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Atomistic modelling study of relaxation processes in polymers: the β-relaxation in polyvinylchloride

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Activation energies related to the β-relaxation process in polyvinylchloride were calculated from atomistic simulations. Pure Boyer and Schatzky crank-shaft type motion seem idealised situations which rarely contribute to relaxation in amorphous polymers. However, the activation energies accompanying other types of local conformational transitions were found in the appropriate range to account for the β-relaxation. Moreover, the present results suggest that local conformational transitions may account for both the β-relaxation as well as the α- or glass transition in polyvinylchloride, whereas motions related to the glass transition involve considerable distortion of the environment next to the conformational transition. The results obtained point out possible answers to long-standing questions concerning the details at the molecular level of the glass-transition and the secondary relaxation mechanism in an amorphous polymer. © 1997 Elsevier Science Ltd.

(Keywords: relaxation; mechanical properties; molecular simulation)

INTRODUCTION

It is well-known that relaxation phenomena[1] in polymers are related to the onset of motion of (parts of) the polymer chain. A typical example is the glass transition. Generally the molecular motion responsible for the relaxation phenomena cover a range of time-scales spanning orders of magnitude. Experimental information on the relaxation phenomena can, for example, be revealed from dielectric spectroscopy measurements[2]. In general, details on the molecular mechanisms involved have been difficult to establish, if obtained at all[3,4]. The nature of the glass transition is one of the most remarkable and still unsolved problems in the theory of the solid state[5]. It is still under review whether activation barriers relating to relaxation phenomena in polymers are dominated by the torsional barrier contribution, i.e. intermolecular effects constitute a minor contribution, or that both play an important role[6–9]. As a typical example, there is a long-standing controversy whether the glass, or α-, transition and the secondary, or β-, transition in main-chain polymers are induced by the same molecular mechanism. Molecular simulations might be valuable in elucidating the nature of the molecular motion involved in relaxation phenomena in polymers. Because the time-scale covered by the relaxation phenomena ranges from less than 10^{-7} s up to hours, it is unfeasible to perform straightforward atomistic molecular dynamics simulations explicitly revealing the molecular motions related to the named transitions. Consequently, if simulations have to teach us something with respect to the molecular motions involved, another approach has to be adopted. One approach involves short time-scale molecular dynamics simulations, typically comprising the nanosecond time range, from which the time-correlation function may be evaluated, for example, for torsional motions[10–13]. The results from these simulations have been compared to available experimental n.m.r. data[14–16]. Recent n.m.r. experiments have allowed for the study of rotational diffusion in polymers over eleven orders of magnitude, i.e. 10^{-11} to 10 s. The results from the simulations have been compared to those of the n.m.r. in the regime of very short time scales. The interpretation of what happens during the mechanical α-transition, i.e. at longer time scales, is therefore dependent on whether short time-scale features are reminiscent of the molecular processes involved at longer time scales. Although the n.m.r. data by themselves extend to a much longer time scale, the interpretation of these data is obviously model dependent, and was often based on a model assuming small-angle reorientational dynamics[14]. More positively, Spiess et al. have argued that the finding that the correlation times as corroborated from n.m.r. experiments obey the WLF equation, indicates that the dynamics monitored by the n.m.r. experiment are intimately linked to the dynamics of the glass transition.

The state-of-affairs summarised above indicates, in our opinion, that not only more but also other types of simulations are required to confirm the character of the molecular motions involved in mechanical relaxation phenomena in polymers. Whereas the full molecular dynamics simulation involving time scales in the range 10^{-7}–10 s is presently totally unfeasible, analysis of the energy barriers corroborated from constrained simulations and adopting the transition state theory may provide us with the essential additional information. Details of the method will be outlined later. This type of constrained simulation is a feasible option aiming at further elucidation of the molecular motions related to relaxation phenomena in polymers, assuming that a sensible model is available for testing and verification.

Simple but practical models have been developed which appear to yield a working relation between the glass

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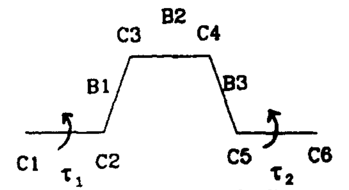
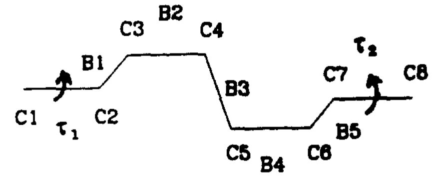


Boyer crank–shaft



Schatzky crank–shaft

Figure 1 Boyer and Schatzky crank-shaft type motion. Rotation over the torsional angles τ_1 and τ_2 is simultaneous (in-phase)

