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On the relationship between stereochemical microstructure and the glass transition temperature (T_g) of poly(vinyl chloride) (PVC): some conclusive evidence given by stereospecific modification with sodium 2-mercaptothiobenzoate

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Abstract

The mechanisms of nucleophilic substitution in poly(vinyl chloride) (PVC) with sodium 2-mercaptothiobenzoate (NaMBT), as studied in recent works, have been outlined. Like substitution with other nucleophiles formerly studied, the reaction proceeds only by the tetrad mmr and the pentad rrmr, the termini of the isotactic and syndiotactic sequences, respectively. In contrast, unlike in those nucleophiles, mmr is found to react exclusively by the mm triad, because the competing reaction by the mr triad proves to be nil with NaMBT.

This is demonstrated to be the reason why the evolution of T_g with substitution, as studied herein, agrees thoroughly with the ratio of mmr to rrmr, contrary to what happened with the nucleophiles that exhibit a minority reaction by the mr triad of mmr. Such a novel quantitative correlation, compared with the more tentative ones obtained previously, allows one to furnish a valuable insight into the prevailing role of stereochemical microstructure in the process of glass transition in PVC.

Keywords: Poly(vinyl chloride); Nucleophilic substitution; T_g

1. Introduction

A considerable amount of work has been devoted in our laboratory to demonstrating that the mechanism of analogous reactions of poly(vinyl chloride) (PVC) is governed by the stereochemical microstructure, as driven by the tacticity [1,4–6]. This microstructure concept includes the average content and length of tactic sequences; the local configurations located at the end of the isotactic and syndiotactic sequences, namely mmr and rrmr, respectively; and the local conformations that are likely in the latter configurations. Of all the reactions studied, it is nucleophilic substitution that has furnished both original basic concepts of the chemical modification of polymers [4,5], and appropriate means of modelling experimentally the microstructure of PVC, so leading to the better understanding of some structure–property relationships [7].

The specific details of microstructure-based mechanisms of substitution have been extensively conveyed [1–6,8]. Basically, it has been demonstrated that: (i) substitution proceeds by the last triad of isotactic sequences, i.e. the mmr tetrad, or by the heterotactic triad at the end of syndiotactic sequences, i.e. that at the rrmr pentad, exclusively. (ii) for these structures to react, the mm and rm triads have to take the $GTTG^-$ and GTTT conformations, respectively. $GTTG^-$ is extremely reactive [8] and can occur only in an mmr structure; the GTTT conformation, of lesser reactivity, can occur in any mr (or rm) triad and, consequently, in any rrmr structure. The availability of either conformation throughout the reaction process is ensured by the occurrence of conformational changes in each structure [8,9], especially in mmr where the equilibrium between the two likely conformations, $GTTG^-TT \Leftrightarrow GTGTTT$, which leans strongly to the right side, ought to be reversed. Such changes in conformation are achieved through selective molecular interactions between the reactive structures and a few solvents, as proved in an earlier work [10]. Owing to the enormous reactivity of the $GTTG^-$ conformation and to the fact that for a given solvent these interactions are different in both nature and strength for the reactive structures, the evolution of the ratio of mmr to rrmr with degree of substitution may be controlled simply by changing the nature of the solvent; in addition, that evolution changes in slope as

