

# Studies on Interfacial Energy and Degree of Miscibility between Polymethylmethacrylates - Polystyrene based Structural Coatings and Emulsions Stability through Computational Molecular Modeling

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## Abstract

*In this present research work, the molecular modeling and the tacticity phenomena of polymers are investigated for industrial coating by means of structural stability of rigid bodies has been utilized to understand the interaction between the polystyrene (PS) and polymethylmethacrylate (PMMA). The polymer composites based coatings and coloring emulsions on rigid structures are potential industrial application, which are promising due to their strength, lightweight, low-cost, chemical stability and tailor- ability. Better understanding of the interface between polymers, ceramics, chemical oxides, metals and metal oxides, as polymers-polymers, polymer – metal oxides interaction will leads to further prospective in this area of research and demanding for various interior and structural coating applications. The calculated interfacial energy reveals that the tacticity plays a significant role in the immiscibility/miscibility of the chosen model systems in addition to the molecular weight. For higher molecular weight system, the decrease in interfacial energy leads to the formation of immiscible system. The experimental observation from these investigations the varying trends in the interfacial energy with molecular weight has been noticed. The interaction of PS with different methylmethacrylate polymers are in progress to understand their order of immiscibility and also to gain the atomistic level interactions.*

**Keywords:** Interfacial energy; PS; PMMA; force field; polymer; immiscibility; coating; structural stability and tacticity.

## INTRODUCTION

The role of polymer composites and coatings in potential industrial applications is promising due to their strength, lightweight, low-cost, chemical stability and tailor-ability of polymer [1-5]. Better understanding of the interface between polymers and ceramics, polymers and oxides, polymers and metals, as polymers-polymers will lead to further prospective in this area of research and demanding for various applications [1-5]. It is important to address the interesting question on how the nature of the interface/ interfacial region does affect the properties of polymers. The interface is the most

important point for initiation of mechanical and chemical properties in polymers [1-3]. The molecular interaction mechanisms between the polymers particularly when the polymers having different tacticity and amorphous state is difficult to quantify and hence to control. Specific studies on modeling polymer materials interface, it is possible to predict various parameters governing the interaction.

It has been known for years that the stereo regularity of polymer chains influences polymer–polymer interaction and due to its availability in isotactic, syndiotactic and

atactic forms of polymethylmethacrylate (PMMA) has been used frequently in the investigation to understand the effect of tacticity on miscibility on different polymers [1-6]. Orientation of side chain *ie* tacticity of polymer has direct the influence on the packing of polymer as well as the physical stability. Polymethylmethacrylate (PMMA) and polystyrene (PS) are one of the simple amorphous polymers, have been used to understand various questions in polymer-polymer interactions [6].

The objective of the most of the modeling and simulation work is to develop an accurate and reliable computational strategy, which can be used to understand and control the interface of any polymers. In this study, isotactic, syndiotactic, atactic PMMA and isotactic, syndiotactic, atactic PS have been selected to predict the interfacial energy of PMMA-PS system. The same tacticity orientation of polymer-polymer interfacial energy of iso PS-iso PMMA, syn PS-syn PMMA, ata PS-ata PMMA are well documented. The interfacial energy of mixed tacticity polymers of iso PS-syn PMMA, iso PS- ata PMMA, syn PS-iso PMMA, syn PS- ata PMMA and ata PS- iso PMMA, ata PS-syn PMMA are also predicted by using molecular modeling and simulation method.

## EXPERIMENTAL SECTION

### *Materials*

Commercial grade poly (methyl methacrylate), sumipex LG grade was procured from Takaroku Shoji Co Ltd, India. The polystyrene polymer was purchased from sisco research laboratories (SRL), India was used as procured. Other polymers and chemicals purchased from Qualigens fine Chemicals, Glaxo India Ltd., India and used without further treatment.

### *Simulation of polymer- polymer interface*

Even though theoretical analysis [7-9] based on the corresponding states theory [10,11] and that of Flory equation-of state thermodynamics [12-14] provided the strong foundations to understand the thermodynamics of compatible polymer mixtures, however deriving atomistic information and these interactions is complicated due to lack of availability of relevant parameterization. Therefore, it is important to develop computational strategy and also to predict the interactions between surfaces of such polymers at the molecular level. Success of using the computer – based molecular dynamics (MD) simulations employing COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field [15] has been demonstrated in various earlier reports [15-18]. In an effort to pursue further a theoretical understanding on polymer-polymer interaction, we have undertaken a detailed study of the interactions of PMMA with polystyrene for the different molecular weights and tacticity.

