as illustrated in Fig. 3. The atom-set was defined primarily through lumping the atoms that move in unison. Furthermore, the effective aggregate charge and the resulting dipole on each super atom was incorporated in making the choices in order to guarantee the preservation of the dielectric properties inherent to the system. To preserve the symmetry in the structure and corresponding charges and dipoles, the oxygen atoms connecting the rings and their corresponding properties were equally shared among the rings.

2.3. Estimation of coarse grain model parameters

The choice of interaction potentials and their parameters, a combination that eventually dictates the dynamics of the system, emerges as the next step. The calculation of force on each interaction site is non-trivial and is pivotal to the success of the model. Various approaches translate particle-particle interaction in different ways to its representative force component.

In a dissipative particle dynamics approach the total force is the sum of a conservative, dissipative and random forces. While the momentum is conserved owing to presence of pairwise forces, the energy of the system is not conserved due to presence of random and dissipative forces. The conservation of momentum suggests the applicability of Navier-Stokes hydrodynamics in a DPD approach.

$$F_{ij}^{\mathrm{DPD}} = F_{ij}^{\mathrm{Conservative}} + F_{ij}^{\mathrm{Dissipative}} + F_{ij}^{\mathrm{Random}}$$

System consisting of components varying widely in timescales governing their motions is suitable to be treated by Brownian

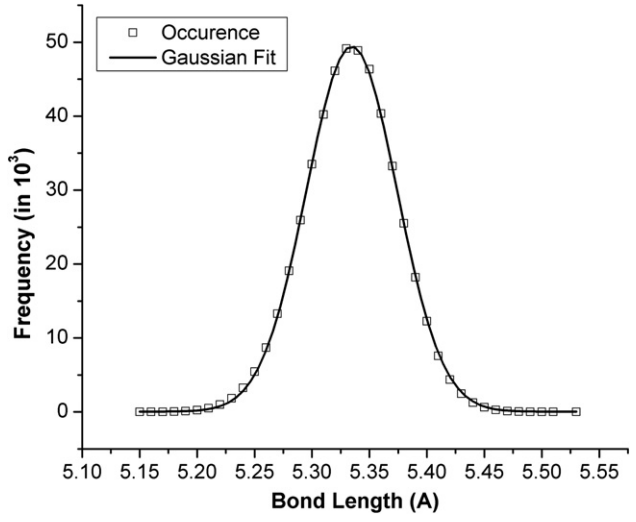

Fig. 4. Energy probability distribution used for determination of the bond stretch parameters.

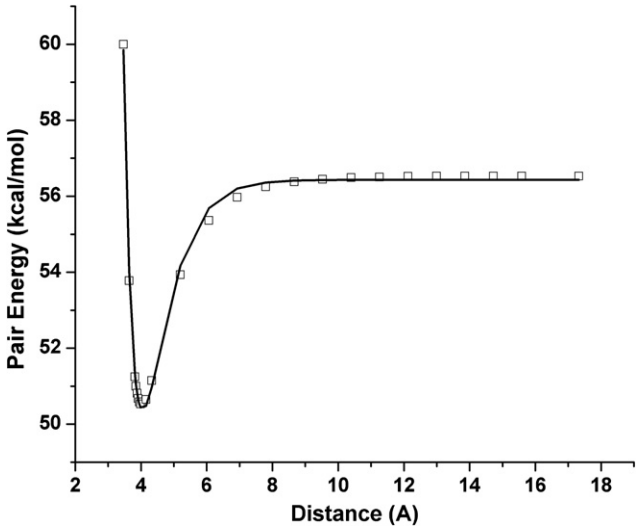

Fig. 5. Pairwise interaction energy data used for determination of van der Waals interaction parameters.

Dynamics [64–66] approach. If the motions of the fastest moving molecules are not of interest their presence is mimicked by a dissipative and random force terms and replaces the Newton's equation of motion by a Langevin equation.

$$F_i(t) = \sum_{j \neq i} F_{ij}^{C} - \gamma p_i + \sigma \xi_i(t)$$

where: the constants γ and σ are function of the system. The approach however conserves neither momentum nor energy implying absence of hydrodynamic behavior at the macroscale.