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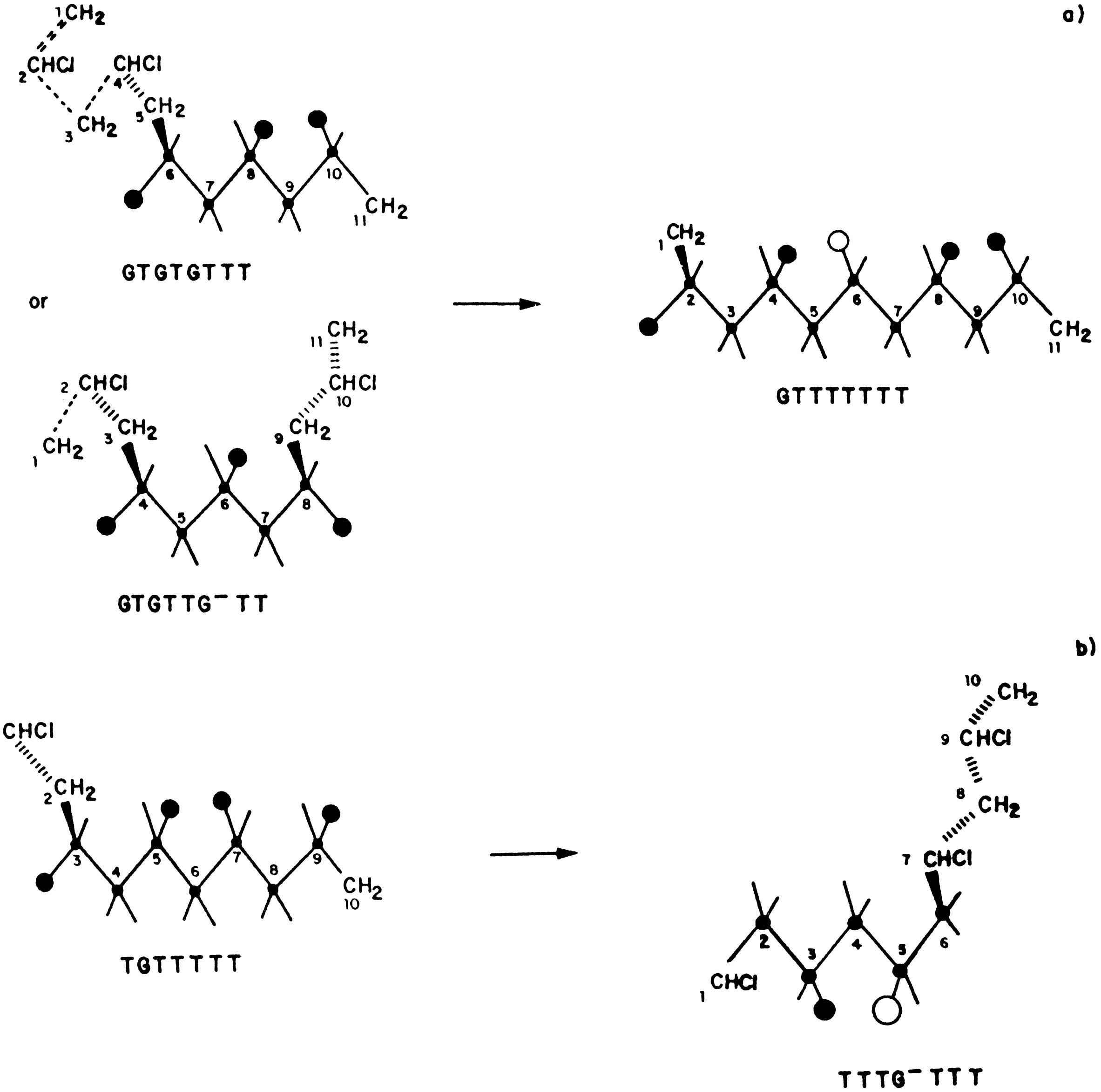

Fig. 1. Conformational changes involved in substitution of PVC on the central C–Cl of: (a) mmmr pentad; (b) rmrr pentad. Cl (●); nucleophile group (○).

the mmr structures, most likely to react, start vanishing, which occurs at conversions ranging from roughly 6 to 10% according to the type of solvent [1–6]. Finally, a small fraction of mmr structures react by the mr triad instead of the mm, at least with sodium benzenethiolate (NaTB) and sodium thiobenzoate (NaTBZ) as nucleophiles [3,4,6].

As a result, three well-defined substitution mechanisms could be established [3–6]: (i) mechanism A applies for the reaction by the mm triad of mmr and involves the simultaneous disappearance of one isotactic triad and one heterotactic triad by exchanging for one nucleophile centered triad and one co-syndiotactic triad, respectively; (ii) mechanism B is substitution by the rm triad of rrmr and involves the elimination of a single heterotactic triad; and (iii) mechanism C relates to substitution by the mr triad of mmr and involves the disappearance of one isotactic triad without yielding either the appearance of one syndiotactic triad as in mechanism A, or the disappearance of one heterotactic triad as in mechanisms A and B [3,6].