### *Computational details*

Molecular modeling and simulations were performed using the MS modeling 3.1 software purchased from Accelrys, San Diego, CA, USA [19]. The simulation methodology includes molecular mechanics (MM) and molecular dynamics (MD) calculations using the Discover module [20]. MD was performed using the COMPASS force field [15], which is one of the first initio force field approaches that has been parameterized and validated using the condensed-phase properties. The minimization was performed using the steepest descent approach followed by the conjugate gradient method. The temperature in all the simulations was equilibrated with the Andersen [21] algorithm. The velocity Verlet [22] algorithm was then used to integrate the equations of motion. The non-bonded

interactions have been calculated using group based method with explicit atom sums being calculated to  $9.5 \text{ \AA}^\circ$ . The tail correction was applied to non-bonded interactions during the MD run. The selected one polymer chain was generated with 10 monomer units. It was minimized and amorphous cells were constructed based on the respective densities of selected polymers. The density of the PMMA and PS having  $1.19 \text{ g/cc}$  and  $1.05 \text{ g/cc}$  respectively [23]. The Microsoft (MS) modeling is used to develop the amorphous model and algorithm is originally developed by Theodorou et al [24] and the method of canning is developed by Meirovitch et al [25]. The isomeric state of rotation (RIS) is used to configure and generate the proposed structure of the combined polymer composites. The un composed and tranquil polymer chain composites was described by Flory et al [26].

In order to avoid excessive overlaps between chains modified conditional probabilities were used, which could account for non-bonded interactions between atoms to be placed and rest of the system. Initial structures were minimized by turning on potential interactions such that more severe overlaps were relaxed first and slowly step by step to reach the minimum through the full potential energy levels. The developed and growing polymer chains were observed for continuous growing of its state which is considered for computation of conditional probabilities. The level of convergence of so designed amorphous cell or unit was lowered to  $0.01 \text{ kcal/mol/\AA}^\circ$  by using the same methodology dealt previously. The molecular dynamics based simulation by using constant volume and temperature (MVT) which is normally considered for new development and investigations. The MVT has been utilized to the system equilibrated with 3D periodicity at  $298 \text{ K}$ . The physical properties of composites was

calculated for last half of the run subject to the system at  $200 \text{ ps}$  of dynamics with the path being saved for every  $0.1 \text{ ps}$  while the dynamics run performed for  $10 \text{ ps}$  in the unit.

### ***PMMA –PS Model***

PMMA-PS slab was constructed using the confined layer (cell type) dialog in the amorphous builder. As a part of the amorphous cell construction, a geometry refinement of the structure was performed. Further, 2D boxes were built using the algorithm as described above, whereupon one tacticity of PMMA and the one tacticity of selected PS slabs were piled up and the box was extended by  $80 \text{ \AA}^\circ$  in the c-direction. In order to pile the cells correctly, other polymer systems were selected such that they have almost the same base-size by choosing 'a' and 'b' cell dimensions to be compatible with those of PMMA. Molecular dynamics and computation based simulation was performed in MVT at  $298 \text{ K}$  with a trimmed correction of external cut-off of  $9.5 \text{ \AA}^\circ$  unit. This assumes that the thin layer and the bulk one were at equal effective pressure because of the system under vacuum space. The constant volume system is assumed even the both polymer systems are expand freely. The both system were let to attained equilibrium state under vacuum for  $30,000$  steps in approximation. These conditions was followed at  $300 \text{ ps}$  of Molecular dynamics run and the induced interfacial energy of polymer layers under interaction was predicted and evaluated at  $18 \text{ \AA}^\circ$  cut-off band length without any tail corrections. The applied cut-off distance gives a consistent and reasonably accurate measure of the total energy of interaction of the two layers. Representative structures of PMMA with the polystyrene emerged in this study are illustrated in Fig.1, Fig 2, and Fig 3. A total of  $600$  energy evaluations were performed for each system ( $300 \text{ ps}$  total simulation time).