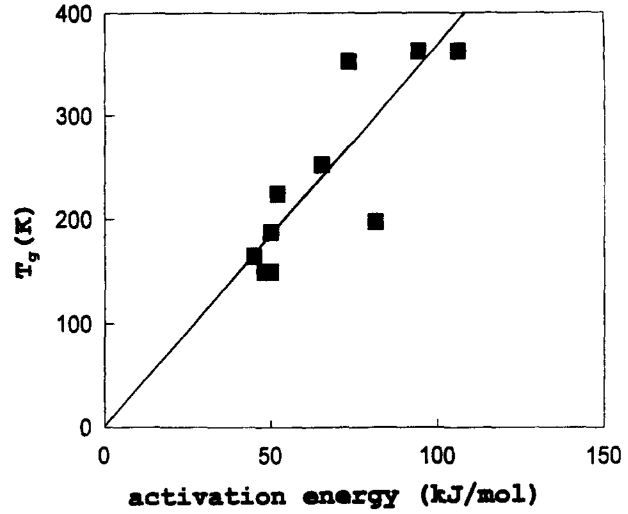


Figure 2 A relation (Ref. [4]) between the glass transition temperature T_g (K) and the calculated activation barrier ΔE_{act} (kJ/mol) according to $\Delta E_{act} = 5E_{\text{cohesive energy density per bead}} + 2E_{\text{rotational energy}}$. The set of ($\Delta E_{act}$, T_g) reads: (1) polyethylene (48;150); (2) polypropylene (65;253); (3) poly(isobutylene) (81;198); (4) polystyrene (94-106;363); (5) polyvinylchloride (73;353); (6) polytetrafluoroethylene (52;225); (7) polyoxymethylene (50;188); (8) polydimethylsiloxane (50;150); (9) polybutadiene (45;165)

transition temperature T_g and a quantity entitled 'activation barrier' of a local molecular motion considered for the secondary or β-relaxation[7–9,17]. It has been assumed that the moving unit involves a relatively small number, n, of beads of the polymer chain, e.g. $n = 2$–5, which is considered the smallest unit for rotation. Known proposed types of motion are the Boyer ($n = 3$) and the Schatzky ($n = 5$) crank-shaft motion illustrated in *Figure 1*, which have the terminal bonds in these sequences lying colinear. As a typical example, five bonds or beads named B1–B5, indicated in *Figure 1*, are rotated as a stiff unit around the bonds indicated by τ_1 and τ_2. When the molecular motion is treated within energy barrier model (Arrhenius-type mechanism) with an activation barrier E_{act}, the transition rate is given by

$$k = A \exp\left[\frac{-\Delta E_{act}}{kT}\right] \qquad (1)$$

A has the character of a collision factor and its value is commonly assumed to be in the range of a low molecular vibrational frequency, e.g. $10^{13}\ \mathrm{s}^{-1}$ (see Ref. [3] for further comments). For a more general account on the description of relaxation behaviour in polymers using Arrhenius plots we refer to the excellent reviews by Heijboer[3,18]. The attractiveness of the Boyer and Schatzky crank-shafts is that the, initial, all-trans structure seems to guarantee a minimum friction to rotation in the bulk polymer environment. The onset of such type rotatory motion is often assumed to be related to relaxation behaviour in polymers.

In the simple model illustrated in *Figure 1* the activation energy E_{act} needs to be quantified. This quantity was previously proposed[4] to be calculated as twice the bond rotation energy around τ_1 and τ_2, respectively, and the additional energy for rotating the centre n beads which was estimated by taking n times the cohesive energy density per bead. Taking $n = 5$ as suggested for the Schatzky crank-shaft

$$\Delta E_{act} = 5E_b(\text{cohesive energy density per bead}) + 2E_\tau(\text{torsional energy}) \qquad (2)$$

A linear relationship between the calculated activation energy ΔE_{act} and T_g was obtained when the number of beads chosen was 5, as illustrated in *Figure 2*. For polyvinylchloride (PVC) the values $E_b = 8.6$ kJ/mol and $E_\tau = 15$ kJ/mol were adopted. The latter value equals the experimental rotational barrier for ethylchloride, C_2H_5Cl. A similar approach as given in equation (2) was presented by Bershtein et al.[9].

It is generally considered that the local motion represented by Boyer or Schatzky crank-shafts[19] is related to the β-transition in PVC rather than to the α- or glass transition. The relation displayed in *Figure 2* can therefore be considered surprising because it suggests a relation between a local motion (crank-shaft) and a non-local collective behaviour which is responsible for the α- or glass transition. However, in a polymer without side chains, both the local motion involved in the β-relaxation and the chain motion involved in the glass transition, must involve main chain motions, and it may be anticipated that a mutual relation exists[20–22]. More strongly it was advocated by Johari[23] that for main-chain polymers the α- and β-relaxations are caused by the same (local) molecular motion. The solution to this problem is possibly related to another problem regarding the explanation of relaxation phenomena. When motion of short sequences of the main chain are responsible for the secondary relaxation phenomenon, and long sequences of the main chain being responsible for the glass or α-transition, one might question why there cannot be active motions involving other lengths of segments of the main chain, i.e. segments involving 7, 9, 11, ... monomer units, resulting in a continuous, monotonically, varying dielectric loss spectrum. Dielectric spectra on, for example, PVC[24,25] clearly show two regimes with two maxima.