For better insight of simulation on polymers using Brownian dynamics various studies can be looked at [67–69].

Lattice Boltzmann method, in similar scenarios dealt by Brownian dynamics, treats the solvent molecules using discretized Boltzmann equation and the hydrodynamics of the solvent molecules is correctly captured.

Field theoretic polymer simulation method pioneered by Fredrickson and co-workers [4,5] uses complex chemical potential field to illustrate the energetic of the system. The approach however fails to capture hydrodynamic behavior as momentum is not conserved. The methodology is restricted to the use of soft

Table 1
Estimated parameters for the developed Coarse Grain Model.

Superatom	Parameters		
	D (Kcal/mole)	α	r_0 (Angstroms)
 (Superatom 1, 3)	3.89	2.7	4.82
 (Superatom 2)	5.52	2.7	4.83
 (Superatom 4, 5)	4.98	2.7	6.26

Table 2
Comparison of the properties obtained from all atom MD and CG Model Simulations.

Sample	Beads	Atoms	ρ gm/cc		Dielectric constant $\langle\varepsilon\rangle$ (Kirkwood–Frohlich Method)	
			MD	CG	MD	CG
10_30	1500	18620	1.28	1.26	3.3	1.81
20_30	3000	37240	1.29	1.25	3.03	4.78
15_40	3000	37230	1.26	1.24	2.63	2.32
30_40	6000	74460	1.26	1.26	3.39	2.28
40_40	8000	99280	1.29	1.24	2.88	3.98
80_60	24000	297760	N/A	1.28	N/A	2.45
100_60	30000	372200	N/A	1.27	N/A	3.49

repulsive potentials and is not expected to describe reptation dynamics [34].

In our work, the polymer system has been defined as a bead model. A polymer model with M chains and N monomers per chain has been designated as M_N polymer in this article. While the energetics arising from chemical bonding has been addressed in a similar fashion as found in literature [7], the non bonded terms were treated in a different manner. Instead of combining them together in a single function [2] the VDW parameters were estimated in the absence of any electrostatic forces. The electrostatic forces were illustrated through monopole-monopole interaction. Furthermore, incorporation of PPPM [70] method ensured efficient incorporation of long range forces.

To demonstrate, the interactions among the super atoms were broken into components and were described by the following hamiltonian:

$$E = E_b + E_{\text{angle}} + E_{\text{vdw}} + E_{\text{coul}}$$

In here the force constant and other parameters were estimated from all atom molecular dynamics simulation of a reasonably sized polymer sample, (30 monomers per chain with 10 chains of (β − CN)APB/ODPA polymer) of single polymer chains of different length for several 5ns runs in canonical ensemble using modified CVFF force field. The dynamics of the monomer at the centre of the chain, least influenced by end effects, was considered for parameter estimation. This ensured development of an atomistically informed CG model. The components of the potential energy expression should be interpreted as follows:

E_b : The "bond" stretch energy was described through a harmonic function (Fig. 4):

$$E_b = \frac{1}{2}k_b(r - r_0)^2$$

k_b represents the force constant and r_0 stands for the equilibrium bond length between two interaction centers. Majority of bead spring models treat bond stretch energy as a harmonic function [2,31,71]. Evidence of rigidly constraining the bead-bead distance [71,72] to freeze the high frequency oscillations is also present in literature. The atom center of masses defining the bead co-ordinates were tracked in the production runs of MD simulation and parameters for bond stretching and angle bending energy were estimated through fitting the frequency distribution curve to a Gaussian distribution of the corresponding energy function. As an example, for bond stretch energy, the following expression was minimized:

$$C_b(k, r) = \int_0^\infty dr P(r) - \frac{\sqrt{\pi}RT}{k_b}\exp\left(-\frac{E_b}{RT}\right)$$

E_{angle}: The angle bending energy was represented in a similar fashion with angle values replacing bond lengths.

$$E_a = \frac{1}{2}k_a(\theta - \theta_0)^2$$

To estimate the VDW parameters, individual set of atoms defining a super atom was interacted with its identical structure with different orientation and distance between the centres. The centre of mass of one set of atoms was kept fixed and the other set of atoms were allowed to move in a constrained fashion. The atoms were not assigned any charges to mimic only the VDW interaction. The pairwise interaction energy was then averaged over time for various distances among the bead centres. The interaction energy as a function of distance was then fitted to the functional form of E_{vdw}. The van der Waals energy, was described through a Morse potential (Fig. 5).