As repeatedly argued [7,11] and as may be easily observed with appropriate atomic models, the above changes of configuration, coupled with the inversion of the carbon configuration characteristic of nucleophilic substitution [8], bring about a significant rearrangement of a particular chain segment. This is illustrated by Fig. 1 showing the implications of nucleophilic substitution on the central CHCl carbon at the mm and mr triads in the mmmr and rrmr pentads, respectively. The corresponding effects on chain interactions and on properties have been published in detail [10]. What is worthy of note for this work is that mechanism C brings about the same conformational changes as mechanism B (Fig. 1), whereas the evolution of microstructure, in terms of loss of isotactic content, which is associated with it, looks like that of mechanism A [11].

The above-cited substitution reaction mechanisms allowed us to endeavour a systematic investigation of stereochemical microstructure as the driving force for a few physical behaviors of PVC, in particular T_g [9–12]. As well-documented elsewhere [11,12], T_g was demonstrated to vary linearly with degree of conversion up to 15% for NaTB and NaTBZ, but with slopes of negative and positive signs, respectively. In addition, the magnitude of the slopes, whether negative or positive, was proved to change with the ratio of mmr to rrmr removed through substitution as controlled by the type of solvent [11]. That, overall, T_g decreases or increases when substituting either the benzenethiolate or thiobenzoate group for chlorine could be expected from the bulkiness and polarity of the respective nucleophiles compared with chlorine [11]. Now, this specific effect of the substituent will depend only on the degree of substitution, and can by no means justify the changes in slope observed [9,11]. Since these changes are paralleled by those observed for the slopes of the variation of mmr/rrmr ratio up to conversions of roughly 6–10% when changing the type of solvent [1–7], both quantities were assumed to be related [11], and it was concluded that the effect of stereochemical microstructure on T_g ought to stem from the occurrence of local or sequential discontinuities along the polymer chain, which would cause fluctuations in excess free volume, local and sequential chain rigidity, and sequential inter-chain interactions to arise [7,11].

Actually, as indicated by Fig. 1 and widely understood [7,11], this sort of structure disruption varies gradually with the mmr/rrmr ratio, i.e. with the stereochemical microstructure, and accordingly, a change in slope of the linear variation of T_g with substitution degree was expected to occur at conversions ranging from 6 to 10% [11]. Nevertheless, experience proved to be otherwise in that a unique slope was obtained up to at least 15% [9,11]. The most reliable explanation was believed to lie in the already mentioned fact that the specific fraction of mmr, which reacts through mechanism C from the outset of the process [4–7] produces, simultaneously, changes in local chain arrangement (Fig. 1), and thence in T_g and in the mmr/rrmr ratio, in a similar way to mechanisms B and A, respectively [11]. Thus the hypothesis was made that the straight line joining the ends of the plots of that ratio vs conversion should be considered as representative of the ratio between the frequency of occurrence of mechanism A and the frequency of occurrence of either of B and C mechanisms, which are the two unique microstructure-based ways to influence T_g. If this hypothesis was true, a straight line would be obtained by plotting the slopes thus measured vs those of the corresponding changes in T_g, and the magnitude of the effect of stereochemical microstructure on T_g could be estimated. As conveyed elsewhere [11] this proved to be so, as firstly, linear behaviors were obtained as expected, and, secondly, the absolute value of the slopes proved to be similar for NaTB and NaTBZ, regardless of both experimental conditions and the sign of the slope.

Therefore these preliminary results lend support to the stereospecific microstructure dependence of T_g, which is permanent in character unlike the effect of the substituent. One appropriate way to ascertain whether this correlation is general in nature is to, on the one hand, investigate the substitution reaction with a nucleophile of bulkiness great enough for the attack on the CHCl carbon at the centre of the mr triad in mmr to be hindered so making mechanism C inoperative. And, on the other hand, to verify whether the evolution of T_g with degree of substitution in the absence of mechanism C holds to that of the mmr/rrmr ratio exhibiting a change in slope at 6–10% conversion, unlike in the case of NaTB or NaTBZ [11]. This would not only demonstrate our prior hypothesis but would also take the stereochemical microstructure-based mechanism of the glass transition process, as proposed in our work [9,11], a conclusive step further. These courses of action, as accomplished through sodium 2-mercaptobenzothiazolate (NaMBT) as a nucleophile of high bulkiness without significant loss of nucleophility, are the subject of the present paper.

