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Local chain configuration dependence of the mechanisms of analogous reactions of poly(vinyl chloride)

4. Nucleophilic substitution with sodium thiobenzoate

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Abstract

The substution reaction of poly(vinyl chloride) (PVC) with sodium thiobenzoate has been performed in two series of solvents differing in molecular structure. One series includes cyclohexanone and the other includes more basic solvents, such as *N*-methylpyrrolidone and *N,N*-dimethylformamide. The evolution of unreacted iso-, hetero- and syndiotactic triad contents with degree of substitution has been followed by ^{13}C NMR spectroscopy. In the former type of solvent, the mm located at the end of long isotactic sequences react exclusively. Then, the heterotactic triad mr is involved in the reaction. The latter type of solvent does not discriminate between either structure from the outset of the reaction, as is the case for the former group of solvents at conversions higher than roughly 7%. Only a small fraction of mmr tetrads reacts occasionally by the central chlorine of its mr triad instead of the mm. Through the foregoing results, the mechanisms of substitution, as proposed in a previous work, have been confirmed to be independent of the type of solvent utilized. The approach to the local configurational nature of the mechanisms is discussed on the grounds of the FTIR results. The same reaction has also been studied in aqueous suspension in the presence of a phase-transfer catalyst. In this experimental system, the behaviour of the modified samples in relation to the evolution of the content of mmr and rrmr structures rather approximates to that obtained for basic solvents. On the whole, the results, as analysed in the light of earlier work, provide some novel ideas on the role of the tacticity-dependent microstructure and the related local conformations in the chemical reactions of PVC. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: PVC; Nucleophilic substitution; Local chain configuration

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1. Introduction

In several previous works, we found that the nucleophilic substitution reactions of poly(vinyl chloride) (PVC) proceed via a stereospecific S_N2 mechanism in that only the last triad of isotactic sequences and the heterotactic triads adjacent to syndiotactic sequences intervene in the reaction. Thus, the reactive sites are the mmr tetrad and the rrmr pentad, exclusively [1][2][3][4]. In order for these structures to react, the mm and rm triads have to take the GTTG$^-$ or GTTT conformation, respectively. GTTG$^-$ can exist solely at mmr sequences, whereas GTTT can be adopted by all the mr triads along the atactic parts. Since all the isotactic and heterotactic triads finished up by reacting under appropriate conditions, it was suggested that the mechanism-determining factor during the reaction would be the conformational change GTGTTT ⇒ GTTG$^-$TT, which provides the highly reactive conformation GTTG$^-$ as long as isotactic sequences exist. Subsequently, the reaction would proceed through the less reactive conformation GTTT in heterotactic parts [3].

On the other hand, we found recently that 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 [2], in aqueous suspension in the presence of a phase transfer catalyst (PTC) [5] or in the melt [6]. Basically, the following has been demonstrated. (a) For a series of solvents like cyclohexanone (CH), methyl ethyl ketone (MEK) and tetrahydrofuran (THF), which will be referred to as type 1, the reaction proceeds only through isotactic mm triads up to conversions of roughly 7–10%; then, the heterotactic rm triads also start reacting. In more basic solvents, like *N*-methyl-2-pyrrolidone (MP), *N,N*-dimethylformamide (DMF) and hexamethylphosphoric triamide (HMPT), which are referred to as type 2, both triads react from the onset of

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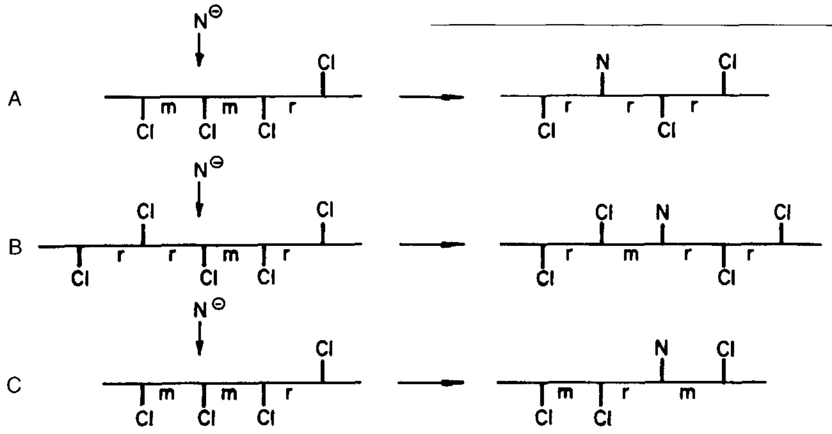
the reaction even if, as is the case for solvents of type 1, when the conversion exceeds 7–10%, the mm triads are preferred [7]. (b) Under reaction conditions where the foregoing conformational change is presumably hindered, e.g., in the melt state or in aqueous suspension with PTC, the behaviour is rather like that of the solvents of type 2 [5][6].