$$E_{\text{VDW}} = D\left\{\left(e^{-0.5\alpha\left(\frac{r_{ij}}{r_0}-1\right)}\right)^2 - 2\left(e^{-0.5\alpha\left(\frac{r_{ij}}{r_0}-1\right)}\right)\right\}$$

r_0 represents the equilibrium distance between two non bonded interaction centres and '-D' represents the corresponding non-bonded energy between the two interaction centres at optimum separation.

The charges on the individual atoms were zeroed out to isolate the effect of the van-der Waals interaction and capture it through the Morse potential. The interaction parameters among unlike beads were subsequently evaluated by combination rule:

$$D_{0,ij} = \sqrt{D_{0,i}D_{0,j}}$$

Table 3
Comparison of mechanical properties from atomistic and coarse grain models.

Model	B (GPa)		C_{11} (GPa)		C_{22} (GPa)		C_{33} (GPa)		C_{44} (GPa)		C_{55} (GPa)		C_{66} (GPa)	
	MD	CG	MD	CG	MD	CG	MD	CG	MD	CG	MD	CG	MD	CG
20_30	12.04	10.38	13.54	12.19	13.38	12.19	13.53	12.27	2.25	2.72	2.01	2.72	2.24	2.83
15_40	10.73	9.00	12.32	10.95	12.24	10.99	12.27	10.97	2.39	2.92	2.26	2.98	2.31	2.95
30_40	9.79	10.85	11.20	12.80	11.04	12.89	11.19	12.90	2.12	2.93	1.88	3.06	2.10	3.08
40_40	11.99	10.82	13.32	12.67	13.38	12.57	13.22	12.69	1.99	2.78	2.08	2.63	1.84	2.81
80_60	N/A	12.50	N/A	14.72	N/A	14.81	N/A	14.82	N/A	3.33	N/A	3.46	N/A	3.48

Table 4
Condensed comparison.

Properties	MD Model	CG Model
$\langle\rho\rangle$(gm/cc)	1.28	1.25
$\langle\varepsilon\rangle$	2.98	3.34
$\langle B\rangle$(GPa)	11.14	10.26
$\langle C_{11}+C_{22}+C_{33}\rangle/3$ (GPa)	12.55	12.17
$\langle C_{44}+C_{55}+C_{66}\rangle/3$ (GPa)	2.12	2.87

$$r_{0,ij} = \frac{1}{2}(r_{0i} + r_{0j})$$

$$\alpha_{0,ij} = \frac{1}{2}(\alpha_{0,i} + \alpha_{0,j})$$

The VDW parameters were further refined iteratively to reasonably match the density and bulk and tetragonal shear modulus of the system as predicted by atomistic simulations through bulk phase calculations of CG model (using the MD simulation of 10_30 polymer system as basis for the atomistic data). The final estimated set of parameters determined after several iterations for the CG model which have been used in this study are presented in Table 1.

The charge on each super-atom was calculated by summing the individual charges on each atom constituting the bead. Since the beads were defined based on the atom sets moving in unison, defining the charge on beads in this fashion is expected to show reasonable representation of the dielectric properties compared to all atom simulation. The electrostatic energy E_{coul} was calculated using point charge-point charge coulomb interactions

$$E_{coul} = \sum_i^N \sum_{j=i}^N \frac{q_i q_j}{r}$$

In order to eliminate truncation errors, long range nature of electrostatic energy and forces were evaluated through PPPM [70,73] method to minimize the loss of dielectric information still not tasking the computational resources (as opposed to full fledged Ewald Summation). The cut off for VDW energy and force evaluations were set to 14 Angstrom.

2.4. Validation of the coarse grain model

The CG model developed as described in the section 2.3 was assessed and validated through comparing the density, stiffness and dielectric properties with its atomistic counterpart [54] for piezoelectric polymer system of various sizes in terms of chain length and number of chains used. The results are given in Tables 2 and 3. Experimental studies for the given polymeric system suggest a density value of 1.34 gm/cc [46] and a dielectric constant value of approximately 3.5 at 10 Hz frequency and 300 K temperature [48].

