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On the relationship between tacticity dependent molecular microstructure and glass transition temperature of poly(vinyl chloride): a novel approach through model polymers with controlled, chemically induced microstructure

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Nucleophilic substitution in poly(vinyl chloride) (PVC) with sodium thiobenzoate (NaTBZ) has been studied in two kinds of solvent. From the evolution of the content of isotactic (**mr**) and heterotactic (**mr**) triads in the unmodified parts of the polymer, as investigated by ^{13}C n.m.r., the reaction was found to behave similarly to that previously studied with sodium benzenethiolate (NaBT) in that only the local configurations **mmr** and **rrmr** at the end of isotactic and syndiotactic sequences respectively are reactive. The same reaction with both nucleophiles has also been studied in aqueous suspension in the presence of a phase transfer catalyst. In all cases the ratio of **mmr** content to **rrmr** content is found to vary according to the experimental conditions, in particular the type of solvent, irrespective of the nucleophile. Accordingly, model polymers having well known tacticity-derived microstructure can be obtained. On the other hand, the evolution of T_g with degree of conversion has been studied by calorimetric measurements. T_g has been found to change linearly with conversion and the correlation between the corresponding rates and the evolution of the ratio between the **mmr** and **rrmr** contents proves to be linear too. From these studies it follows that T_g depends on two well defined factors: one, variable in character, is the nucleophile nature; the other is the microstructure in terms of the isotactic and syndiotactic sequences and, especially, the local configurations and conformations at the end of them. Interestingly, this effect is permanent in character and is independent of the substituent. The results that we have obtained provide new concepts on the involvement of some specific molecular microstructural features in the T_g phenomenon.

(Keywords: PVC; T_g; nucleophilic substitution)

INTRODUCTION

Current and recent work of our laboratory has been focused on tacticity dependent molecular microstructure as the major driving force for the mechanism of analogous reactions of PVC[1,2]. We endeavoured first to provide novel ideas on the chemical modification of polymers and, secondly, to prepare model polymers of well defined molecular microstructure. The microstructure concept, as considered in our work, includes the average content and length of tactic sequences; the local configurations located at the end of 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 the nucleophilic substitution that has provided the best means of modelling, experimentally, the molecular microstructure of PVC, thereby opening original prospects in the field of relationships between structure and physical properties.

This reaction has been extensively documented elsewhere[3–6]. Basically, it has been demonstrated that: (i) the 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) in order for these structures to react, the **mm** and **rm** triads have to take the **GTTG$^-$** or **GTTT** conformation respectively. They are, in fact, very reactive species and can occur only in the **mmr** and **rrmr** structures. Such a requirement involves the occurrence of conformational changes in each structure so as to ensure the availability of the above reactive conformations throughout the reaction process[1,6]; and (iii) although the **GTTG$^-$** isotactic triad conformation is extremely reactive compared to the **GTTT** heterotactic triad conformation, the evolution of the ratio of **mmr** to **rrmr** with degree of substitution may be straightforwardly controlled by changing the nature of the solvent or the additives, depending respectively on whether the reactions are carried out in solution or in the melt[5–7]. The basis of such behaviour lies in the fact that, as demonstrated recently, the molecular interactions

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between the reactive structures and a few solvents, esters and polyesters are different in both nature and strength[8].

In addition to the foregoing points, it should be noted that every act of substitution not only involves the disappearance of one **mmr** or **rrmr** structure but, owing to the inversion of the configuration of the carbon, characteristic of the S_N2 mechanism, substantially alters the configuration and the related conformation of the adjacent triads, thereby bringing about a significant rearrangement of a definite chain segment. This is illustrated in *Figure 1* which shows the implications of the nucleophilic substitution reaction on the central CHCl carbon at **mm** and **rm** triads in **mmmr** and **rrmr** pentads respectively, as deduced from earlier results. From mere inspection it follows straightforwardly that in each case the sequence, whether isotactic or syndiotactic, associated with the reactive structure is shortened. Actually, the end segments of those sequences, as depicted on the left side of *Figure 1*, completely disappear by exchanging with those on the right side as the result of a single act of substitution at carbons 6 and 5 for the isotactic and the heterotactic sequence respectively. As a result, one isotactic **mmmr** pentad under conformation involving chain bends (**GTGTGTTT** or **GTGTTG^{-}TT**) is converted into an all-*trans* sequence. In principle this would have to imply an increase in local chain rigidity and a higher ability for interchain interaction through consecutive H···Cl bonds. In contrast, substitution on the **rrmr** pentad causes an all-*trans* syndiotactic sequence to depart from regularity. As clearly depicted by *Figure 1*, this involves a decrease in both the local chain rigidity and the ability to interchain sequential interaction through consecutive H···Cl bonds. In addition, it should be noted that one isotactic or syndiotactic sequence is necessarily shortened as the result of substitution on the **mmmr** or **rrmr** pentad; then, some