The basis of such behaviour lies in the fact that, as demonstrated recently, the molecular interactions between the reactive structures and a few solvents, esters and polyesters are different in both nature and strength [8]. Solvents like CH and MEK (type 1) are able to complex specifically the mmr structure taking the $\mathrm{GTTG^{-}TT}$ conformation, thereby making it possible to displace the conformational equilibrium $\mathrm{GTGTTT} \rightleftarrows \mathrm{GTTG^{-}TT}$, which usually lies on the left side, to the side of $\mathrm{GTTG^{-}TT}$ conformation. In contrast, solvents like MP and DMF (type 2) scarcely displace this equilibrium and, owing to their less electron donor and higher hard-basic character than the former group of solvents, they interact with mmr and rrmr structures in more parallel ways [8]. This has been widely explained on the basis of the electron donor–acceptor concept and hard–soft acid–base (HSAB) theory [9].

By comparing quantitatively the microstructural changes with degree of substitution on PVC with sodium benzenethiolate (NaBT) and taking into account the characteristics of the S_N2 mechanism, the following stereospecific mechanisms were proposed to operate:



Mechanisms A and B take place when the substitution occurs either via the mm triad of the mmr tetrad and via the mr triad of the rrmr pentad, respectively. Mechanism C arises from the reacted triad mr in the mmr tetrad even though, in fact, most of the mmr structures have been proven to react by mechanism A [3].

Encouraged by these findings, we became interested in exploring the influence on the proposed mechanisms of the nucleophilic group which is substituted for chlorine atoms. To do this, we studied the substitution reaction of PVC in solution with both type of solvents using sodium thiobenzoate (NaTB), a similarly bulky nucleophile with much higher capability of interacting with hydrogen atoms than NaBT. In addition, we studied the same reaction in aqueous suspension in the presence of tetrabutyl ammonium bromide (TBAB) as PTC so as to avoid any interaction of PVC with solvents.

2. Experimental

2.1. Materials

The PVC sample studied was prepared by the bulk polymerization process at 90°C, using 2,2′-azodiisobutyronitrile (AIBN) from Fluka as initiator. The number-average molecular weight ($M_n = 18\,000$) was determined at 34°C in CH using a Knauer membrane osmometer. This polymer was previously found to be quite bernoullian in character. Therefore, the probability of occurrence of tactic sequences, whether isotactic or syndiotactic, is extremely low. Since the crystallinity of PVC is considered to depend on the content of these sequences, in particular the syndiotactic, we believe it reasonable that the crystallinity of the PVC sample as used in this work should be nil in practice. 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. 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 phosphorus pentoxide for 4 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 (TB; Fluka) were purified by fractional distillation under nitrogen. A reagent grade of TBAB (Fluka) was used without further purification.

2.2. Preparation of NaTB

A solution of 1.74 g (58.0 mmol) of sodium hydride oil dispersion (80%) in 40 ml of THF was added dropwise to a well-stirred solution of TB (6.75 g, 48.9 mmol) in 40 ml of THF under a nitrogen atmosphere. The mixture was refluxed for 4 h, then filtered and the solvent evaporated in vacuo. 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.

2.3. Substitution reaction of PVC with NaTB in solution

PVC (1.85 g, 29.6 mmol, based on monomeric unit) was dissolved in 109 ml of solvent (CH, DMF or MP). Then, 5.33 g (33.3 mmol) of NaTB in 122 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 vacuo at 50°C.

2.4. Substitution reaction of PVC with NaTB 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 NaTB 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. IR (film): 1660 (S–C=O); 1580 (aromatic); 775 (S–C); 690 (COS) cm^{-1}. ^{1}H NMR (dioxane): δ 8.12–7.60 (m; 5H, monosubstituted aromatic), 4.50 and 2.2 (protons of unreacted PVC).