## RESULTS AND DISCUSSION

### *Interfacial Energy*

The calculated interfacial interaction energies for PMMA-PS for same tacticity are presented in Table 1. It can be seen from the table that tacticity has profound effect on the calculated values of interfacial energy. It is also interesting to note that interfacial energy increases with molecular weight for isotactic systems. For both syndiotactic and atactic combinations, the interfacial energy initially increases with molecular weight and then decreases. High molecular weight of polymer related to the immiscible nature is clear from this observation. This may be attributed to the orientation of functional groups informing the interface leading to lesser extent of interaction. With a view to understand how different tacticity combinations, influence the calculated interaction energy, an attempt has also been made to obtain the interfacial energy for different tacticity combinations. The calculated interaction energy of the layers with different tacticity combinations is presented Table 2. It is evident from the results that combinations of different tacticity have significant effect on the calculated interfacial energy. The changes in the variation may be related to the arrangement of different functional groups at the interface regions.

### *Structural interpretations*

The interfacial interactions between the two layers contain several contributions apart from forces associated with the polar and non-polar parts of the segments. There may be significant contributions from the dipolar interactions originating from the polar parts of the ester groups, if the chains can approach each other closely enough. The interfacial interactions and its differences are confronted and important to explain and discuss the characteristic conformations of isotactic, syndiotactic and atactic forms of PMMA polymer composites has been carried out through this investigation. The previous prediction

on PMMA composite includes the work of Sundar Rajan et al [27, 28] for the isotactic Polymethylmethacrylate.

The major and important conformation on polymer bindings are corresponds to (simply small twisted) trans-trans C-C successive conformations on polymer composite bonds. The other conformations are also significant which may contribute, since the differences in induced energy levels are not huge. The isotactic PMMA is quite flexible and backbone of polymer isotactic composites. The composite syndiotactic polymethylmethacrylate polymer is predicted as a very much preference for all-trans backbone conformation. The backbone conformation's energy level is much greater, which resulting a dominant trans-backbone sequence. At the interface between the composites, the energy levels of these polymer macromolecules will be a affected strongly by their asymmetric surroundings.

The structures of PMMA and PS before and after minimization in the isotactic, syndiotactic and atactic arrangements are shown in Figure.4 and Figure.5. The initial models of PMMA and PS have been considered to be linear with a torsion angle of around  $180^\circ$  in all stereo chemical arrangements. It is evident from the results that bond distances and bond angles are deviate from the standard values after minimization for both PMMA and PS composites. In addition to this observation it can be noted that due to planarity of the C=O group in PMMA composite, an increase in the strain is observed. There is a significant change in the torsion angles of the main chain after minimization. It can be noted from the figures that there is drastic change in the structure of isotactic PMMA when compared to the syndiotactic PMMA. Due to balancing of strain energy in both directions with respect to the backbone there is not much of structural

variation in the syndiotactic arrangement. In, PS the phenyl rings orient in such a way to minimize the energy for different structures.

Different interface models obtained after energy minimization are shown in Figure 4 and 5. It is very important to point out the lateral interactions in different systems which are strongly related to the orientation effects of functional groups at the interface. In the polymer-polymer interface regions,  $\pi$  (PS)... $\pi$  (PS),  $\pi$  (PS)...CH<sub>3</sub> (PMMA) and  $\pi$  (PS)...O=C (PMMA) are the important interactions involved in the stabilization of composite interface in addition to the hydrophobic forces on the polymers. Hence local structural variations in these interface models significantly influence the calculated interactions energy values.

## CONCLUSION

The investigation demonstrated that the interaction between the two polymers

depends on the tacticity and the orientation of various functional groups at the interface plays a significant role in the interaction process. It is evident from the results that the lateral interaction between the two layers strongly related to the structure of the two layers and the nature of both polar and non-polar parts polymers significantly contributes to the interaction. As reported, high molecular weight PMMA and PS blend composites are immiscible. Such an observation can be noticed from the decreasing trend in the induced interfacial energy with the molecular weight. The interaction of PS with different methylethacrylate polymers are in progress to understand their order of immiscibility and also to gain the atomistic level interactions. With these results and reports new kinds of structurally stabled and longlasting coatings and emulsions can be formulated and used for domestic and industrial applications.