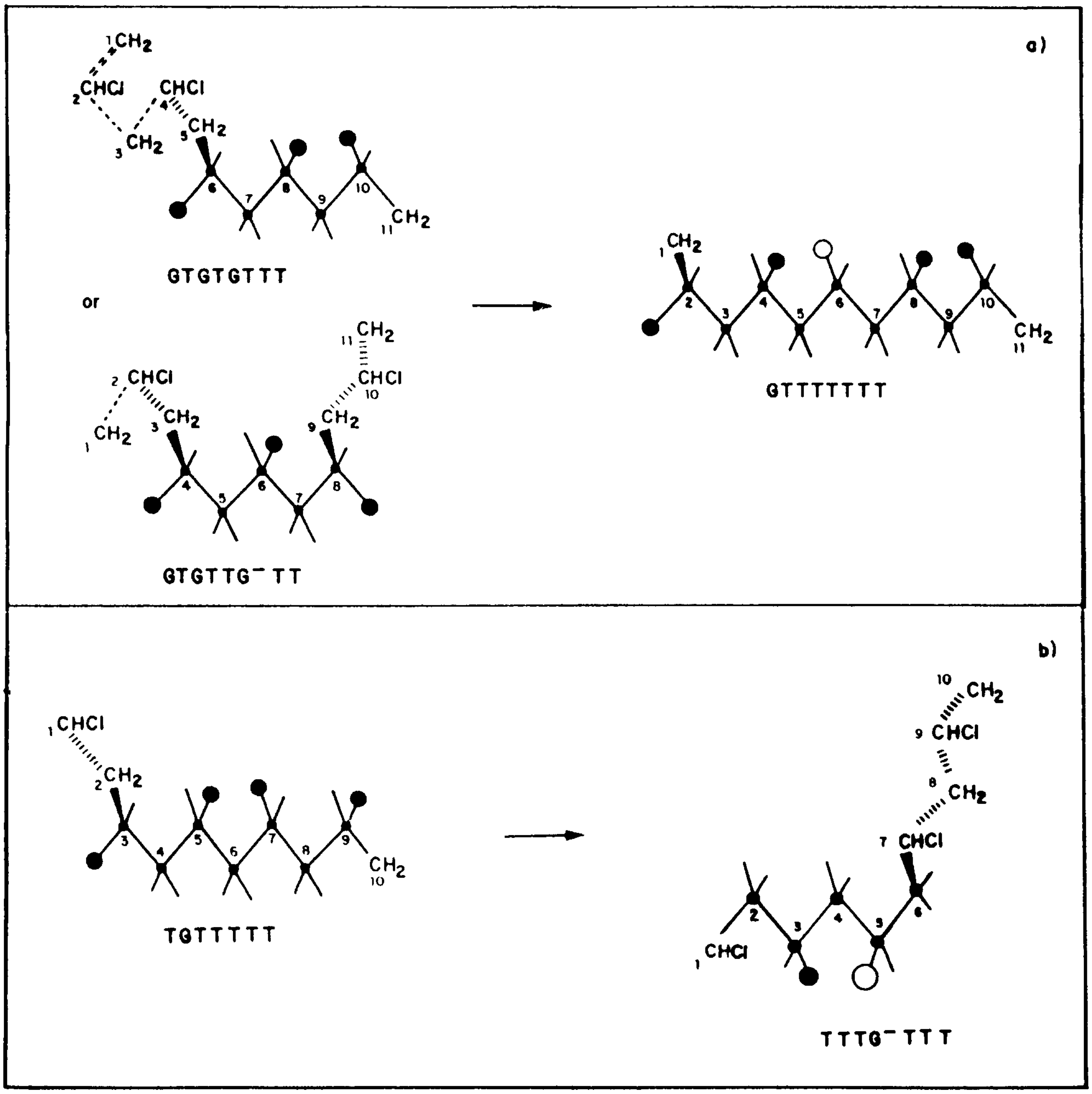

Figure 1 Conformational changes involved in substitution of PVC on the central C–Cl of: (a) **mmmr** pentad; **(b) rmrr** pentad. Cl (●); benzenethiolate group (○)

characteristics relevant to the length of the sequence, such as the ability to form consecutive H· · ·Cl bonds so determining the strength of the interchain sequential interaction, and the overall rigidity of the sequence, will be substantially changed. This is more important for the syndiotactic sequence, where those characteristics are particularly enhanced.

On the other hand, it may be inferred from *Figure 1* that the reaction involves severe changes in the free volume associated with the **mmmr** or **rrmr** pentads and with the isotactic or syndiotactic sequences at the end of which those pentads are found.

To these implications, affecting the polymer chain itself, may be added the influence of the nucleophile group which is substituted for chlorine atoms. This should be considered in the way that the bulkiness and polarity of the incorporated substituent may be substantially different from those of chlorine. Unlike the changes in the polymer chain, the effect of the new substituent on any behaviour of the polymer will depend only on the degree of substitution.

Therefore, the stereospecific substitution reaction makes it feasible to prepare model PVC samples with varying characteristics such as: (i) the content of **mmr** and **rrmr** structures at the end of long isotactic and syndiotactic sequences respectively, by exchanging them for chain segments of different flexibility or rigidity; (ii) the average length of isotactic and syndiotactic sequences; (iii) the amount of sequential intermolecular interactions through consecutive H· · ·Cl bonds; (iv) the free volume fluctuations along the chain; and (v) the bulkiness and polarity of the nucleophile group incorporated into the chain. As extensively published, these changes may be performed in a controlled way by utilizing appropriate substitution conditions[1,5,6].

It is commonly admitted that the microstructure, as a whole, has a strong influence on T_g[10] and other properties of polymers. Nevertheless, the specific microstructure derived from tacticity has been scarcely considered, apart from some work in our laboratory[10,11]. With respect to T_g of PVC, a few attempts to correlate it with overall tacticity have been made[12]. Overall, these authors concluded that T_g increases with increasing syndiotacticity, but no information as to the reason for that behaviour at molecular level was conveyed.