2.5. ^{13}C NMR spectroscopy

The tacticity of both the starting and modified polymers was measured by means of ^{13}C NMR 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 (volume ratio 2:1). The spectral width was 2500 Hz; a pulse repetititon of 3 s and 16k 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 digital planimeter, as well as by means of the built-in electronic integrator.

3. Results and discussion

As shown in a preliminary work [10], the incorporation of the thiobenzoate group into the PVC was followed by UV spectroscopy. The degree of substitution of the reaction was determined by measuring the absorbance at 266 nm in the UV spectrum. A calibration curve was obtained previously by plotting the absorbance at 266 nm vs. conversion for a series of samples after modification to conversions ranging between 0.5% and 20% at least three times measured by microanalysis of the content of chlorine and sulfur. Some of the conversion values thus obtained were checked using ^{1}H NMR spectroscopy, which accounts for the accuracy of the calibration curve [10]. This procedure resulted in a straight line passing through the origin of coordinates.

Fig. 1 shows the evolution of conversion curves at stoichiometric concentration for the two types of solvents [CH (type 1); MP and DMF (type 2)]. In agreement with expectations, both the fast period rate and the final conversion of the reaction increase with the dipole moment of the solvent, i.e. with its ability to complex the cation of the nucleophile without solvating the anion appreciably, so that the latter should increase strongly in nucleophility. The complete parallelism between the reactivity depending on the type of utilized solvent and that obtained previously with benzenethiolate [2, 11] makes it reasonable to suppose that the mechanisms are alike.

An overview of the evolution of the ^{13}C NMR spectrum with substitution is given by Fig. 2. From comparison with the spectrum of the unmodified PVC, it may be concluded that the substitution involves the appearance of new signals at 59.4–59.7 ppm, very close to the syndiotactic triads of unmodified PVC, and around 60.2 ppm, when the degree of substitution increases (not included in Fig. 2). Some minor bands at 58.7, 58.4 and 57.8 ppm can also be observed. The remaining bands are those of pure PVC and no appreciable change in position is observed, though some broadening of syndiotactic triads is noticed.

The most salient feature is, on the one hand, the ability to

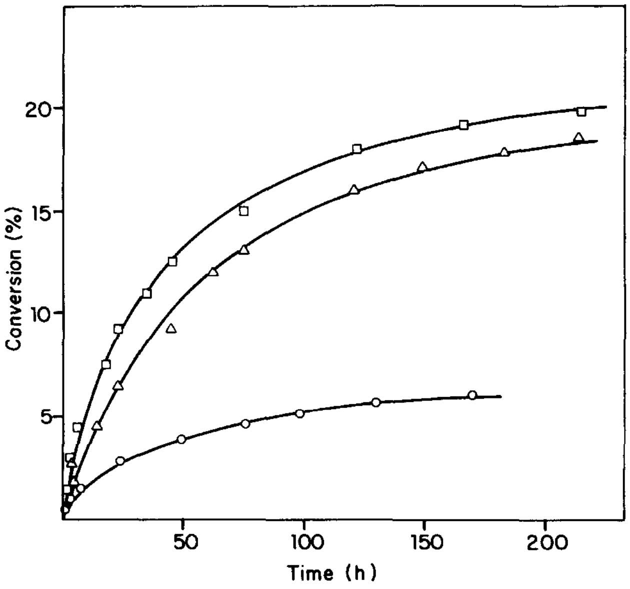


Fig. 1. Nucleophilic substitution on PVC with NaTB at 40°C in different solvents: (○) CH; (△) DMF; (□) MP.

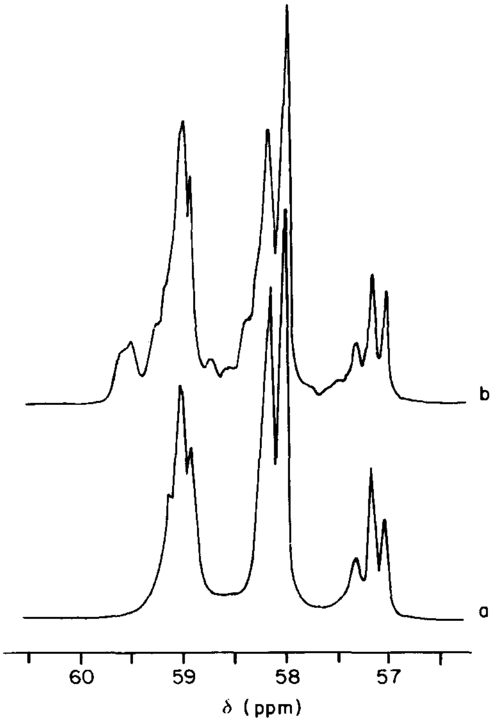


Fig. 2. ^{13}C NMR spectra (methine carbon region) of: (a) virgin PVC; (b) PVC after 7.5% substitution with NaTB in DMF.