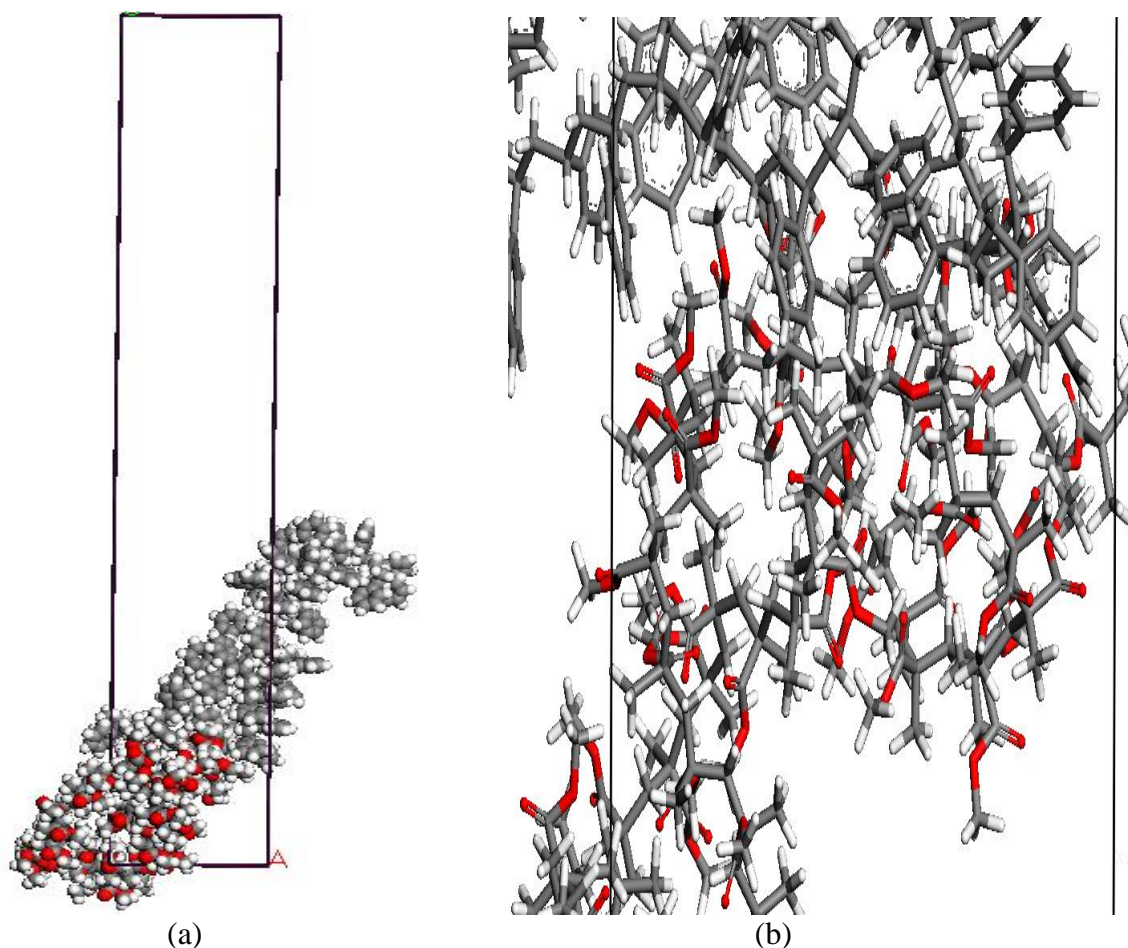
**Table 1:** Interaction energy for the layers of same tacticity

Sl.No	Degree of Polymerization	PMMA		Polystyrene		Interaction energy (kcal/mol)
		Tacticity	M.Wt	Tacticity	M.Wt	
1	10	Isotactic	1000	Isotactic	1040	-20.911(2.451)
2	20	Isotactic	2000	Isotactic	2080	-25.652(3.780)
3	30	Isotactic	3000	Isotactic	3120	-46.074(4.681)
4	40	Isotactic	4000	Isotactic	4160	-51.356(5.631)
5	50	Isotactic	5000	Isotactic	5200	-53.068(6.679)
6	10	Syndiotactic	1000	Syndiotactic	1040	-20.922(2.561)
7	20	Syndiotactic	2000	Syndiotactic	2080	-28.251(3.297)
8	30	Syndiotactic	3000	Syndiotactic	3120	-42.059(3.221)
9	40	Syndiotactic	4000	Syndiotactic	4160	-48.457(4.695)
10	50	Syndiotactic	5000	Syndiotactic	5200	-18.166(7.119)
11	10	Atactic	1000	Atactic	1040	-28.834(3.714)
12	20	Atactic	2000	Atactic	2080	-34.258(4.867)
13	30	Atactic	3000	Atactic	3120	-46.922(7.649)
14	40	Atactic	4000	Atactic	4160	-61.002(5.256)
15	50	Atactic	5000	Atactic	5200	-20.783(6.057)