Evidently the model exemplified here is a super simplified model. One simplification is by taking just 5 beads only. Secondly, the environment was taken account of by incorporating the cohesive energy density per bead. This simple approach seemed a good first estimate as illustrated by the relation displayed in *Figure 2*. However, in a dense polymer system it is not the entire cohesive energy density that is lost when rotating the unit depicted in *Figure 1*, and, secondly, the effect of rotating this unit might extend a considerable distance from the rotating unit. A fully atomistic simulation on the dense polymer allows for these effects. In the present paper we will discuss the results from such simulations obtained on a fully atomistic model representing amorphous PVC. In order to propose a certain characteristic motion in PVC which might account for the motional phenomena observed by the dielectric and n.m.r. spectroscopies, and which simultaneously lead to a more detailed, i.e. an atomistic, picture of this type of motion related to relaxation phenomena in glassy polymers, we have performed an atomistic simulation study of crank-shaft-like motion in PVC. Initially, we have adopted the crank-shaft-type motion depicted in *Figure 1* as an appropriate physical model. Concerted rotation around bonds related to τ_1 and τ_2 will be carried out by varying the angles τ_1 and τ_2 stepwise. Because, as we will see later, pure crank-shafts are hardly found present in the amorphous polymer structure, motions starting from conformations which do not have their initial terminal torsional angles equal to or very close to 180° will be referred to as (n-bond) conformational transitions, which are most likely characterised by the terminal dihedral angles τ_1 and τ_2. In analogy to the Boyer and Schatzky crank-shaft type motions, we may thus refer to a three- or a five-bond conformational transition, respectively.

ATOMISTIC MODEL AND SIMULATION METHOD

A PVC box was created according to the method proposed by Theodorou and Suter[26]. The DISCOVER version 2.9.5 program was used as implemented in the Biosym/MSI software*. A single PVC chain of 200 monomers with a meso-diad ratio of 0.55 was considered. The ratio of 0.55 was assumed on basis of the n.m.r. data of Barendswaard and Litvinov[27]. The density of this material was given as 1.38–1.40 g/cm. Adopting this density in our simulations, the cubic unit cell had a length of 24.63 Å when using a 200 monomer polymer chain as the elementary building block of the polymer. A bulk polymer was simulated by applying periodic boundary conditions to the unit cell.

In order to describe the interactions in atomistic detail, an all-atom force field of the form

$$E_{\text{pot}} = \sum_b [K_2(b-b_0)^2 + K_3(b-b_0)^3 + K_4(b-b_0)^4] + \tag{3}$$

$$\sum_\theta [H_2(\theta-\theta_0)^2 + H_3(\theta-\theta_0)^3 + H_4(\theta-\theta_0)^4] +$$

$$\sum_\phi [V_1[1-\cos(\phi-\phi_1^0)] + [V_2[1-\cos(2\phi-\phi_2^0)]$$

$$+ [V_3[1-\cos[1-\cos(3\phi-\phi_3^0)]] +$$

$$\sum_\chi K_\chi \chi^2 + \sum_{i>j} \frac{q_i q_j}{r_{ij}} + \sum_{i>j} \epsilon_{ij} [2(r_{ij*}/r_{ij})^6]$$

was employed, with $r_{ij} = [(r_i^6 + r_j^6))/2]^{1/6}$ and $\epsilon_{ij} = 2\surd(\epsilon_i \epsilon_j r_i^3 r_j^3/[r_i^6 + r_j^6]$. The successive terms in the above equation are the bond stretch term (b), the valence angle term (θ), a three-term Fourier expansion of the torsional potential (ϕ), an out-of-plane term (χ), a Coulomb term, and finally a Lennard-Jones 9–6 potential for describing the van der Waals interactions. All force field parameters were taken from the known consistent valence (CV) and CFF91 force fields previously developed by Hagler et al., respectively[28,29]. In the CVFF the van der Waals term is represented by a Lennard-Jones 6–12 potential and there are no higher order terms in the stretch term or in the valence angle term. We emphasize therefore that no specific fitting has been carried specific for PVC, i.e. the force field employed is a generic force field for organic and polymer molecules. Cross-terms have not been taken into account.