On the basis of the foregoing results on nucleophilic substitution reactions, we have recently endeavoured to correlate T_g with the evolution of microstructure, as described above, with the degree of substitution. The first research work dealt with PVC modified with sodium benzenethiolate (NaBT). The results, published elsewhere[11], are illustrated in *Figures 2* and *3* which show the evolution of both the percentage loss of isotactic triads with conversion (*Figure 2*) and T_g with conversion (*Figure 3*). Taking into account that **mm** and **mr** triads in **mmr** and **rrmr** structures are the only ones to react, the percentage loss of the latter triad may be calculated by subtracting that of the **mm** triad from conversion. Thence the slopes of *Figure 2* will be representative of the ratio of **mmr** to **rrmr** removed in accordance with the processes depicted in *Figure 1*. These slopes are higher than 0.5 up to conversions of about 20%. On the other hand, they are higher for cyclohexanone (CH) than for N-methyl pyrrolidone (MP) as solvent. Thus, the reaction occurs more often by **mmr** and this behaviour is accentuated in CH compared to MP. At conversions higher than 20% the slopes are lower than 0.5, which indicates that the reaction by **rrmr** structures increases abruptly, presumably because the **mmr** structures become depleted[11]. This reaction period will not be considered here.

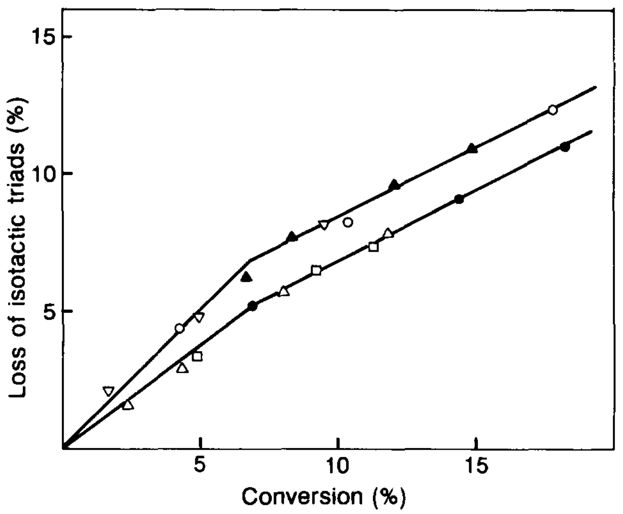

Figure 2 Loss of isotactic triad content vs conversion of PVC after substitution reaction with NaBT in various solvents: CH (○); THF (▽); MEK (▲); DMF (△); MP(□); hexamethyl phosphoric triamide (HMPT) (●)

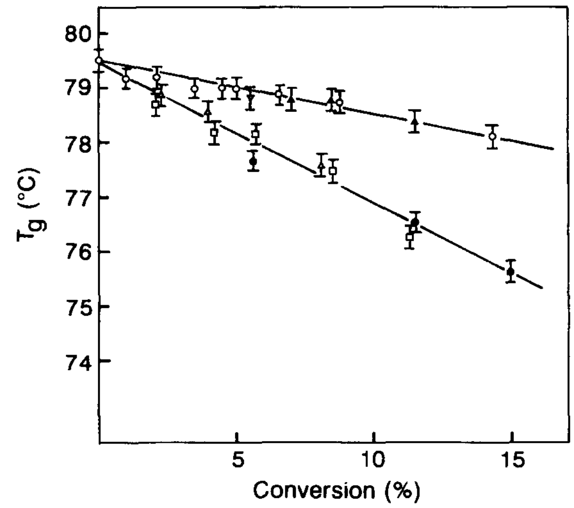

Figure 3 Evolution of glass transition temperature with conversion of PVC after substitution reaction with NaBT in various solvents: CH (○); THF (▽); MEK (▲); DMF (△); MP (□); HMPT (●)

As can be seen from *Figure 3*, up to 20% conversion the overall linear decrease of T_g is much more accentuated for MP solvent. It must be emphasized that such a difference cannot be due to the effect of the nucleophile itself.

Benzenethiolate is bulkier and less electron-donor than chlorine. Nevertheless, as is easily observable with appropriate atomic models, its size is not great enough for any of the likely local conformations characteristic of PVC (*Figure 1*) to be hindered. This aspect, together with the lower ability of that group to give hydrogen bonds, suggests that the trend of T_g with increasing benzenethiolate content will be toward progressive decrease. As is shown in *Figure 3*, this agrees with experience.

As previously argued[11], the results of *Figure 3* strongly suggest that T_g is related, at least to some extent, to two well differentiated microstructural factors. One factor is that of the particular **mmr** terminal of isotactic sequences no shorter than a heptad. Their conversion into a more rigid segment exhibiting less excess free volume (*Figure 1* and references 1, 5, 6) would probably cause T_g to increase but for the reverse effect of the benzenethiolate group, which causes that increase in T_g to be balanced or surpassed. The slight decrease in T_g observed in CH (*Figure 3*) presumably obeys this circumstance[11]. The other factor is the **rrmr** located at the end of syndiotactic sequences. As illustrated by *Figure 1* and explained previously[11], the terminal chain segment is converted into another of higher flexibility and excess free volume. Besides, the associated syndiotactic sequences are shortened and the occurrence of sequential interchain interactions through consecutive H···Cl bonds will be reduced. As a result a decrease in T_g should be expected. The results given in *Figure 3* for MP as solvent clearly agree with this hypothesis.