2. Experimental section

2.1. Materials

The PVC sample used was prepared at 60°C by the bulk polymerization process, using 2,2′-azodiisobutyronitrile (AIBN) as initiator, and taken to conversion of 11%. The average molecular weight ($M_n = 40,000$) was determined at 34°C with solutions in CH using a Knauer membrane osmometer. The solvent (cyclohexanone, CH) was purified as already described [3]. 2-Mercaptobenzothiazole (MBT) (Fluka) was purified by repeat recrystallization from benzene.

2.2. Preparation of NaMBT

A solution of 1.08 g (36.0 mmol) of sodium hydride oil dispersion (80%) in 30 ml of THF was added dropwise to a well-stirred solution of MBT (6 g, 36.0 mmol) in 30 ml of THF under nitrogen atmosphere. The mixture was refluxed for 2 h, then filtered, and the solvent evaporated in vacuo.

2.3. Substitution reaction of PVC with NaMBT in solution

Two grams (32.0 mmol, based on monomer unit) of PVC were dissolved in 125 ml of CH and 6.24 g (33.1 mmol) of NaMBT in 125 ml of CH were added to the polymer solution. The mixture was stirred and heated at 60°C under an inert atmosphere. At appropriate reaction times,

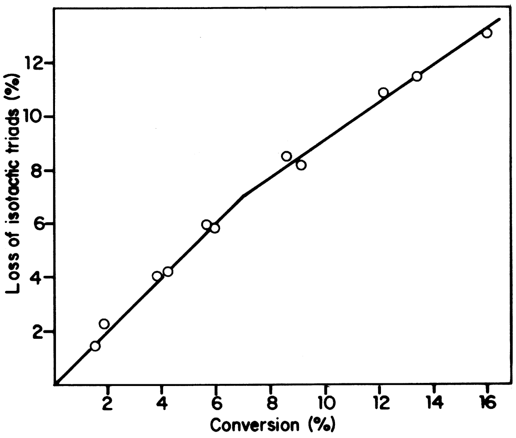

Fig. 2. Loss of isotactic triad content vs conversion of PVC after substitution reaction with NaMBT in CH.

samples were precipitated with methanol, the products were purified from THF into methanol, filtered and then dried at 40°C. The samples were characterized by UV spectroscopy to determine the degree of substitution from the intensity of the mercaptobenzothiazolate 281 nm band. A calibration curve had been previously obtained from the absorbance at 281 nm for samples modified to well-defined extents, as measured by microanalysis of the content of Cl, S and N. Some of these values were checked by ^{1}H NMR spectroscopy, which accounts for the accuracy of the calibration curve [14]. The UV spectra were determined in a Perkin–Elmer 554 UV–Vis spectrophotometer at room temperature with a 1 cm^{-1} path length cell.

2.4. ^{13}C NMR spectroscopy

The tacticities of the starting and the modified polymers were measured by means of ^{13}C NMR decoupled spectra obtained at 90°C on an XL-300 Varian instrument, operating at 75.5 MHz using dioxane-d$_8$ as solvent. The spectral width was 2500 MHz; a pulse repetition rate of 3 s and 16K data points were used. The relative peak intensities were measured from the area of the integrated peaks, calculated by means of an electronic integrator. The complete data have been already published [13].

2.5. Calorimetric measurements

Powdered samples, in amounts ranging from 8 to 10 mg, were encapsulated in aluminium pans. The calorimetric measurements were carried out with a Perkin–Elmer differential scanning calorimeter (DSC), DSC-4, coupled with a thermal analysis data station. Dry nitrogen was used as purge gas. Temperature and enthalpy calibration was achieved with indium. The T_g was taken as the midpoint of the intersection from the glassy to the liquid state. All measurements were obtained at a heating rate of 10°C/min. The reproducibility of duplicate runs of samples with well-defined T_g was better than ±0.2°C. The initial onset of the change of slope in the DSC curve was also taken into account.