After the formal construction of the box, the polymer chain in the box was subjected to energy minimisation techniques in order to find an energetically favourable structure. This process partly involved the use of molecular dynamics simulations, i.e. simulated annealing at T = 400 K, which allows for passing over small energetic barriers while searching for a lower energy structure. In the calculations the long-range van der Waals interactions beyond a certain distance were neglected. This was accomplished by defining a distance cut parameter ('cutdis'); van der Waals interactions over a distance longer than this given distance are entirely neglected. In order to avoid discontinuities in energy and energy derivatives, simply cutting the non-bonded interactions has to be avoided. The incorporation of a switching function causes the van der Waals interaction to decrease smoothly to zero. The switching function causes the van der Waals interactions to decrease in a continuous way from the full potential to zero over an interval given by the switch distance parameter ('swtdis'). Finally, since during the simulation atoms might move into or out of the distance range set by the distance cut parameter, a buffer width is defined, outside the distance cutoff range, in which the atom positions are updated in every cycle of the calculation. This buffer width is given by the difference between the cut distance parameter ('cutdis') and the cutoff parameter ('cutoff') in the DISCOVER program. Numerically, parameter settings 'cutoff = 8.5 Å', 'cutdis = 7.5 Å', and 'swtdis = 1.5 Å' have been used.

The energy minimised unit cell was subsequently taken as the starting point for further simulations involving forced conformational transitions. The rotational energy profile associated with these conformational transitions is calculated by stepwise simultaneous variation of the torsional angles τ_1 and τ_2. Each of these torsional angles is being defined by four main chain carbon atoms, namely *Figure 1*. Force field minimisation at fixed τ_1 and τ_2 combinations were carried out in two steps. Firstly, a steepest descent minimizer was employed until the maximum derivative was less than 0.1 kcal/Å, and subsequently a conjugate gradient optimizer was applied until the maximum derivative was less than 10^{-3} kcal/Å. Initially, torsion angle increments of $\Delta\tau$ = 6° were tried. However, immediately after each increment in τ the van der Waals energy rose enormously, leading to a very large scatter in minimised energies as a function of τ and meaningless energy profiles. Reasonably continuous energy profiles were obtained after resetting $\Delta\tau$ to 1°. After some testing it turned out that a step size of 2° was an acceptable compromise. The latter value was adopted in the calculations reported in this paper.

RESULTS

The torsional potential for the monomer C–C bond

Because the main chain conformational barrier is one of the crucial quantities in the planned simulations, we initially

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* Models developed using software programs from Biosym/MSI—computed with the DISCOVER force field program and displayed using the INSIGHTII molecular visualisation program

evaluated the rotational energy profile for ethylchloride, C_2H_5Cl. The energy profiles were calculated using both the consistent valence force field (CVFF) and the CFF91 force field, whereas for each of these force fields one set of calculations did include the charges (Coulomb term), whereas another set was generated in which the charges were set to zero (no Coulomb term in the force field). We obtained calculated rotational barriers of 14.1 kJ/mol for the CVFF without charges, 14.1 kJ/mol for the CVFF with charges, 13.0 kJ/mol for the CFF91 without charges and 17.3 kJ/mol for the CFF91 with charges. When these values are compared to the experimental barrier for ethylchloride, i.e. 15.1 kJ/mol, we conclude that the CVFF calculated barriers are most, and sufficiently, close to the experimental value. We subsequently decided to continue the polymer simulations employing the CVFF force field without charges after considering the following. The value of the rotational barrier itself is well represented while neglecting the Coulomb term in the force field employed. Coulomb interactions are long range and therefore proper convergence has to be accounted for. In a bulk polymer, however, screening of the Coulomb potential takes place and, therefore, a distance dependent dielectric constant ought to be included as practised by, for example, Smith et al.[30]. Smith et al., however, also showed that the pair distribution function for a PVC melt is independent of inclusion of Coulombic interactions.

Rotational energy profiles of conformational transition-type motion in bulk PVC

Starting from the energy minimised PVC box, an arbitrary set of two torsions τ_1 and τ_2 was chosen representing a three-bond conformational transition. Because the actual initial values for τ_1 and τ_2 were 176.29° and 171.47°, respectively, this conformational transition is very close to a true, co-linear, Boyer crankshaft which has these angles set at exactly 180°.

From the rotational energy profile of the three-bond conformational transition, a barrier to rotation of 45.2 kJ/mol was obtained. This value may be compared to the value obtained from the previously mentioned simple model, namely equation (2), approach yielding $\Delta E_{\text{act}} = 3E_b + 2E_\tau$

Figure 3 Typical five-bond conformational transitions studied in amorphous PVC. The centre bond in the yellow monomers indicate the bonds corresponding to the torsional rotations τ_1 and τ_2