Further support for these conclusions was given by comparing the evolution of both microstructure and T_g for substitutions carried out at temperatures between 5°C and 60°C and under standard conditions at 25°C on PVC samples of different microstructures. Indeed, it was evidenced that in every case T_g is lower as the contribution of the reaction by **rrmr** increases[11].

Behaviour similar to the foregoing has been recently found by other authors by modifying PVC with various nucleophiles in solvents of the type used in our work[13]. Actually, they found T_g to depend on the type of solvent in a similar way to that of our work[5]. However, these authors attributed such behaviour mainly to the occurrence of two distinct types of polymer–solvent interaction. Depending on the ability of the solvent to form gels with PVC, the polymer chains would become more or less ordered in solution and such a potential morphology would remain unaltered after precipitation with methanol. It is notable that no data as to either the nature of the polymer–solvent interactions or the type of morphology was conveyed[13]. Instead, in recent and current work we have demonstrated that the interactions between PVC and a few solvents, esters and polyesters are governed by the tacticity dependent local microstructure in that the higher the gel forming character of the solvent (in general solvents bearing isolated carbonyl groups), the more specific is the interaction through the **mmr** terminal of long isotactic sequences. In contrast, more basic solvents such as MP scarcely discriminate between **mmr** and **rrmr** structures[8].

As discussed earlier, these specific interactions make it feasible to conduct the substitution reaction specifically through either **mmr** or **rrmr** or both, in a controlled manner, at least up to conversions of about 20%. The implications are that the flexibility characteristic of the **mmr** or **rrmr** structures prior to substitution (intrachain interactions), the local excess free volume relevant to them and the ability to provide consecutive H···Cl bonds of the long isotactic and syndiotactic sequences at the end of which those structures are found (interchain interactions), are strongly modified as the result of substitution. Therefore it is certainly the strong change in the chemical microstructure of **mmr** or **rrmr** structures and of the associated tactic sequences that emerges as the driving force for the T_g of PVC after modification. Further evidence for these conclusions has been provided by studying the effect of substitution on the thermal degradation and on various physical properties of PVC[14–16]. In addition, as will be seen later, the substitution reaction run in the absence of solvents proves to behave similarly to that in solution from a qualitative point of view[6,7].

These well documented findings have not been considered in the work cited earlier[13]. Still, some of the results concerning the evolution of both the overall tacticity and T_g with conversion agree, to a considerable extent, with our results except for the solvent dependence of the polymer microstructure after substitution reaction as unquestionably stated in our work[1,6]. As will be seen below, some recent results proving the influence of the local vicinity on the reactivity of both **mmr** and **rrmr** structures have provided further evidence on this matter, in that they allow one to explain the reason why a unique linear variation of T_g corresponds to two distinct linear **mm** triad removal rates up to conversions of about 20% (*Figure 3*)[1,2].

This original result led us to investigate further the extent to which the tacticity dependent microstructure, as considered in our work, is one permanent determining factor of T_g of PVC, compared to other factors of variable effect, in particular the substituent. To do that we first studied the substitution reaction with sodium thiobenzoate (NaTBZ), a similarly bulky nucleophile of much higher capability of interacting with hydrogen atoms than NaBT. In addition, we studied the substitution reaction with both nucleophiles in aqueous suspension in the presence of tetrabutylammonium bromide as phase transfer catalyst so as to avoid any interaction of polymer with solvents. We then examined the evolution of T_g with conversion, seeking to separate the contributions of microstructure and nucleophile to the change in T_g for the purpose of providing new evidence of the involvement of molecular microstructure in the physico-chemical processes which control T_g.

EXPERIMENTAL

Materials

The PVC sample used in this investigation was prepared by the bulk polymerization process at 90°C, using 2,2′-azodiisobutyronitrile (AIBN) from Fluka as initiator. The number-average molecular weight ($\bar{M}_n = 18\,000$) was determined at 34°C in CH using a Knauer membrane osmometer. Tetrahydrofuran (THF) was distilled under nitrogen with aluminium lithium hydride (Carlo Erba) to remove peroxides immediately before being used. MP was purified by drying over calcium hydride overnight and distillation. N,N-Dimethylformamide (DMF) was dried by adding 10 vol.% of benzene which had been dried over calcium dihydride. The benzene–water azeotrope was removed by distillation at atmospheric pressure. DMF was purified by shaking with phosphorous pentoxide for four days. It was then washed with potassium hydroxide pellets and distilled at 47°C at 14 torr. The middle fraction of the distillate was used. CH and thiobenzoic acid (TBZ) (Fluka) were purified by fractional distillation under nitrogen. A reagent grade of tetrabutylammonium bromide (TBAB) (Fluka) was used without further purification.

Preparation of sodium thiobenzoate (NaTBZ)

A solution of 1.29 g (43.0 mmol) of sodium hydride oil dispersion (80%) in 30 ml of THF was added dropwise to a well-stirred solution of TBZ (5 g, 36.2 mmol) in 30 ml of THF under nitrogen atmosphere. The mixture was refluxed for 3 h, then filtered and the solvent evaporated in vacuum. The product was recrystallized from 2-propanol. All the reactions were carried out using a freshly prepared thiobenzoate so as to avoid the occasional risk of either hydrolysis or oxidation.