Note that MD simulation was not performed for larger systems (80_60 and 100_60). However the CG model produced consistent results and successfully demonstrated insensitiveness towards scaling issues.

In addition to density and dielectric constants, elastic stiffness coefficients of various systems were estimated and compared as demonstrated in Table 3. Analysis of Tables 2 and 3 shows that the estimated densities, dielectric constants and stiffness coefficients are in reasonable agreement between all atom MD and CG simulations. A condensed (averaging properties from different samples) comparison is presented in Table 4. The 10_30 polymer system was not considered to generate the property average, since it was used as the basis for parameterizing the CG model.

Additionally, we inspected polymer characteristics at the chain level to evaluate the CG model in terms of polymer chain dynamics. Table 5 compares the average end to end distance and the radius of gyration for a chain in each of the polymer systems studied. The basis of the model development, the 10_30 polymer system, showed good agreement in $\langle R_e\rangle$ and $\langle R_g\rangle$ values considering its atomistic counterpart as expected (Note that, the chain end to end distance and radius of gyration values from all atom MD simulations, naturally, were not used as target values in parameterization). The 20_30 polymer system, having the same chain contour length also showed reasonable agreement for these two chain properties considered. On contrary, systems with 40 monomers per chain were found to be scattered and relatively stretched then their fully atomistic MD simulation counterpart. We also observe that chain movement is more in case of CG representation of the polymer system. The absence of rotational degrees of freedom in the CG model forces the beads to respond only in translational motion as an outcome of various interactions. This is expected to result in more movement of the beads leading to such observation. This in turn affects the equilibrated chain morphology and its $\langle R_e\rangle$ and $\langle R_g\rangle$ in a CG model. Similar response is expected when the CG model is subjected to external perturbation. In the atomistic case rotational ability of rings and group of atoms also plays a role to counter external perturbation. Nonetheless in all cases the ratio between $\langle R_e\rangle$ and $\langle R_g\rangle$ are similar for both models across all polymer systems.

Overall, the observed agreement in physical, mechanical and dielectric properties for polymer systems of various sizes between MD and CG model validated our model development approach. This signified reliability of the approach and led to further computational experiments with our CG model.

3. Dynamic stress test of polymer models

3.1. Step stress test

Polymers exhibit viscoelastic behavior. Dynamic mechanical analysis [74] is an experimental technique used to investigate and comprehend this particular phenomenon in polymers. Here we have attempted to observe polymer dynamics in a similar fashion at a smaller scale. The rapid response created through such computational experiment is expected to serve as the foundation for the response observed at the macroscopic scale.

In response to external perturbation the changes in the internal configuration in a polymer system happen in three different scales [75].

Table 5
Comparison of polymer chain properties from atomistic and coarse grain models.

	μ_{R_e} (A)		σ_{R_e}		μ_{R_g}(A)		σ_{R_g}		μ_{R_e}/μ_{R_g}	
	MD	CG	MD	CG	MD	CG	MD	CG	MD	CG
10_30	53.18	51.77	24.47	20.17	26.03	23.19	4.13	3.99	2.04	2.23
20_30	49.29	58.14	22.36	27.23	22.68	31.7	3.93	11.67	2.17	1.83
15_40	46.28	81.63	15.86	32.6	24.67	43.29	4.38	12.3	1.88	1.89
30_40	52.15	83.95	22.94	39.83	24.98	41.47	4.46	14.63	2.09	2.02
40_40	55.39	83.35	18.41	46.29	26.28	40.57	4.33	17.06	2.11	2.05