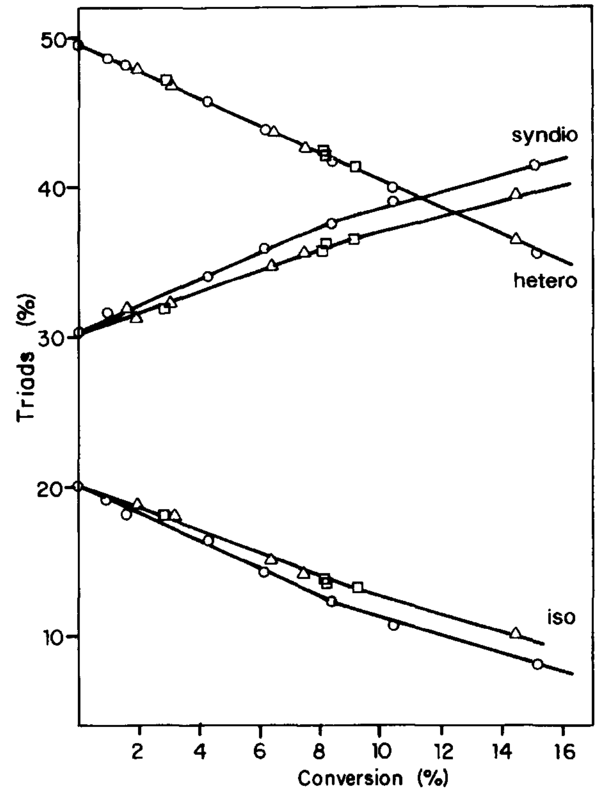


Fig. 3. Evolution of the content of the tactic triads with conversion for different solvents: (○) CH; (△) DMF; (□) MP.

differentiate the bands that are relevant to the modified polymer units from those of the unreacted polymer for the purpose of a reliable measure of the polymer composition. On the other hand, an accurate evaluation of the content of the syndiotactic, heterotactic and isotactic triads and of the isotactic pentads in the unmodified parts of the polymer should be ensured for the reactivity of the local configurations to be stated. As can be seen from Fig. 2, this is the case for the polymers modified with NaTB, even if, unlike in the reaction with NaBT, dioxane-d_8 could not be used as solvent because of the overlapping of the signals. The only negative implication of this arises from the non-resolution of the mmmr isotactic pentad, which makes it impossible to discriminate, experimentally, between the rmmmrx and mmmmrx (x = m or r) heptads.

In the light of the foregoing work, we assume that the bands at 59.4–59.7 ppm and around 60.7 ppm are due to the polymer unit after modification. On the contrary, the small bands at 58.7, 58.4 and 57.8 ppm might be due to long-range steric effects on the ^{13}C NMR chemical shifts induced by the changes in local microstructure that occur in the vicinity of the heterotactic triad as the result of substitution. The same argument should hold for the broadening of the syndiotactic band according to the above-quoted results.

Fig. 3 shows the evolution of the content of each triad, as calculated by measuring the areas of the respective bands, with the degree of substitution. Actually, until a conversion as high as 8% is reached, the decrease of isotactic triad content occurs in an almost symmetrical way to the increase of syndiotactic triad content, which accounts for both changes being concomitant. Clearly, these effects during the early stage of the reaction are of significantly less intensity for solvents of type 2. In contrast, a unique linear behaviour is observed for the decrease of heterotactic triad content irrespective of the type of solvent for the overall reaction.

It is worth noting that the curves in Fig. 3 are quite similar to those obtained for the reaction with NaBT, which is surprising since the reactants are quite different in reactivity. Hence, the substitution reaction of PVC is demonstrated to be stereoselective for the two nucleophiles studied so far.

Another salient point that is worth emphasizing is that, here again, there are two groups of solvents quite distinct in behaviour. On the other hand, type 1 represented by CH and type 2 by DMF and MP showed a similar evolution of the content of the tactic triads with conversion (Fig. 3) to that found for NaBT [3]. With regard to this subject and taking into account the high reactivity of the isotactic triad relative to the heterotactic in S_N2 substitution [7], it may be inferred from the foregoing results that, during the early reaction period, the substitution in solvents of type 1 occurs exclusively by a highly reactive fraction of isotactic triads, and then the reaction by heterotactic triads begins competing.