Substitution reaction of PVC with NaTBZ in solution

1.7 g (27.2 mmol, based on monomeric unit) of PVC was dissolved in 100 ml of solvent (CH, DMF or MP). Then 4.9 g (30.6 mmol) of NaTBZ in 112 ml of the same solvent was added to the polymer solution. The mixture was stirred and heated at 40°C under an inert atmosphere. At appropriate reaction times, samples were precipitated with methanol, the products were purified from THF into methanol, filtered and then dried in vacuum at 50°C.

Substitution reaction of PVC with NaTBZ in water suspension catalysed by TBAB

In 50 ml ultrapure water (Milli-Q reagent water system), 0.15 g (9.3×10^{-3} mol l^{-1}) of TBAB and 4.22 g (0.57 mol l^{-1}) of NaTBZ were dissolved and then 1.78 g (0.57 mol l^{-1}, based on monomeric unit) of PVC samples were suspended. The mixtures were shaken at 60°C under nitrogen. After precipitation with methanol, the samples were reprecipitated from THF into methanol, washed and finally dried under vacuum at 50°C. A similar method has been used for NaBT as nucleophile.

The degree of substitution in both systems was determined from THF solutions by measuring the absorbance at 266 nm in the u.v. spectrum. A calibration curve was previously obtained from the absorbance at 266 nm by ^{1}H n.m.r. spectroscopy for samples modified to known extents.

^{13}*C n.m.r. spectroscopy*

The tacticity of both the starting and modified polymers was measured by means of ^{13}C n.m.r. decoupled spectra obtained on an XL-300 Varian instrument, operating at 75.5 MHz and 90°C. The samples were examined as 10 wt% solutions in mixtures of 1,4-dioxane-d_8/1,2-dichlorobenzene (vol. ratio 2:1). The spectral width was 2500 Hz, a pulse repetition of 3 s and 16 k data points were used. In all the experiments, 20 000–25 000 scans gave a very satisfactory signal/noise ratio, and the calculations were carried out by measuring the relative areas of the different peaks of the methynic carbons with a compensating planimeter as well as by means of the built-in electronic integrator.

Calorimetric measurements

The polymer samples, in amounts ranging from 8 to 10 mg, were encapsulated in aluminium pans. D.s.c. measurements were carried out with a Perkin Elmer differential scanning calorimeter, 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 between the intersection from the glassy to the liquid state. All measurements were obtained at a heating rate of 10°C min^{-1}. 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 d.s.c. curve was also taken into account.

RESULTS AND DISCUSSION

Figure 4 shows the removal of **mm** triad vs conversion for the substitution reactions with NaTBZ as nucleophile. Note that the corresponding disappearance of **mr** triads can be easily estimated by subtracting that of **mm** triads from the whole conversion[11]. Clearly, the effect of the solvents is of the type obtained for NaBT (*Figure 2*)[5,11]. Indeed, there are two distinct types of behaviour, depending on whether the reaction is carried out in solvents bearing isolated carbonyl group, namely CH and ethyl methyl ketone (MEK), or in solvents where an unshared pair of electrons, usually in a nitrogen atom, is in a conjugated position with the double bond of carbonyl function[5]; this is the case with MP, DMF, etc. The main difference between both types of behaviour lies in the fact that in the former solvents the slope is unity during the early step while in the latter the slope is between 0.5 and unity. This indicates that there is a fraction of isotactic triads of such a high reactivity that they are either the only or the most likely species to react up to total depletion, depending on the type of solvent.

During the second step, going up to conversions of roughly 20%, both slopes tend to be similar and are higher than 0.5. Thus the remaining isotactic triads are not as different in reactivity from the heterotactic as are the specific isotactic triads that react, whether exclusively or preferably, during the early stage (*Figure 4*).

At conversions higher than 20% the slopes proved to be similar and lower than 0.5, irrespective of the solvent, just as in the case of NaBT[11]. As shown recently, at this conversion range neither **mmr** nor **rrmr** is associated with isotactic or syndiotactic sequences respectively[11]. Therefore no significant change in the tacticity induced microstructure should be expected and the variation of T_g should be due mainly to the progressive substitution of nucleophile groups for chlorine atoms. This is the reason why this stage will not be considered herein, our purpose being to examine the relationship between chain microstructure and T_g.

The results of *Figure 4* are quite similar to those obtained for NaBT (*Figure 2*). Thus the mechanism of substitution, as widely explained[1,11], is shown to hold thoroughly for NaTBZ, and, in addition, the influence of

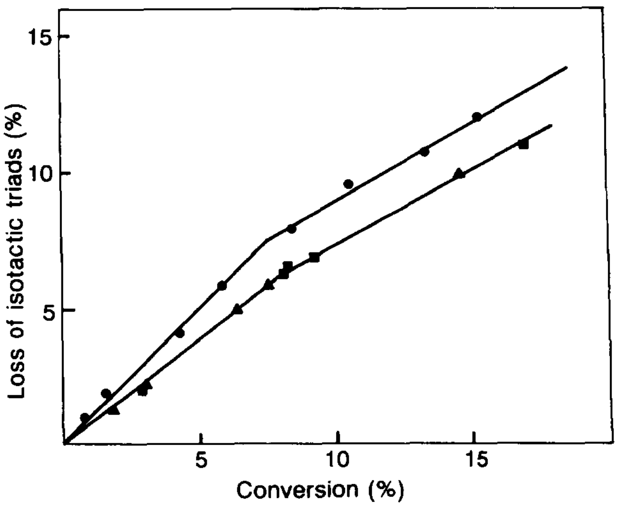

Figure 4 Loss of isotactic content vs conversion of PVC after substitution reaction with NaTBZ in various solvents: CH (●); DMF (▲); MP (■)

the solvent on the mechanism of substitution is evidenced. It then follows that for any degree of substitution the changes in chain microstructure ought to be independent of the type of nucleophile and so should represent the permanent contribution of the chain microstructure to the overall properties of the polymer, in particular the T_g.