3. Results and discussion

Both the nucleophilic substitution of PVC with NaMBT in cyclohexanone as solvent, and the implications as regards the changes in stereospecific microstructure of the polymer have been completely described in earlier work, to which the reader is referred [13,14]. So, only those specific matters that may be helpful for the elucidation of the effects of changes in stereospecific microstructure on T_g will be considered herein.

Fig. 2 depicts the percent loss of isotactic triads with conversion. As extensively argued [3–7], this behavior is of the type obtained when the only reactive species are the mm triad in mmr associated with any isotactic sequence and the mr or rm triad located mostly at the rrmr associated with syndiotactic sequences, and only infrequently at a definite fraction of mmr. These processes follow the occurrence of the substitution mechanisms A, B and C, respectively. Bearing in mind the implications of each of them [3–7] it may be inferred that the slopes of Fig. 2 will be representative of the ratio of the mmr that has reacted by mechanisms A or C to the rrmr that has reacted through mechanism B for any conversion. As was the case for the nucleophiles NaBT [3–5] and NaTBZ [6], the reaction in CH involves two distinct linear steps (Fig. 2). The corresponding slopes are unity and between 0.5 and unity, which indicates that there is a fraction of mmr structures of such a high reactivity that they are the only ones to react during the early stage, while the remaining mmr which react during the second stage are not as different in reactivity from the competing rrmr structures as are the former, extremely reactive mmr. These were demonstrated to be associated with isotactic sequences at least 1 heptad in length [3]. Thus, from a qualitative point of view Fig. 2 agrees with the behavior found previously for NaBT [3–5] and NaTBZ [6].

However, from mere inspection, a little difference between NaMBT and the other nucleophiles is apparent. Actually, comparing the results of Fig. 2 and those obtained for NaBT [3–5] and NaTBZ [6], it is evident that the conversion at which the change in slope is produced is somewhat greater (roughly 1% higher) and that the slope of the second period is substantially higher for NaMBT. As a first approximation, this difference is an indication that the discrimination between the mmr and rrmr reactive species is somewhat sharper in the case of NaMBT. A possible explanation lies in the fact that the hindering of the nucleophile attack, which usually arises when increasing the bulkiness of the nucleophile, should be more marked for rrmr than for mmr [8,13]. Now, a steeper decrease in frequency of occurrence of reaction by rrmr during the second period,

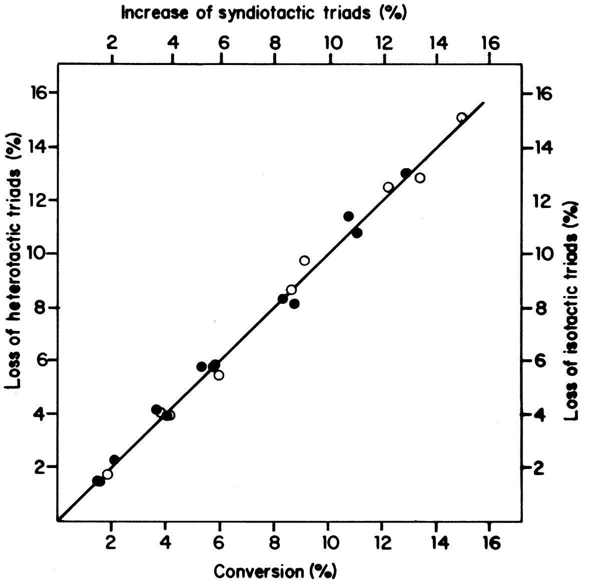

Fig. 3. Loss of heterotactic triad content vs conversion (○) and loss of isotactic triad content vs increase of syndiotactic triad content (●) of PVC after substitution reaction with NaMBT.

relative to mmr, would have to result in an increase of slope. As illustrated by Fig. 2, this agrees with experience.

It is notable that a similar effect of nucleophile bulkiness is expected for the reaction of mmr by its mr triad (mechanism C), but as a consequence of the above quoted implications of mechanism C, compared to mechanisms A and B, that reaction should produce neither any change in mm triad loss nor any alteration of the slope of the second stage [3]. Thus, whether or not mechanism C operates cannot be concluded from the results of Fig. 2, even if they agree with our expectation that the reaction by the mr triad in mmr should be restricted or unlikely, relative to the mm triad.