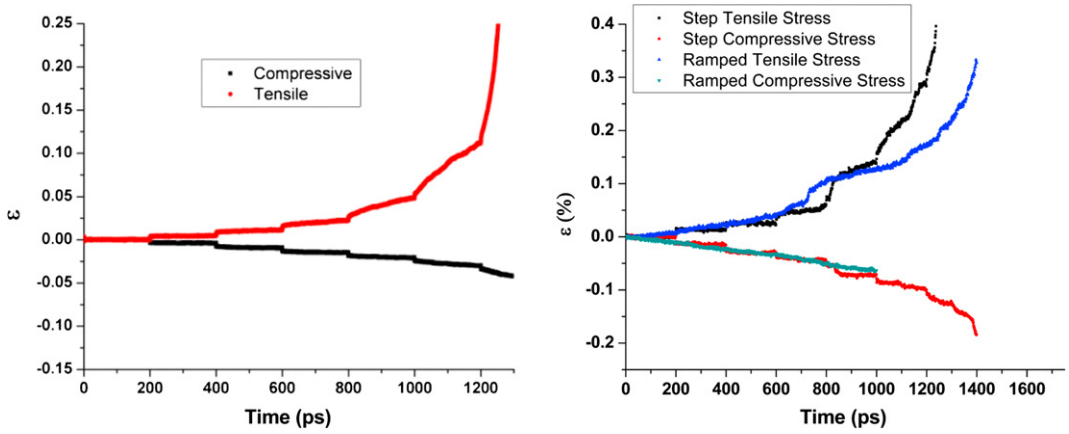

Fig. 6. Instantaneous strain response observed for CG (left) and MD (right) model.

- Long range change in chain contour rearrangement.
- Local rearrangements of a group of atoms.
- Reorientation of bonds on the chain backbone.

The wide range of timescales over which the structure evolves is related to these responses.

In the previous section, we have showed that the developed model could estimate polymer properties reasonably well. The CG model's capability was subsequently examined to represent polymer dynamics and its time dependent behavior. Axial stress, both compressive and tensile, was applied in *z* direction of the polyimide and the response was measured. Stress was applied in steps with increment of 500 atmospheres (~50 MPa) and the system was allowed to relax for 200 ps in between under the given constraints. The experiment is similar in nature to creep test with a larger stress rate.

Fig. 6 illustrates the instantaneous response of 100_60 model polyimide from compressive and tensile step stress. The application of step stress produces a spontaneous response from the polymer chain in the form of instantaneous strain. In similar lines with its atomistic counterpart (simulation of a 30_40 polyimide system), we observe stiffer compressive elastic and yield modulus. The dearth of available space for molecular rearrangement of polymer chains undergoing compression lead to such phenomena.

Furthermore, plastic flow of the polymer chains at higher stress levels and transition from elastic to plastic domain was accurately predicted by the model in agreement with its full atomistic MD counterpart results*. As the stress on the polymer system increases polymer chains strive to counter the external force initially by elastically stretching in the applied stress direction. In the process the chains get stretched and start disentangling. Increment of stress initiates the flow of chains. The strain response clearly shows the increment in strain rate with larger stresses in the plastic region. A similar phenomenon takes place in the atomistic model. However the presence of rotational movement of rings, group of atoms counters a part of the external stress. As a consequence the change in strain rate observed is steeper in the developed CG model.

Similar instantaneous responses were observed for other CG model polymer sets (10_30, 20_30, 30_40, 40_40 and 80_60) as well as their atomistic counterpart and are not presented here.

3.2. Work hardening

Work hardening refers to strengthening of a material through the increase of material's dislocation density. It is also known as strain hardening. As stress is applied on a system beyond its elastic limit; based on the stress level and the application time, it develops permanent deformation through dislocations. As more dislocations are formed, these dislocations acts as a resistance to further creation of dislocations and in turn plastic deformation.

Limited studies exist inspecting the work hardening phenomena in polymers at the nanoscale level [76–78]. However,