On the other hand, the contribution of the nucleophile to the average change in T_g will be variable in nature, depending on its bulkiness and polarity. Thiobenzoate is a hindering group and, unlike the benzenethiolate group, possesses a carbonyl function which is capable of creating H···O=C bonds of higher stability than that of H···Cl bonds[8]. Both effects should favour the interchain interactions and, consequently, the trend with increasing degree of substitution would be towards an increase of T_g. It is notable that, as already indicated, this effect is independent of the permanent effect that changes in microstructure have on T_g.

The variation of T_g with the degree of substitution for the reactions with NaTBZ in various solvents is depicted in *Figure 5*. Clearly, in both types of solvent T_g is higher as the conversion increases, but unlike the effect of NaBT (*Figure 3*) the effect of NaTBZ is more accentuated in CH than it is in MP or DMF solvents. The explanation for such behaviour lies in the fact that both nucleophile and microstructure are able to influence T_g, whether in parallel ways or in opposite ways, depending on the nucleophile and the reaction conditions.

In an attempt to demonstrate that the foregoing original knowledge of the outstanding role of PVC microstructure is more general in nature, we have studied the same substitution reaction in the absence of solvent, whether in aqueous suspension using phase transfer catalysts or in the melt state in the presence of a number of interacting agents, either polymeric or not. The implications of the latter process as regards changes in T_g in relation to microstructure will be published in a separate paper[7].

As for substitutions in aqueous suspension, the disappearance of **mm** triads is plotted against conversion in *Figure 6* for both NaBT and NaTBZ nucleophiles. Here again two well differentiated slopes are obtained. Comparing this behaviour to that obtained in solution (*Figures 2* and *4*), it is apparent that the substitution is in both cases the same in nature. From a quantitative point of view the plot of removal of **mm** triads vs conversion approximates rather to that obtained for MP as solvent. It must be observed, however, that the measured percentages of **mm** triad loss and conversion refer to the total weight of polymer. Taking into account that the reaction takes place presumably at the outer part of the polymer particles, in the solid state, the real values for those quantities might be somewhat different, at least at higher conversions.

Note that no appreciable difference between the nucleophiles can be observed.

The changes in T_g with degree of conversion for the above quoted reactions in aqueous dispersion are shown in *Figure 7*. T_g proves to decrease and to increase linearly for NaBT and NaTBZ as nucleophile respectively, and, although not shown in the figure, that behaviour was proved to hold up to conversions around 20%, even if some deviations appeared incidentally from roughly 15%, doubtless because of the uncertainties derived from the phase heterogeneity of the reaction medium. Be that as it may, the results of *Figures 6* and *7* are of the nature obtained for the reaction in solution[11]. The foregoing modes of behaviour for, on the one hand, the evolution of microstructure, as on average indicated by the percentage loss of **mm** triads, and, on the other, the changes in T_g with degree of conversion, prove to be common to all the sets of reaction utilized, including the type of nucleophile up to conversions around 20%. Interestingly, the superiority of the **mmr** structure relative to the **rrmr** structure in reacting, and, consequently, the ratio between the respective contributions of both structures to the whole degree of substitution, can be evaluated through the slopes of the straight lines obtained when plotting the removal of isotactic triad against conversion. This has allowed us to demonstrate that the ratio of **mmr** content to **rrmr** content for any conversion is governed by either the solvent or the interacting agent, depending on the conditions under which the reaction is run, thereby making it possible to

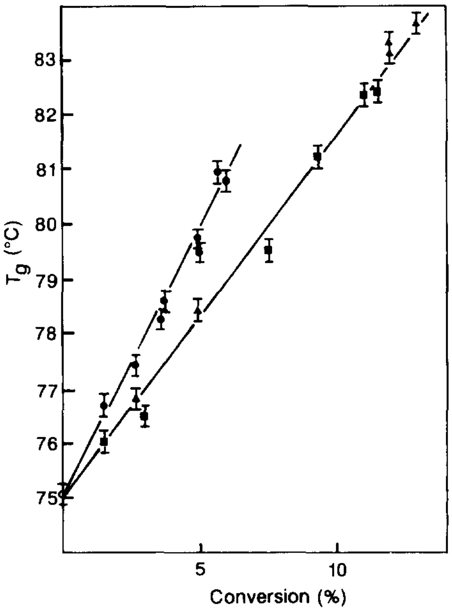

Figure 5 Evolution of glass transition temperature with conversion of PVC after substitution reaction with NaTBZ in various solvents: CH (●); DMF (▲); MP (■)