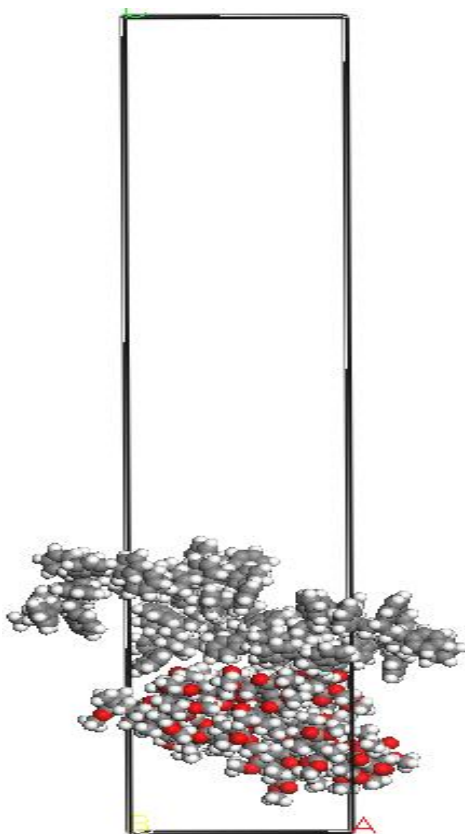


**Table 2:** Interaction energy for the layers of different tacticity

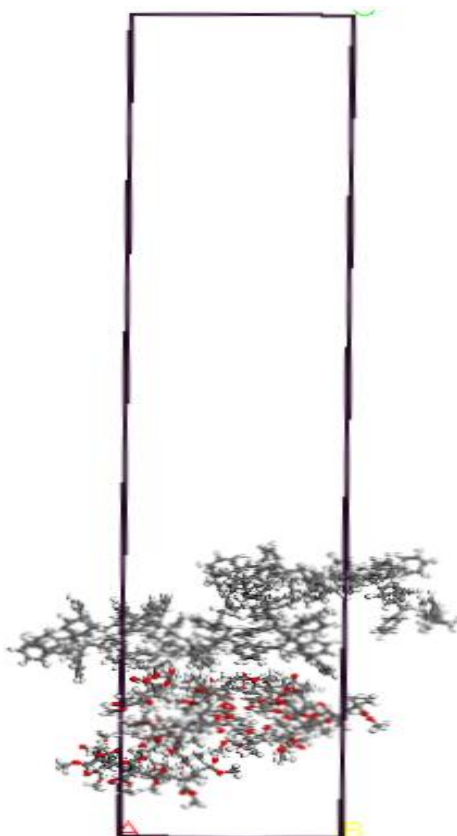
Sl.No	Degree of polymerization	PMMA		Polystyrene		Interaction Energy (Kcal/mol)
		Tacticity	M.Wt	Tacticity	M.Wt	
1	40	Isotactic	4000	Syndiotactic	4160	-39.114 (5.083)
2	50	Isotactic	5000	Syndiotactic	5200	-52.258 (13.038)
3	40	Isotactic	4000	Atactic	4160	-45.176 (5.38)
4	50	Isotactic	5000	Atactic	5200	-41.405 (5.193)
5	40	Syndiotactic	4000	Atactic	4160	-29.438 (13.814)
6	50	Syndiotactic	5000	Atactic	5200	-50.684 (9.150)
7	40	Syndiotactic	4000	Isotactic	4160	-37.772 (4.065)
8	50	Syndiotactic	5000	Isotactic	5200	-47.405 (4.381)
9	40	Atactic	4000	Isotactic	4160	-58.996 (13.138)
10	50	Atactic	5000	Isotactic	5200	-57.528 (13.069)
11	40	Atactic	4000	Syndiotactic	4160	-59.647 (4.528)
12	50	Atactic	5000	Syndiotactic	5200	-50.493 (11.186)