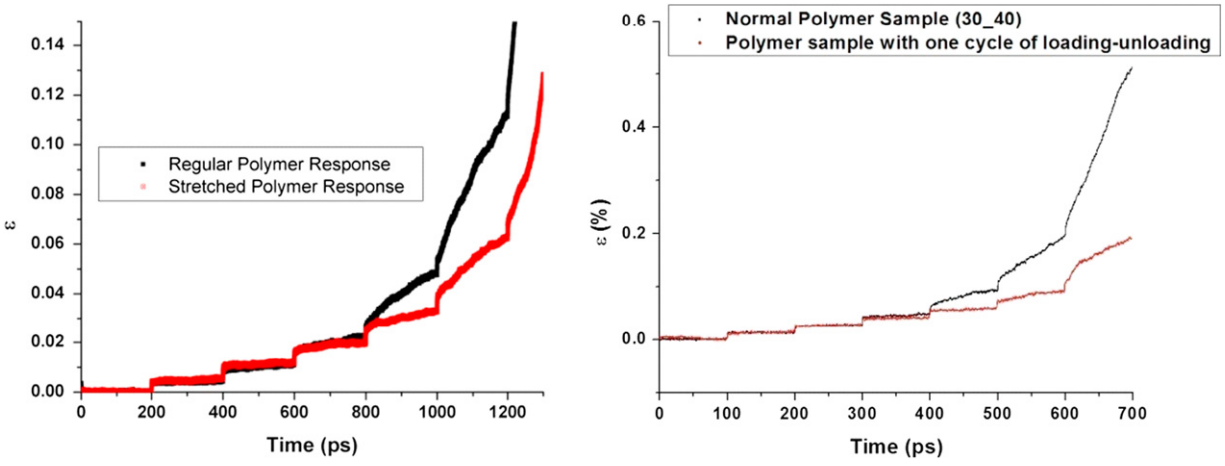

Fig. 7. Work hardening observed in CG (left) and MD (right) model.

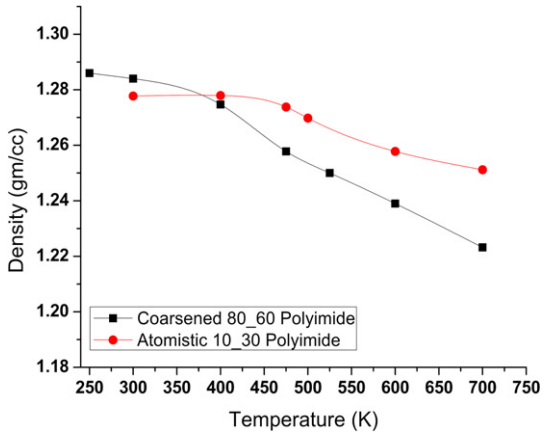

Fig. 8. Temperature dependence of density.

the constitutive modelling of polymer's viscoelastic behavior is expected to benefit largely from information gained at this scale. As an extension of the computational experiments performed as demonstrated in the previous section, the CG model simulations were further analyzed in light of loading-unloading axial stress tests.

The stretched polymer sample in the plastic domain was allowed to relax back under zero pressure condition and was subsequently subjected to second cycle of loading. The applied stress pattern was identical to the one described in the section 3.1. Same approach was also taken in removing stress from the system in steps and help it relax back to a zero stress structure. Identical responses were noted within the elastic region of the polymer samples. The CG model successfully illustrate the work hardening effect in the polymer system in the plastic domain as seen in atomistic simulation. Fig. 7 shows the effect of work hardening in the 100_60 polymer sample. The first loading process made the polymer chains favourably aligned with the 'z' direction (applied stress direction) developing chain ordering parallel to this direction and hence losing the system's isotropy (as amorphous materials are). As a consequence in the second loading cycle, following transition into the plastic domain, the aligned polymer sample showed more resistance to the applied stress than the initially built equilibrated sample (hence increased crystallinity effect). The difference in the acceleration of the flow behavior of chains is clearly noticed in the simulation [54]. The absence of rotational degrees of freedom in the CG model allows the chain only to flow in the direction of the applied stress. On the contrary in the all atomistic model part of the adjustment in response to the external perturbation is expected to be done through ring flipping and rotation of group of atoms, as a consequence the flow is of lesser magnitude.

4. Thermal properties

One of the fundamental rational for chosing (β − CN)APB/ODPA polymer over other piezoelectric polyimide for this study is its thermal stability as pointed out earlier [48,54]. To complement that in a computational approach it is important that the developed model predicts glass transition like behavior in amorphous piezoelectric polymer system accurately. Fig. 8 compares the thermal expansion behavior of 10_30 polyimide as fully atomistic model (18620 atoms) and 80_60 polyimide described by coarse grained model (24000 super-atoms equivalent to 297600 atoms).