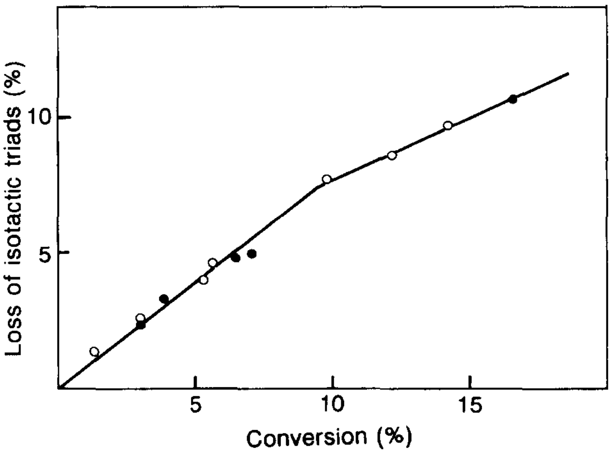

Figure 6 Loss of isotactic content vs conversion of PVC after substitution reaction in aqueous suspension in the presence of TBAB with different nucleophiles: NaBT (○); NaTBZ (●)

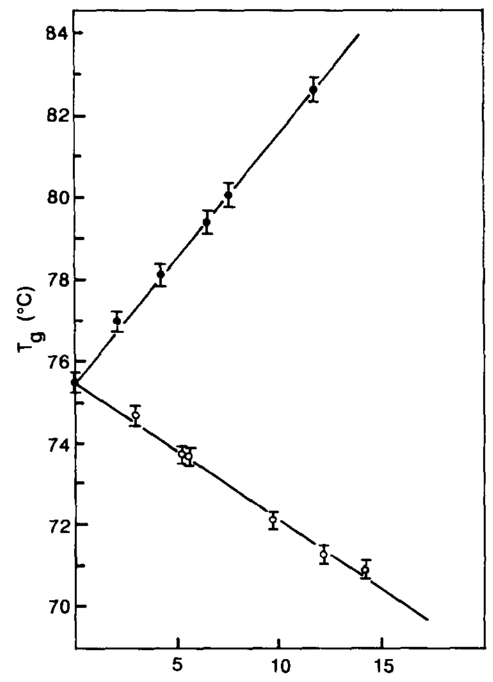

Figure 7 Evolution of glass transition temperature with conversion of PVC after substitution reaction in aqueous suspension in the presence of TBAB with different nucleophiles: NaBT (O); NaTBZ (●)

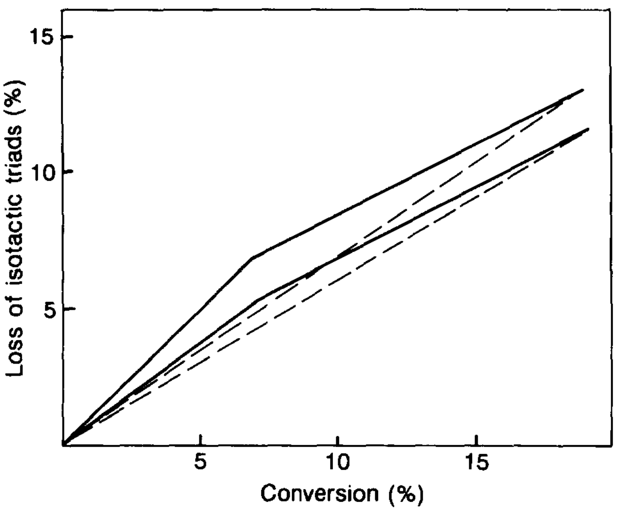

Figure 8 Data of *Figure 2* for substitution with NaBT at 25°C (——); loss of **mm** triad from any **mmr** but that in **mmrrr** sequence (- - - -) (see text)

prepare polymers with well defined tacticity dependent microstructure[1,2].

When attempting to correlate the changes in T_g with those in microstructure during substitution up to 20% conversion, a difficulty arose in that a single straight line is observed for the former implication whereas the latter one is characterized by two well defined straight lines (*Figures 2, 4* and *6*), the slope of which changes with the reaction conditions. This problem has just been solved through two recent courses of action where the reactivity of both **mmr** and **rrmr** structures and the reaction mechanism for the former structure have been demonstrated to depend strongly on the local environment in which the reaction takes place[2]. It is notable that the **mmr** structure, unlike the **rrmr**, possesses two different reactive sites, namely the central –CHCl– group of the **mm** and **mr** triads. Consequently, even if the **mm** triad is much more sensitive to nucleophilic substitution than the **mr** triad[1,2], some of the **mmr** tetrads should be assumed to react by the **mr** triad instead of the **mm**. This proved to be so for the **mmr** followed by at least two **r** diads, i.e. the **mmrrr** sequence, presumably because there is not a long isotactic sequence by the left side[2]. The implication is that one **mm** triad disappears without yielding the parallel disappearance of one heterotactic triad, which is characteristic of the reaction of either **mmr** by **mm** triad or **rrmr** structures[1]. It is thence the incidental occurrence of this particular mechanism that creates the linear behaviour of higher slope during the early stage of substitution, where no or little reaction by the **rrmr** structure takes place[1].

Turning to the corresponding evolution of T_g, it must be emphasized that the reaction by **mmrrr** ought to involve the same change in microstructure as the reaction by **rrmr** at the end of a syndiotactic sequence (*Figure 1*)[11] even if **mmrrr** is reckoned neither as **rrmr** nor as **mmrm** for the overall computation of **mm** and **mr** triads in the polymer after substitution (*Figures 2, 4* and *6*). Consequently, only two kinds of effect of microstructure on T_g, as depicted in *Figure 1*, and a single linear behaviour with a slope consistent with the relative contribution of each effect should be expected. As shown by *Figures 3, 5* and *7*, these implications agree with experience.

