

Chapter 8 Concluding Chapter

8.1 Forewords

Much work has already been undertaken to explain the origins of relaxations in polymers. Many details remain unexplained, however, and this work sought to develop simulation techniques to throw light on the matter. This chapter summarises what was achieved during this PhD. We shall review the reasons for undertaking the work, review what was achieved and suggest avenues for future research.

8.2 Reasons and Objectives

Polymers undergo many dielectric and mechanical relaxations. Although the origin of these relaxations is not fully understood yet, it is believed that they are created by local rearrangement of the structure. In polymers with side groups, rearrangement in the side group is believed to be responsible for some of the relaxations. To understand how the side group motion influences the relaxations, experiments and simulations have been undertaken to investigate the properties of polymers.

The smallest side group that can be rotated, the methyl group has an energy barrier to its rotation of a few kJ mol^{-1} (e.g. 8.4 kJ mol^{-1} in PVME) and rotates quickly. It was studied experimentally by quasi-elastic neutron scattering in PMMA[1] and PVME[2]. These works were later confirmed by molecular simulations performed in our group at the University of Leeds [3-5]. After these successful methyl group studies it was decided to investigate whether the motions of larger groups could be simulated. The methoxy group in PVME was the ideal candidate. Some crude simulations suggested that the methoxy rotation could be responsible for the β relaxation observed by dielectric spectroscopy[6]. Moreover, the dielectric spectrum of PVME was available in literature[7, 8]. The PVME model generated by Saelee had been successful in predicting the x-ray scattering spectrum of PVME and its methyl motions. Hence it was known that reasonable simulation cells could be constructed.

However, the methoxy group is large. As large groups tend to rotate slowly MD simulations were not appropriate to simulate the methoxy group. Other techniques were required. The Quasi-Static method had been used in parallel with MD simulations while studying the methyl motions[3-5] and achieved good results for this group but needed to be tested on a larger group. The umbrella sampling method had also been used to study

the rotation of the ester side group[9]. However, this method failed to predict relaxation strength correctly. A lack of rearrangement in the environment was blamed for this. It was believed that MD simulations implemented in the umbrella simulations were too short compared to real dynamics to let the system accommodate the group in the new site. The energy of the new site was too high and the strength of the relation too small to be observable. If the umbrella sampling method had difficulty in providing a sufficient rearrangement, it was doubtful that the QS method which is based on minimisation could provide the rearrangement needed. However, the speed of computers has improved much since Smith et al's published their article in 1992[9]. Longer MD runs in the umbrella sampling simulations might have been able to produce the necessary rearrangement.

Polymers without side groups, such as polyethylene, also show several relaxations. For this type of polymer, the relaxations can only come from the backbone. Simulation tools to investigate relaxations in backbone chains need to be developed. A protocol which search for the transition state in the backbone has been developed by a co-worker Taining Liang. This protocol has been tested on a short linear chain.

8.3 Models

The method used to create the cells was similar to the one used by Dr Saelee[4, 5] to study the methyl group in PVME. Initial cells at low density and high temperature were generated using a combination of well-known algorithms (Chapter 2). Those cells were then cooled by MD simulations at constant pressure to the temperature of 150 K. Intensive QS simulations were performed to rotate the methoxy groups. The umbrella sampling simulations were less successful.

8.4 Summary of the Results

8.4.1 Quasi-Static simulations

8.4.1.1 Energy profiles and structure

The study of the methoxy group rotation began with the Quasi-Static simulations. The methoxy group energy profiles varied greatly and were usually strongly asymmetric. The *trans* conformation of the methoxy group was on average 4.44 kcal mol⁻¹ above the *syn* conformation but could vary for individual groups from about -1 kcal mol⁻¹ up to about 11 kcal mol⁻¹ where it cease to be a minimum state. We

thought that the strong asymmetry might be due to asymmetric chain configurations. We investigated the influence of the triad tacticity on the energy profiles. Our hypothesis was invalidated as it was found that the local tacticity has little effect on the energy profile. The variety of profiles originates from the environment.

8.4.1.2 Static analysis

Using a simple model, the static dielectric susceptibility generated by the rotation of the methoxy group was calculated. Somewhat unexpectedly, the susceptibility found was reasonably high and close to the experimental value:

s	χ	\pm	$\Delta\chi$	T / K
Experimental	0.12	\pm	0.01	118 to 158
9.5 QS	0.068	\pm	0.010	150
12 QS	0.101	\pm	0.015	150
3-site	0.121	\pm	0.014	150
Integral	0.096	\pm		143
Uncorrelated	0.109	\pm	0.014	150
Correlated	0.093	\pm	0.013	150
RRDM	0.085	\pm		138 to 248

Table 8.1: Susceptibility created by the rotation of the methoxy group in PVME.