In order to confirm the outstanding role of solvents in the nucleophilic S_N2 substitution in PVC with NaTB, Fig. 4 shows the disappearance of mm triads with conversion.

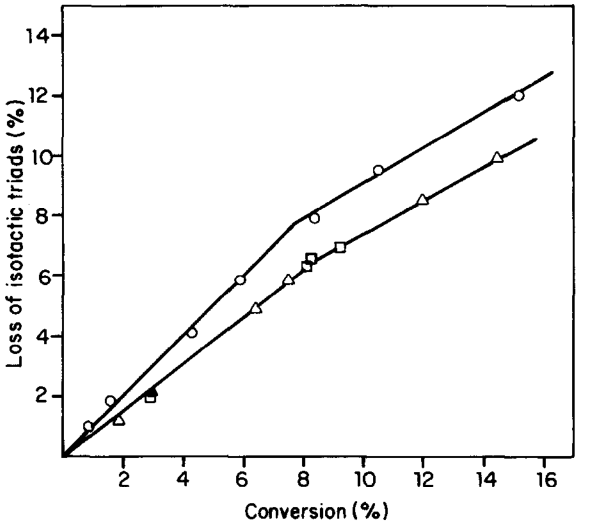


Fig. 4. Evolution of loss of isotactic triads with conversion of PVC after the substitution reaction in various solvents: (○) CH; (△) DMF; (□) MP.

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 mmr triad from the overall conversion. Notably, from the corresponding slopes it follows straightforwardly that the main difference between both behaviours lies in the first step, where the slope is unity for CH and less than unity for DMF and MP. Thus, the reaction occurs more often by mmr, and this behaviour is accentuated in CH compared to DMF and MP. Once again, the results obtained with NaTB are an accurate confirmation of our previous results on the conduct of both types of solvents with NaBT as nucleophile [3]. Accordingly, this important conclusion appears to be general irrespective of the type of nucleophile utilized.

On the grounds of the above-quoted recent results [3, 8] (and this work), these specific interactions make it feasible to conduct the substitution reaction specifically through either mmr or rrmr or both, in a controlled manner. The interaction through the mmr terminal of long isotactic sequences is more specific. In contrast, more basic solvents such as DMF and MP scarcely discriminate between mmr and rrmr structures.

The configurational changes depicted in Figs 3 and 4 emerge from mechanisms A and B. Now, if these mechanisms were the only ones operative, then the evolution of the isotactic triad loss versus the syndiotactic triad increase and that of the heterotactic triad loss versus conversion ought both to be linear with a slope of unity; moreover, if a single mechanism operates for each of the mmr and rmrr configurations, these linear behaviours should be independent of the type of solvent.

The extent to which the experimental results fulfil these conditions is shown in Figs 5 and 6. Clearly, a slight deviation from the theoretical expectations is apparent. Actually, as shown in Fig. 5, there is a small fraction of isotactic triads that disappears without the corresponding appearance of syndiotactic triads. Consequently, even though mechanism A proves to be highly predominant, a small fraction of mmr tetrad seems to behave otherwise. The same argument applies for the reaction through rrmr pentads. As shown in Fig. 6, there is a small fraction of rrmr that reacts by a mechanism other than mechanism B, in that a number of acts of substitution do not involve heterotactic triad depletion.

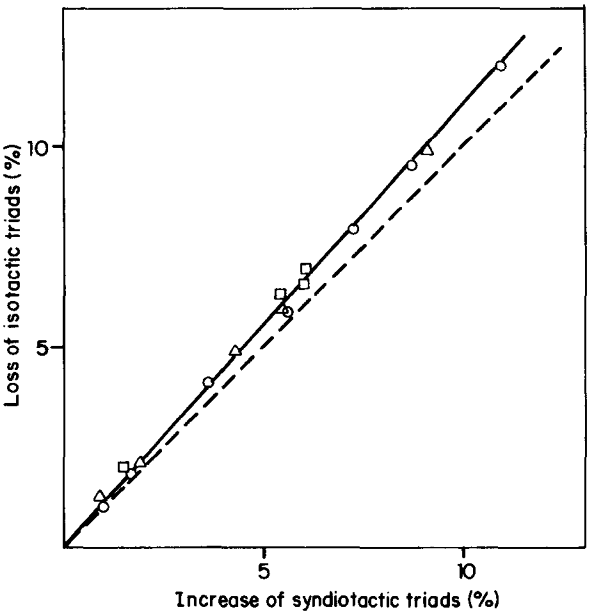


Fig. 5. Evolution of loss of isotactic triads with increase of syndiotactic triads in various solvents: (○) CH; (△) DMF; (□) MP.