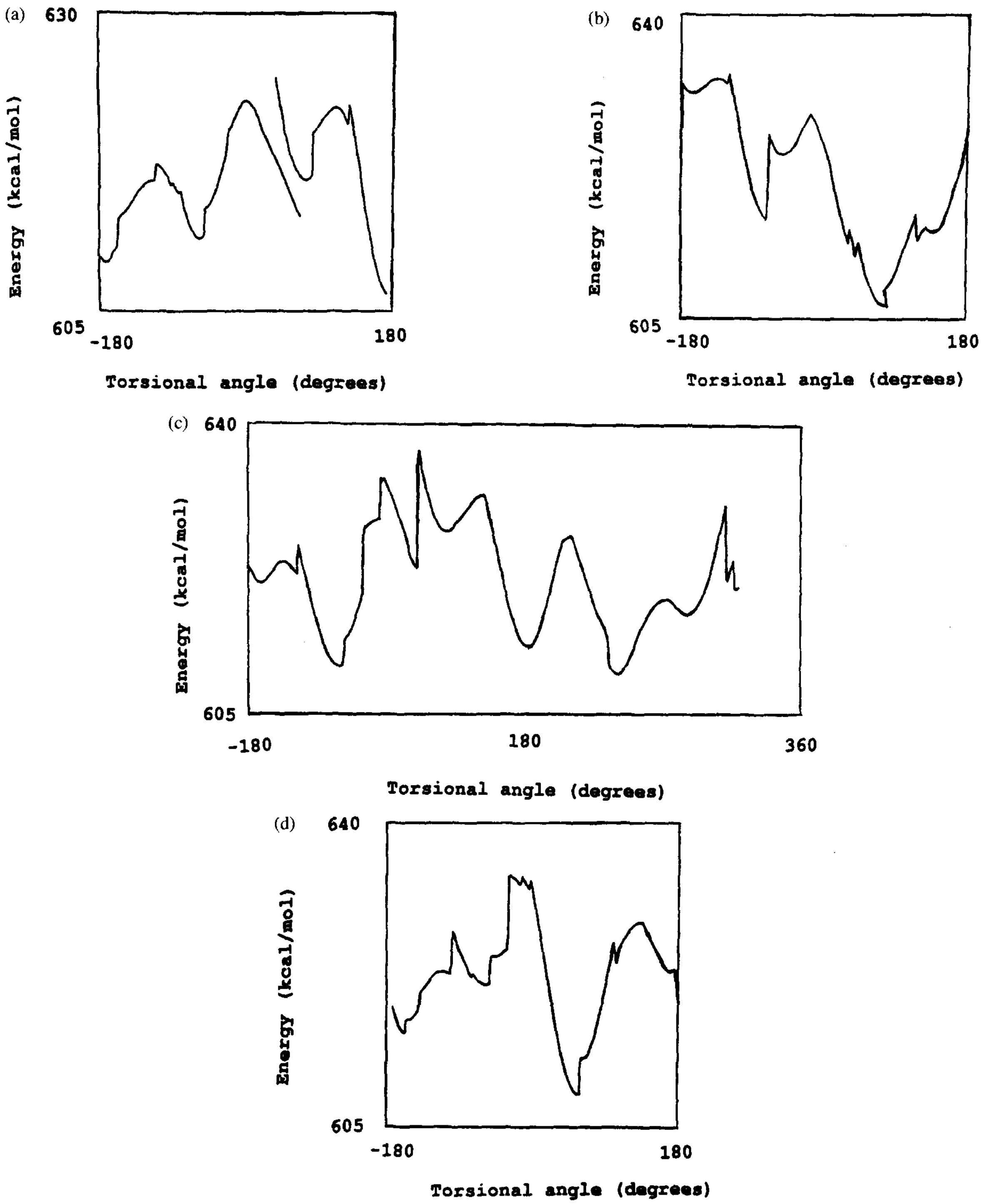

Figure 4 Torsional energy profiles for five-bond crank-shafts. The total energies in units of kcal/mol as they originated from the force field program DISCOVER have been retained in order to keep the values verifiable by other investigators. The non-continuous behaviour in (a) is caused by the fact that energy was rising considerably when starting at $\tau_1 = 180°$ and subsequently decreasing this angle stepwise. When starting from a smaller value for τ_1 the curve $-180°$ to $+70°$ was obtained. These features are a result of the different local environments at $\tau_1 = 70°$ for the structures corresponding to the two seperate curves displayed

= 55.8 kJ/mol. The value of 45.2 kJ/mol corroborated from the present atomistic simulations is not unique, i.e. the local environment of the rotating unit will affect the actual barrier height, as will later be demonstrated for five-bond rotations. Next, a five-bond conformational transition was studied. Some typical five-bond five-bond conformational transitions studied have been marked in *Figure 3*, in which the torsional rotations (τ_1 and τ_2, see *Figure 1*) are around the central bond in the yellow monomers. The calculated torsional energy profile for a five-bond conformational transition is shown in *Figure 4a*. This conformational transition comprised the monomer sequence from the formerly discussed three-bond conformational transition, with the same first torsion $\tau_1 = 176.29°$. Like in the simulation of the three-bond conformational transition, the five-bond conformational transition simulation was started at $\tau_1 = 176.29°$ and this angle and its counterpart five bonds away were simultaneously varied in a stepwise manner (step size 2°). The potential energy curve was found not continuous near $\tau = 70°$ (see *Figure 4a*), which is caused by the fact that energy was rising considerably when starting at $\tau_1 = 176.29°$ followed by a step-wise decrease of this torsional angle. When reversing the direction of the steps, which implies increasing the angle τ_1 across 180°, the torsional energy profile for the torsional angle range $-180°$ to $+70°$ was obtained. The difference in energy profile between forward and backward scanning the torsional angle is caused by differences in local environments at $\tau_1 = 70°$ for the structures corresponding to the two separate curves displayed. The final results show a profile showing three local maxima, with three different barrier heights. The actual values are 34 kJ/mol, 49 kJ/mol and 67 kJ/mol. Again one may wish to compare these values with the value $\Delta E_{\mathrm{act}} = 3E_{\mathrm{b}} + 2E_{\tau} = 73$ kJ/mol calculated from the simplistic model of equation (2).