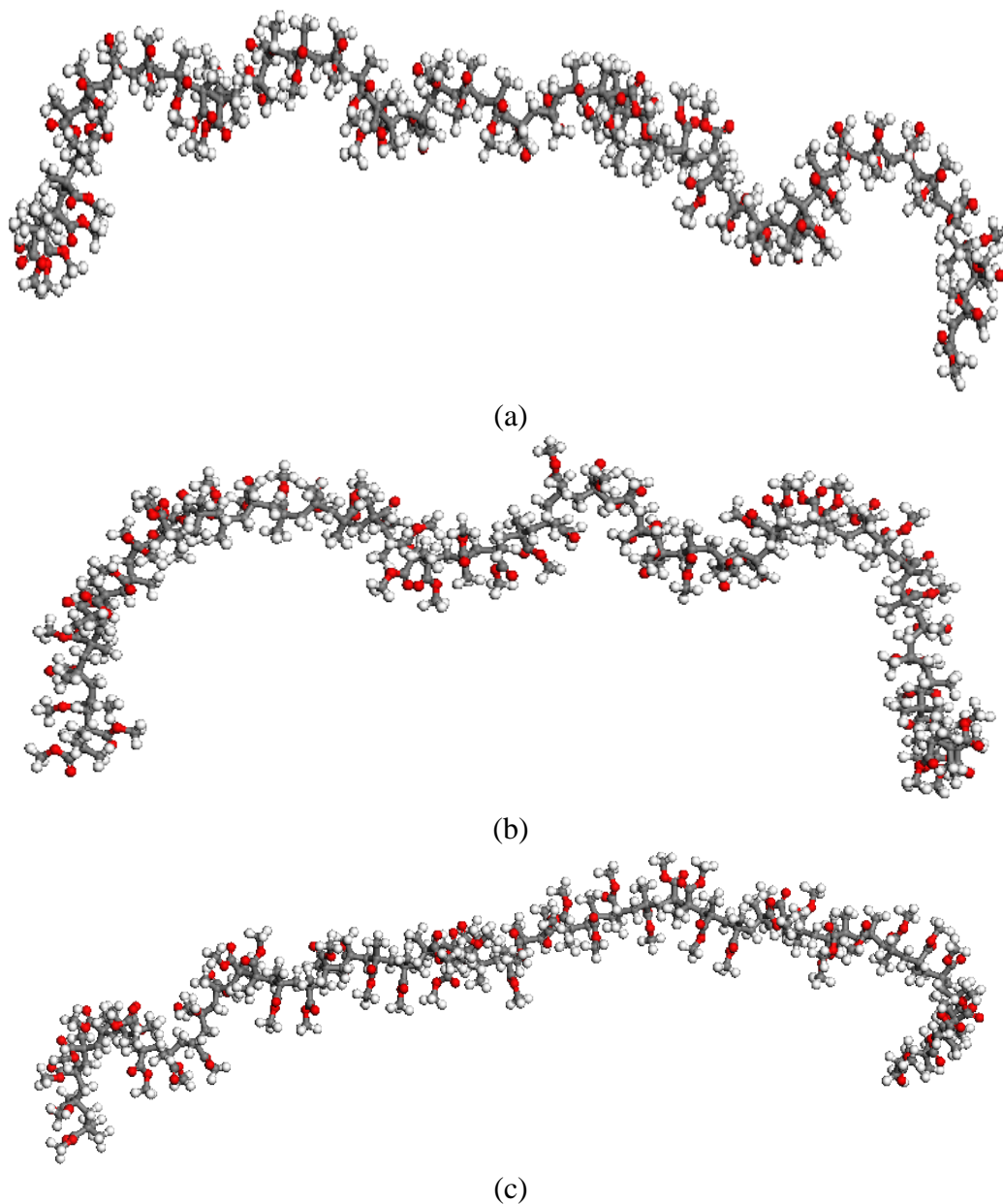
**Fig 1.** (a) A representative structure of Iso-PMMA interacting with Iso-PS of 50 Polymer (b) closed pictorial representation of interacting Iso PS –Iso PMMA of 50 Polymer