The results shown in Figs 5 and 6 are very similar to those found for NaBT [3]. Consequently, even if the mm triad is much more sensitive to S_N2 substitution than the mr triad [1], some of the mmr tetrads should be assumed to react through the mr triad instead of the mm (mechanism C). In this connection, it is worth emphasizing that, as illustrated in Figs 5 and 6, the reaction mechanisms for mmr and rrmr structures should be independent of the type of solvent.

Basically, the results presented herein confirm the previously proposed influence of local configurations on PVC reactivity and convey specific information about the role of such configurations and of the local conformations that are likely in them, in the interaction phenomena concerning PVC.

With the purpose of providing further evidence of the foregoing local configuration-based mechanisms of substitution reactions, the evolution of the ν(C–Cl) bands of the modified samples have been studied by FTIR spectroscopy. It is necessary to analyse the evolution of the FTIR spectrum of PVC, in particular the 600–700 cm^{-1} region, during the substitution reaction studied, and then to compare the sequential order and the number of distinct conformationally sensitive vibration modes of the C–Cl bond before and after substitution, calculated theoretically in the light of the stereospecific mechanisms presented elsewhere [12].

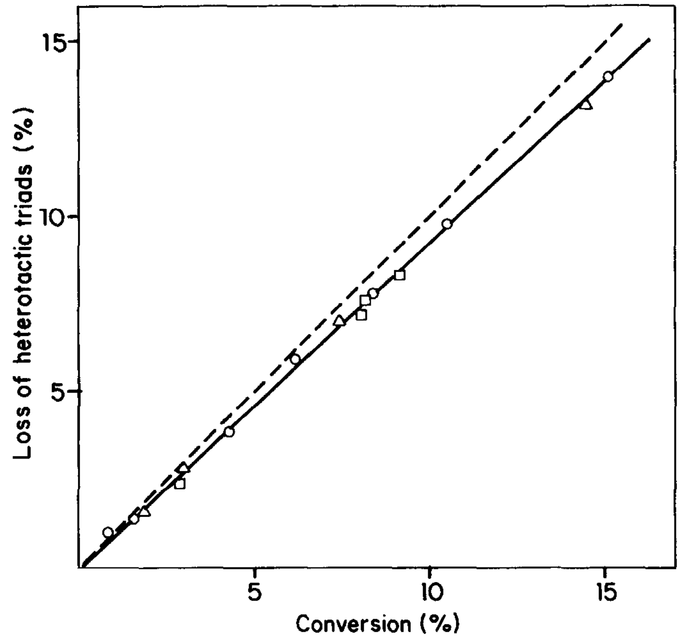


Fig. 6. Evolution of loss of heterotactic triads with conversion in various solvents: (○) CH; (△) DMF; (□) MP.

Fig. 7 shows the evolution of the 600–1800 cm^{-1} region of the FTIR spectrum with nucleophilic substitution. Firstly, the bands at 653, 690 and 775 cm^{-1} correspond to the absorption of the thiobenzoate group in the modified polymers. Secondly, no change in position of the 615 and 637 cm^{-1} bands is observed. Consequently, it is interesting to focus our attention on these bands to account for the changes in local microstructure derived from nucleophilic substitution.

Following the assignment of the different types of C–Cl bond and the changes in their respective sequences, as was proposed in earlier work [12], mechanism A gives rise to the appearance of the $(S_{HH})_b$ mode and, consequently, an increase in intensity of the 615 cm^{-1} band would have to occur. (The suffix stands for the *trans* substituents on both C–C bonds adjacent to the C–Cl bond). In contrast, in the second period of reaction (after 8%), when the reaction takes place via mr triads (mechanisms B and C), the $(S_{HH})_a$ modes disappear and, hence, a decrease of the band at 637 cm^{-1} would arise.