Mechanism C requires that the mm triad disappears without yielding both the appearance of one syndiotactic triad and the disappearance of one heterotactic triad so departing from mechanisms A and B [3]. If mechanisms A and B were the only operative processes, then the plots of heterotactic triad loss vs conversion and that of isotactic triad loss vs syndiotactic triad increase would both have to be linear, with a slope of unity [3,4]. If it proves otherwise, i.e. if departures from a slope of unity occur, then the occurrence of mechanism C will be established. Such was the case for NaBT [3] and NaTBZ [6] as nucleophiles, where slopes lower and greater than unity were found for those plots, respectively.

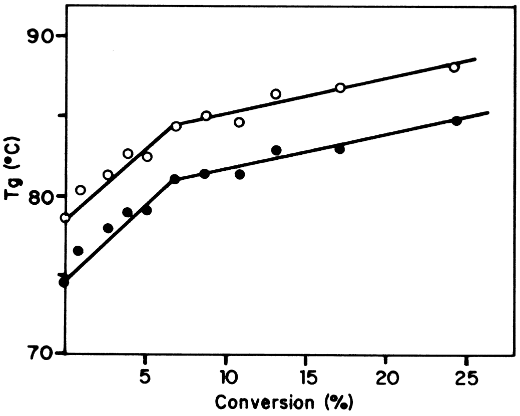

Fig. 4. Evolution of glass transition temperature with conversion of PVC after substitution reaction with NaMBT. (○) Midpoint; (●) onset.

The plots obtained for NaMBT are shown in Fig. 3. They both fit into linear behavior, and unlike the slopes for NaBT and NaTBZ, the slope is exactly unity. Accordingly, mechanism C is to be discarded simply. Correspondingly, the discrepancies between mechanisms C and A, both involving mmr structures, in changing the local chain configurations and conformations [3–5] ought to be discarded too.

Ascertaining this objective was crucial for a reliable correlation between the evolutions of tacticity–microstructure and T_g to be determined experimentally. Actually, in the absence of mechanism C, the slopes of Fig. 2 will be representative of the relative contributions of two processes of substitution only, namely mechanisms A and B, each producing a well-defined change in local configuration and conformation (Fig. 1). Now, if each of the mmr and rrmr structures after substitution has a unique effect on T_g, then the evolution of T_g with substitution degree will parallel that of the microstructure (Fig. 2), contrary to what happened when mechanism C operated, as was the case for NaBT and NaTBZ where the evolution of those quantities was found to fit into one and two linear behaviors, respectively, within the 0–15% range of conversion [9,11]. Thus, the T_g-determining effect of the stereospecific microstructure will be unambiguously disclosed.

Interestingly, Fig. 4 shows that expectation agrees thoroughly with experience in that two straight lines, instead of one, are produced. Therefore T_g is found to vary with substitution degree in a similar way to the ratio between the extents to which the mmr and rrmr structures intervene in the substitution reaction. In this connection the difference in slope prior to and after around 7% conversion clearly indicates that the overall T_g-increasing effect of substitution, doubtless related to the bulkiness and polarity of the substituent [13], is better balanced by the reverse effect of the implications of substitution through mechanism B than it is by the parallel effect of the implications of mechanism A (Fig. 1). This gives evidence in favor of the tentative correlations obtained for NaBT and NaTBZ nucleophiles [11]. It is worth noting that such a specific correlation cannot be due to any feature but the implications of substitution whether by mechanism A or mechanism B, reflected by Fig. 1. In effect, if the changes in T_g were the result of a pure change in chemical composition or of the nature of the nucleophile, a steady variation should be observed.

Therefore, the foregoing results not only assess that there is a permanent effect of the stereochemical-microstructure on T_g regardless of the remaining chemical features, but also lead to a better understanding of the molecular microstructure-based mechanisms of the processes which are responsible for T_g. Actually, the variation in local configuration and conformation as a result of substitution (Fig. 1) involves specific fluctuations in excess free volume, rigidity, mobility and sequential inter-chain interactions through consecutive H...Cl bonds. Consequently, a novel insight into the specific sites where the T_g-determining set of molecular motions originate, may be approached, thereby opening useful prospects for more comprehensive theoretical studies in this important field.

Acknowledgements

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