Because of a large energy difference between the *trans* and *syn* conformation, most of the methoxy groups have a very low polarisability. However, few groups have similar energy in the two states. Those a few groups are highly polarisable and give PVME its susceptibility. Typically, 4% of the groups contribute more than 90% of the susceptibility. Because those groups are rare, many methoxy groups have to be rotated by Quasi-Static method to find the few that will polarise the medium.

In similar work previously undertaken[9], too few groups were rotated to find the few highly polarisable groups. Then, the susceptibility was strongly underestimated. A lack of rearrangement in the environment was blamed for this. It was in fact due to the variety of the energy profiles.

A correlation study was performed. Although non-exhaustive, it suggested than strong correlation may exist between close highly polarisable groups. As highly polarisable groups are sparse, the effect of the correlations is limited.

8.4.1.3 Dynamic analysis

The dielectric loss curve as a function of the frequency has been reconstructed. The simulated dielectric spectrum seems to fit the experimental β relaxation curve. Using similar analysis to the experimentalists, we manage to predict the mean activation energy, standard deviation, and attempt prefactor with reasonable accuracy.

Analysis of the correlation between the prefactor and energy barriers of individual groups showed that the spreading of the loss peak is caused by a distribution of energy barriers rather than a distribution of attempt prefactors. The RRDM model assumed a unique prefactor. This hypothesis is confirmed.

Because of the closeness between the experimental β loss curve and the one generated by rotation of the methoxy group, it is reasonable to believe that the rotation of this group is responsible for a sub-glass β relaxation in PVME.

8.4.2 Umbrella sampling simulations

We estimated that around 40 hours of CPU time are necessary to obtain from umbrella sampling simulations the energy profile of one methoxy group. It would take a horrendous time to rotate the 1488 groups that have been rotated by Quasi-Static simulations.

Irreversible paths are common when a complex system is forced. The umbrella sampling method is blind to irreversible shifts and gives an unreal energetic profile.

As the Quasi-Static method was already giving satisfactory results, we decided to give up further research on the Umbrella Sampling method.

8.4.3 Backbone study

The protocol developed by Taining Liang to search for the transition state was tested on a small chain. Comparisons with MD simulations showed that the method could predict relaxations in the backbone chain. The expected modes were correctly predicted. The method is also much faster and cost less memory than the valley walking or other methods.

8.5 Suggestions for Future Research

The study of correlations between the methoxy groups suggested that correlations existed between close and highly polarisable groups. However, this study was not

exhaustive. How the environment behaves once a methoxy group has rotated remains obscure.

The Quasi-Static method worked for PVME. It showed that the methoxy group was responsible for the β relaxation of PVME. However, only a small fraction of the groups really contributes to the process. More research is needed to determine whether other branched polymers have similar behaviours. A good candidate for this type of research could be Poly(epichlorohydrin)(PECH) as experimental data for this polymer are widely available[8, 10-13].

The transition state search protocol has been validated on a small carbon chain. Taining Liang had begun tests on a larger molecule in a cubic cell. More work is required to validate the method on large molecules. The method could also be used to search for relaxations in large side groups where a simple Quasi-Static simulation would fail.

Finally, our work concerned only dielectric relaxations. There is a formal correspondence between dielectric relaxations and mechanical relaxations (Table 8.2). Simulations of molecules in cells with minimisations of the lattice volume could be used to investigate mechanical relaxations.

Spectr.	Ensemble	Free Energy		Pertubating Energy	Fluctuation		Response	
		Name & Notation			Fluctuation of	Notation	Name & Notation	
Diel.	NVT	Helmholtz	F	$-\mu \cdot E$	Dipole	$\langle \mu^2 \rangle$	Susceptibility	χ
Diel.	NPT	Gibbs	G	$-\mu \cdot E$	Dipole	$\langle \mu^2 \rangle$	Susceptibility	χ
Mech.	NVT	Helmholtz	F	$-P\delta V$	Volume	$\langle V^2 \rangle$	Compliance	J
Mech.	NPT	Gibbs	G	$V\delta P$	Pressure	$\langle P^2 \rangle$	Modulus	Y

Table 8.2: Correspondence between dielectric and mechanical relaxations.

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