On the grounds of the foregoing results, the slope of the straight line joining the ends of the plot of **mm** loss vs conversion (*Figure 8*) should be considered as representative of the ratio between the two unique changes in microstructure which are able to influence T_g, namely those affecting either all the **mmr** save the ones related to the **mmrrr** sequence or the **rrmr** along with the **mmrrr** sequence. Therefore, by plotting the slopes thus measured as indicated in *Figure 8*, vs those of the corresponding changes in T_g, an approximate but reliable evaluation of the influence of microstructure on T_g, which is permanent in character and independent of the more conjectural influence of the substituent, should be obtained. This correlation is illustrated in *Figure 9* for all the substitution conditions utilized. By inspection, and within the experimental uncertainties, it follows straightforwardly, first, that the slope is positive or negative for NaTBZ or NaBT respectively. Thus the trend with increasing conversion is toward an increase or a decrease in T_g, depending on the nature of the substituent. Secondly, the absolute value of the slope is surprisingly similar for both nucleophiles. This is the more significant as: (i) the quantitative change in T_g with conversion varies strongly with the nature of the nucleophile (*Figures 3, 5* and *7*); and (ii) substitution by **mmr** (except for the one associated with the **mmrrr** sequence), and the substituent, can influence T_g in parallel ways or in opposite ways, depending on whether the latter is NaTBZ or NaBT respectively, while the reverse holds true for substitution by **rrmr** or **mmrrr**. Besides, the relative contributions of these processes can be regulated by the reaction conditions (*Figures 2–7*)[1,11]. Yet it is worth noting that the substitution conditions cannot alter the individual substitution mechanisms themselves[1,7]. Thus the molecular microstructure of PVC after substitution to any degree, under a given set of reaction conditions, will be independent of the nucleophile used.

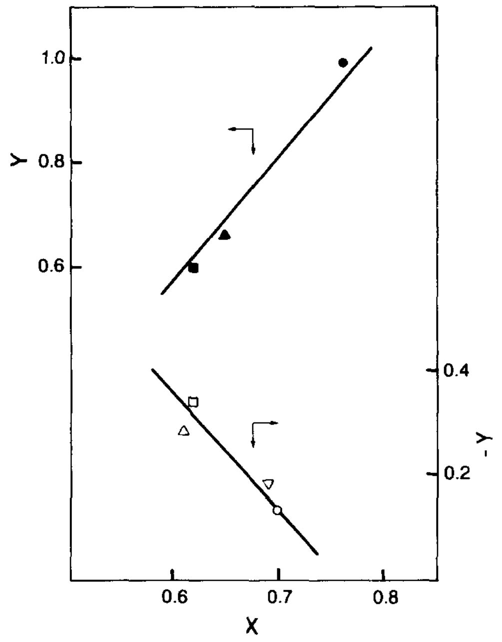

Figure 9 Relationship between the evolution of microstructure (slopes like that of the dashed line of *Figure 8* in *Figures 2*, *4* and *6* [X]) and the change in T_g (slopes of *Figures 3*, *5* and *7* [Y]) during substitution reaction: (○, ●) CH, 25°C; (△, ▲) MP, 25°C; (□, ■) aqueous suspension, 60°C; (▽) CH, 60°C[11]. NaBTZ: filled symbols; NaBT: empty symbols

Overall, the foregoing results strongly suggest that the T_g of PVC after substitution up to roughly 20% depends on two independent molecular factors. One factor is the substituent that has been substituted for chlorine. Clearly, its influence varies with both the degree of hindering character and the ability to create interchain hydrogen bonds. The other factor is the microstructure as defined in our work. Interestingly, the results of *Figure 9* clearly indicate that T_g varies with microstructure, keeping to a unique rate regardless of the remaining molecular features that are likely to contribute to its value. Furthermore, that rate happens to be large enough for the tacticity dependent microstructure to be reckoned as a determining factor for the prevailing T_g.

In addition to that relationship, the results obtained herein provide some novel ideas on the mechanisms at molecular level of the physical processes involved in the T_g transition. Both the intramolecular and the intermolecular interactions appear to depend on the tacticity dependent microstructure. In regard to the former interactions, it has been shown how the conversion of the **mmr** at the end of isotactic sequences into a chain segment, more rigid and with lower excess free volume (*Figure 1*), causes the T_g to increase, probably because the associated isotactic sequence becomes fastened by its end. In fact, **mmr** after substitution appears to be much more inclined to form H···Cl bonds than the same structure prior to substitution. As argued above, the reverse behaviour applies to the **rrmr** terminal of syndiotactic sequences. On the other hand, the fluctuations of local free volume as the result of the conformational changes which are characteristic of the substitution reaction (*Figure 1*) and the consequential changes in T_g happen to relate both **mmr** and **rrmr** structures.

As to the microstructure dependence of the intermolecular interactions, this may also be inferred from the foregoing results. The significant decrease in T_g when the reaction by **rrmr** with nucleophile NaBT progresses has been shown to be accompanied by a progressive decrease in H···Cl bond facilities (*Figure 1*), so indicating the importance of the sequences that are capable of forming consecutive H···Cl bonds; this has been considered in the way that those sequential interactions are connected with the length of the syndiotactic sequences.

Finally, to the above considerations may be added that in the two substitution processes, as reflected in *Figure 1*, a single act of substitution causes the sequence adjacent to the reactive species to be substantially shortened, thereby affecting the interchain interactions and thence the T_g.

The results obtained herein give further support for the high significance of tacticity dependent microstructure in the T_g of PVC. Some work attempting to extend the above conclusions to other polymers is currently under way.

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