**Fig 2.** A representative structure of Syn PMMA interacting with Syn PS of 50 Polymer

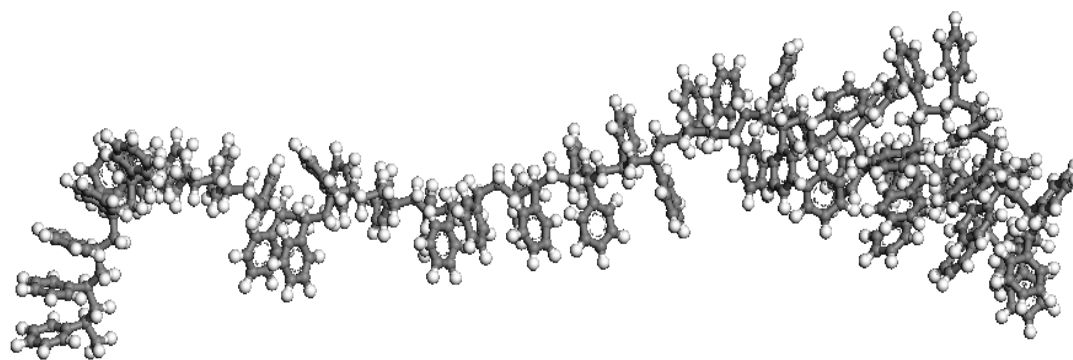


**Fig 3.** A representative structure of ata PMMA interacting with ata PS of 50 Polymer

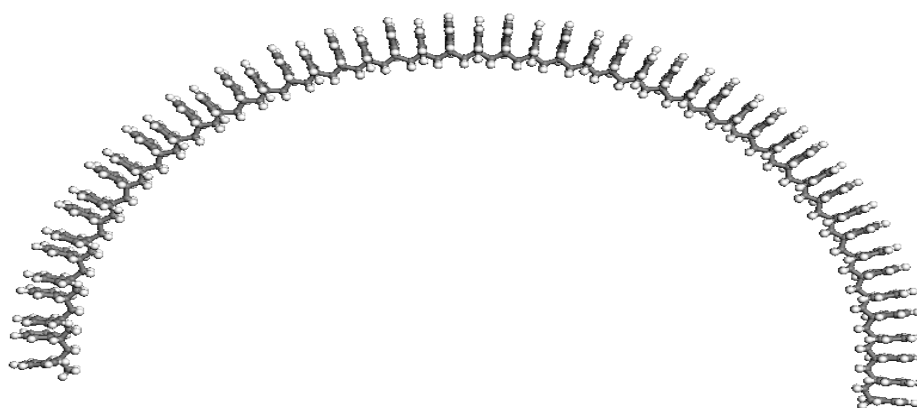


**Fig 4.** (a) Minimized structures of isotactic PMMA 50 Polymer (b) Minimized structures of syndiotactic PMMA 50 Polymer (c) Minimized structures of atactic PMMA 50 Polymer

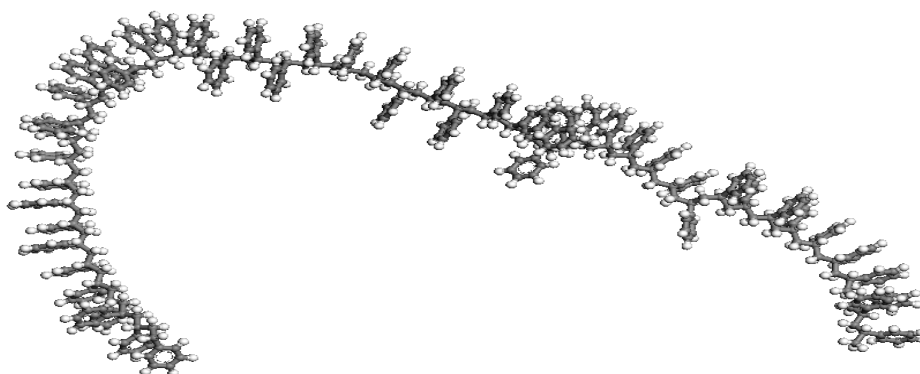




(a)



(b)



(c)

**Fig 5.** (a) Minimized structures of isotactic PS 50 Polymer (b) Minimized structures of syndiotactic PS 50 Polymer (c) Minimized structures of atactic PS 50 Polymer

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