The few data obtained from atomistic simulations seem to indicate that the barrier height for conformational transitions does not necessarily simply increases with increasing length of the rotating unit. Even for a single value of n, e.g. $n = 5$, a considerable spread in energetic barriers is observed. Interestingly, true Boyer or Schatzky type crank-shafts with all-trans sequences are not a requirement to have three- or five-bond conformational transitions with acceptable energetic barriers to relate to the β-relaxation process in PVC. The intermediate torsional angles (initial values before rotation of the unit) in the five-bond conformational transition studied took the values $\tau_{\mathrm{B1}} = 168.7°$, $\tau_{\mathrm{B2}} = -178.8°$, $\tau_{\mathrm{B3}} = -99.5°$, $\tau_{\mathrm{B4}} = 171.5°$, and $\tau_{\mathrm{B5}} = 79.7°$ (see *Figure 1*).

In order to obtain further details on the effect of the local environment on the energy barriers, we have studied another three five-bond conformational transitions in the same bulk PVC structure, which have been marked in *Figure 3*. The rotational energy profiles obtained for these five-bond rotations have been displayed in *Figure 4b–d*. It is evident from the potential energy profiles shown that energy minimisation at each consecutive torsional angle increment is often a pain: some spiky features remain. The corresponding local energy barriers, calculated by taking the energy difference between local minima and local maxima while the spiky features were disregarded, are 48, 69, 95 and 108 kJ/mol for *Figure 4b*, 39, 54, 58, 68, 78 and 96 kJ/mol for *Figure 4c*, and 51, 86 and 105 kJ/mol for *Figure 4d*. This set of values shows an even larger spread in activation barriers for the five-bond conformational transitions than previously obtained.

DISCUSSION

We have considered conformational transitions in amorphous PVC. For the three-bond transition our local geometry had torsional angles initially at (see *Figure 1*) $\tau_{\mathrm{B1}} = 168.7°$, $\tau_{\mathrm{B2}} = -178.8°$ and $\tau_{\mathrm{B3}} = -99.5°$, respectively, whereas for the first of the four five-bond transitions the corresponding values were $\tau_{\mathrm{B1}} = 168.7°$, $\tau_{\mathrm{B2}} = -178.8°$, $\tau_{\mathrm{B3}} = -99.5°$, $\tau_{\mathrm{B4}} = 171.5°$, and $\tau_{\mathrm{B5}} = 79.7°$. The attractiveness of the pure Boyer and Schatsky crank-shafts is that the initial essentially all-trans structure seems, at least in principle, to guarantee a minimum resistance of the bulk polymer environment against rotation. The question arises whether true Boyer and Schatzky crank-shafts have smaller rotational barriers and therefore truly determine the three- and five-bond conformational transitions in practice. Rather than selecting a Boyer and Schatzky crank-shaft in the amorphous polymer structure and subsequently calculating the corresponding rotational energy profile, we have enumerated the number of Boyer and Schatzky crank-shafts in the PVC unit cell of *Figure 1*. The enumeration was accomplished in the following way. Referring to *Figure 1*, a minimum requirement for a sequence to be entitled a Boyer or Schatzky crank-shaft, i.e. both bonds belonging to τ_1 and τ_2 being practically colinear, is that the angles C1C2C5 and C1C2C6 should both be close, and for a pure Boyer crank-shaft be equal, to 180°, whereas the angles C1C2C7 and C1C2C8 should be equally close for a Schatzky crank-shaft. For the three-bond torsion we selected for our actual calculations, the angles found were C1C2C5 = 137.3° and C1C2C7 = 139.2°, respectively, showing immediately that we do not have a proper Boyer crank-shaft. For the three-bond Boyer type crank-shaft this minimum requirement was not met for any torsional angle after visiting 300 torsional bonds, and we found only three cases of a possible Schatzky crank-shaft after having visited over 200 different torsional bonds. These numbers imply that the concentration of Boyer and Schatzky crank-shafts is pretty low and, in fact, too low to be held responsible for macroscopically observed relaxation phenomena. On the other hand we have seen that more general three- and five-bond conformational transitions involve rotational energies that are well within the range of activation energies corroborated from, for example, dielectric spectroscopy. These types of transitions are therefore suggested to be the basis for the molecular motion responsible for some of the relaxation phenomena in amorphous polymer systems.