The experimental glass transition temperature for the studied polyimide system has been estimated to be close to 500 K [79] and is close to the atomistic simulation estimation (Fig. 8). However, we observe that the CG model shows earlier glass transition like behavior and higher expansion coefficient relative to full atomistic model. For temperatures below glass transition, a typical volumetric thermal expansion coefficient estimated through the CG model for this polymer system. It is in the order of $10^{-4} \sim 10^{-5}$/K which agrees well with the observation for atomistic case, Fig. 8.

The observation of an early glass transition temperature in case of the CG model relates to the elimination of several rotational degrees of freedom existed in the full atom model. The thermal energy assists the acceleration of the glass transition of the sample as no energy is being spent on the rotation of the rings. This is similar to our observation in mechanical property characterization where the full mechanical energy is used for translational motion of the chain in the CG model, leading to an earlier flow of chains in the

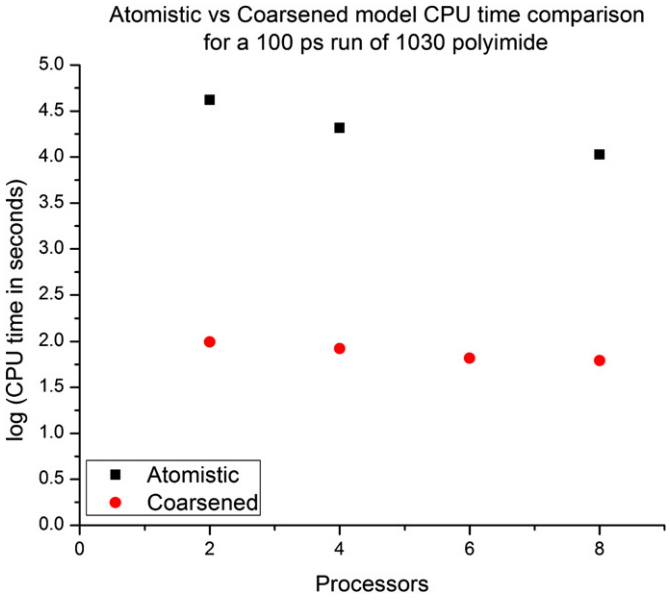

Fig. 9. CPU time comparison semi log scale.

plastic domain. Overall, we observe that estimation of thermal properties through developed CG models predicted similar thermal behavior of the polymer system compared to its atomistic counterpart.

5. Computational gain

Prominent gain in CPU time was achieved through coarsening our polymer system. We observe in Fig. 9 that the CG model developed shows a 200–300 times gain in terms of CPU time while predicting the polymer behavior in reasonable agreement with its atomistic equivalent as demonstrated in earlier sections. The apparent reduction in gain for higher number of processors is due to the higher percentage contribution of communication time between the processors as oppose to the calculation of the model itself.

6. Concluding remarks

In summary, we have developed an atomistically informed coarse grain model of a piezoelectric polyimide that could successfully describe mechanical, dielectric, thermal, chain and time dependent properties of the system. The developed coarse graining methodology for piezoelectric polymer systems emerged as an attractive approach to address longer time and length scale problems. The successful time dependent response prediction has the potential of improving the foundation of constitutive modelling. The advantages come at the price of averaging out individual atom property and their interactions. A two to two-and-half orders of magnitude gain in terms of computational time and an order of magnitude gain in system size through implementation of the model offer considerable rewards.

Barring the effect of rotational degrees of freedom, the model has shown exceptional promise. The absence of these rotational degrees of freedom resulted in underestimation of glass transition temperature. It also lead to overestimation of flow behavior observed through step stress tests. However the model successfully produced outcomes agreeing sensibly with its atomistic counterpart in terms of equilibrium properties, chain properties, mechanical, and dielectric properties. Additionally time dependent properties as plastic behavior and work hardening phenomenon were also successfully demonstrated. The substantial gain in terms of CPU time and the opportunity to extend the system sizes is encouraging. The developed method shows promise of reliably access the domain not readily accessible to fully atomistic MD simulations for a piezoelectric system through coarsening.

Appendix. Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.polymer.2010.03.060.

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