The energy barriers corroborated from the profile depicted in *Figure 4* suggest that activation barriers for five-bond conformational transitions are certainly not always dominated by the contributions from the main chain C–C rotational barriers only (2 × 15 = 30 kJ/mol in the present case). All energy barrier values obtained have been collected in *Figure 5*, from which a slight maximum in the range around 60 kJ/mol seems to be suggested. Some of the barriers obtained after rotating a five-bond torsion fall in the range where we expect the glass transition, i.e. around an energy barrier of 100 kJ/mol or a time scale of seconds (all referring to ambient or slightly elevated temperature). Regarding the relation between the computed activation barriers and experimental dielectric spectra, the following comparison can be made. From Figure 6 of Ref. [3], showing Arrhenius plots of the secondary maxima for

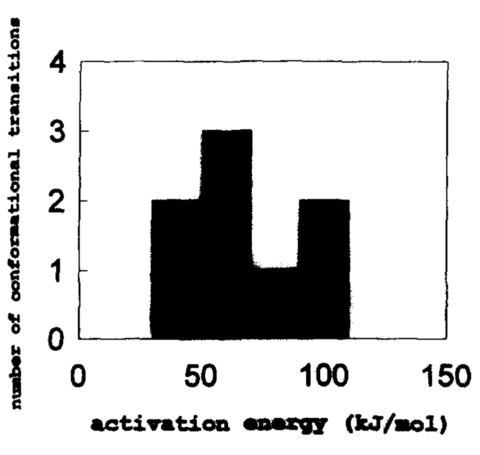

Figure 5 Number of five-bond conformational transitions in amorphous PVC per range of activation energies. Individual data points shown were derived from the potential energy curves shown in *Figure 4*. Although the statistics are insufficient to draw definite conclusions, there is a first indication of the presence of a maximum near 60 kJ/mol (β-transition range) and a lower maximum near 100 kJ/mol (α- or glass transition range)

several polymers, i.e. for PVC the β-transition, we corroborated that for PVC $\log\nu = 6.2$ at $T = 400$ K. This implies $\nu = 10^{6.2}$. With the pre-exponential factor set at 10^{13} (collision rate, see also Ref. [3]), we obtain $\exp\{-\Delta E/kT\} = 1.6.10^{-7}$, and $\Delta E/kT = 15.7$. Herefrom, at $T = 400$ K, $\Delta E = 52.0$ kJ/mol. The maximum obtained from the dielectric spectra is in reasonable agreement with the maximum in the density we find from *Figure 5* (around 58 kJ/mol when we average over the numbers between 50 and 70 kJ/mol). The range of 50–70 kJ/mol corresponds to a frequency range of 3×10^6–7×10^3 Hz, i.e. 10^{-4}–3×10^{-7} s, which matches well with the full width at half height of the dielectric loss curve related to the β-relaxation process in PVC reported by Steeman et al. (Figure 4 in Ref. [24]).

Concerning the spatial displacement of the polymer structure during a conformational transition, it was observed that even far from the area where this conformational transition takes place atoms may be displaced as much as 3 Å, which implies that the matrix is much more elastic than commonly considered on basis of the, generally assumed, more likely Boyer and Schatztky crank-shafts. The apparently relative ease of displacement of far-away atoms might be consistent with the observation[3] that the β-loss peaks in amorphous polymers are only slightly sensitive to changes of free volume corroborated from the experimentally observed insensitivity on cooling rate[31].

The relatively high activation energies (around 100 kJ/mol) observed for each of the five-bond conformational transitions (*Figure 4*) are expected to involve, apart from the two rotational barrier contributions due to C–C bond rotation ($2 \times 15 = 30$ kJ/mol), a substantial contribution from other terms in the potential equation (equation (3)). These high barrier values observed directly touch the question whether these high barriers are a consequence of local motion only (the five-bond conformational transition), or that a much longer part of the main chain is involved. We have analyzed the 95 kJ/mol barrier from *Figure 4b* and the 105 kJ/mol barrier from *Figure 4d*. The torsional angles were measured along the main polymer chain in order to reveal the extent to which these torsional angles are affected by the local five-bond conformational transition. The torsional angles measured have been collected in *Table 1*. From these data it is concluded that only those main chain torsional angles which are close to the conformational transition are seriously affected during rotation. Qualitatively, this result is in agreement with simulations on polyisoprene reported by Moe and Ediger[11], and by the n.m.r. data on atactic polypropylene presented by Schaefer and Spiess[16]. When we combine this observation with the representation in *Figure 5*, this provides evidence for the model, forwarded by Johari[31], that the secondary and primary relaxation in main chain polymers are intimately connected, i.e. they result from the same molecular origin. It contradicts general statements (Ref. [1], p. 108) that activation models which involve local motion only correspond to secondary relaxation phenomena. Our observations imply the β-transition involves energy changes consisting of torsional energy and local non-bonded energy terms, whereas for the motions responsible for the α-transition significant changes in the long-range non-bonded interactions are involved. The latter finding seems to agree with the statement that correlation–time distributions are related to spatial inhomogeneities[32–34] suggesting that the structure of the local environment determines the character of the conformational change, and from there whether it falls within the domain of either the α- or the β-type transition. The reported findings also seem to agree with the results from simulations similar to ours, performed on polyethylene[35].

Table 1 Torsional angles along main polymer chain around the five-bond crank-shaft for two situations, both involving a high energetic barrier. The two left-hand columns refer to the 95 kJ/mol barrier from Figure 4b, whereas the two right-hand columns refer to the 105 kJ/mol barrier in Figure 4d. τ_1 and τ_2 are the torsional angles corresponding to conformational transitions as illustrated in Figure 1 for the Boyer and Schatzky crank-shaft

95 kJ/mol barrier torsional angles (see Figure 4b)		105 kJ/mol barrier torsional angles (see Figure 4d)	
At minimum energy	At barrier height	At minimum energy	At barrier height
−175.5	−168.6	179.5	176.5
43.3	48.4	−60.3	−57.0
65.5	60.2	−62.7	−57.6
−169.0	174.3	−60.9	−61.6
69.4	70.7	−56.7	−61.6
−101.4	−93.2	170.1	−176.0
165.6	158.2	174.7	−174.0
166.9	173.5	71.2	91.9
−174.3	176.3	169.3	−165.1
−179.5	−176.8	−172.5	−168.4
74.0	171.4	56.9	−2.9 τ_1
−178.0	−164.6	72.8	107.4
77.9	−19.6 τ_1	−72.4	−68.5
−167.8	−131.8	−157.5	−179.7
−53.5	−46.3	172.3	148.1
170.2	163.6	−74.3	−41.1
−60.2	−48.5	170.5	111.2 τ_2
−172.9	−164.9	−94.7	−75.2
−154.6	120.4 τ_2	−69.6	−69.0
−151.5	−162.0	−74.3	−63.5
99.5	173.2	−51.2	−42.1
−70.6	−72.7	−69.2	−69.5
−85.4	−93.2	160.7	163.1
−173.8	176.6	−81.0	−85.0
63.3	62.9	−75.0	−76.4
81.3	82.1	153.6	155.5
−66.6	−71.1	73.0	72.4
−55.2	−57.7		
−64.2	−63.7		
−64.0	−63.2		
−161.3	−162.7		
73.5	72.1		

Finally, we would like to address the fact that energy barrier values calculated atomistically should be considered upper-estimates of the barrier heights. The reason for this is mainly that proper energy minimisation after each consecutive torsional bond increment is not ensured. In reality, i.e. accounting for the dynamic behaviour of the polymer explicitly, molecular dynamics should be incorporated in the simulations. This would normally tend to have the effect of smearing out jumps in energy as they were encountered in our simulations. However, it would be difficult, if at all possible, to estimate the length of the dynamics simulation to be pursued. If we could apply dynamics for a really long period (time scales of minutes), the structure would always tend to return to the same minimum energy conformation. If the simulation is too short, its effect will be negligible. The length of the simulation will be determined by the local environment of the rotating unit. Because, as we have seen for the case of five-bond rotation, there are several distinct barrier heights connected to this type of rotation with a time scale ranging over several orders of magnitude, a suitable choice of length of dynamics simulation does not seem possible. The procedure we have followed in the present paper seems, to us, to be the best alternative presently available.

CONCLUSIONS

Fully atomistic simulations have been performed aiming at understanding the molecular motion related to the α- and the β-relaxation process in the amorphous phase of PVC. First, the relevance of Boyer and Schatzky crank-shaft motion was investigated. Both types of motion were found unimportant, i.e. these particular structures have a very low probability of occurrence in the amorphous PVC structure. On the other hand, three- and five-bond conformational transitions are found to be possible from an energetic point of view. Moreover, it was found that the activation energies thus obtained relate to the appropriate frequency range of secondary maxima determined by dielectric spectroscopy. We thus propose that localised conformational transitions may be held responsible for the β-relaxation process in amorphous PVC and many other types of main chain secondary processes (polyethylene, polyethyleneterephthalate, etc.).

Analysis of the changes in torsional angles along the main polymer chain upon conformational transitions has revealed that a local five-bond transition may result in activation energies responsible for the secondary relaxation process, but also for much higher activation energies (100 kJ/mol) related to the glass transition. This suggests a strong similarity between the molecular motions involved in the glass transition and the secondary transition in polymers, respectively.

In conclusion, we have suggested an atomistic interpretation of the β-relaxation process as well as the glass transition in PVC based on a fully atomistic model, explicitly taking account of the bulk structure of amorphous PVC. Although more definite and more detailed conclusions await further simulations, we believe it has been shown in the present paper that such an approach is very feasible on the basis of static simulations, i.e. without explicitly simulating polymer dynamics, and that further simulations of this type are expected to provide more detail on relaxation phenomena in polymers.

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