The experimental changes of the bands at 615 and 637 cm^{-1} can be observed in Fig. 7. Within experimental uncertainties, an increase in the absorbance ratio $A_{615\ \mathrm{cm}^{-1}}/A_{637\ \mathrm{cm}^{-1}}$ with degree of substitution can be appreciated, particularly in the 2–9% range. This increase is not large enough for an unambigous conclusion to be drawn. At conversions over 9%, the resolution of the 637 cm^{-1} band is poor owing to both its low absorption as the conversion increases and the overlap with the 653 cm^{-1} absorption. Therefore, the above changes are difficult to observe. Actually, these peculiarities are the same as those found in the substitution. reaction with NaBT [12]. Consequently, the proposals in the foregoing work [12] are valid for the results presented herein, in such a way that the experimental behaviour of the ν(C–Cl) bands is found to be in close agreement with theoretical expectations, thus providing an interesting approach to the local configurational nature of the mechanisms of reactions of PVC.

As was argued previously [2, 5], the way to control the evolution of the ratio of mmr to rrmr with degree of substitution was made possible by changing the type of the

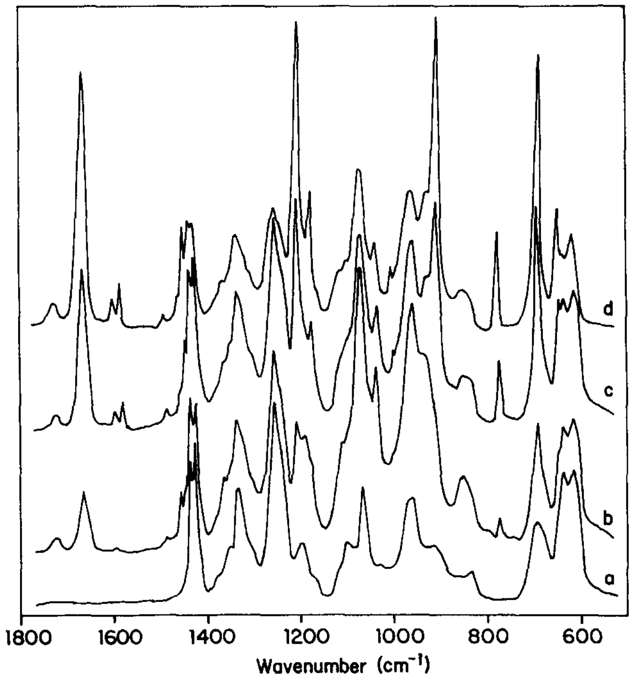


Fig. 7. Evolution of IR spectra with conversion: (a) 0%; (b) 1.6%; (c) 3.0%; (d) 8.4%.

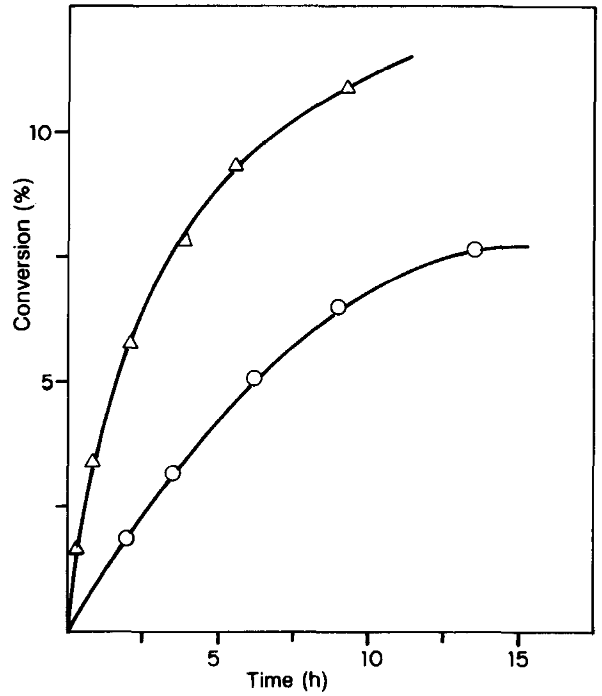


Fig. 8. Nucleophilic substitution on PVC with NaTB at 60°C in aqueous suspension at different concentrations of TBAB: (○) 3.1 × 10^{-2} mol l^{-1}; (△) 6.2 × 10^{-2} mol l^{-1}. [PVC]/[nucleophile] = 1 mol mol^{-1}.

solvent in solution reactions or by carrying out the reaction in aqueous suspension in the presence of a PTC.

With regard to the latter reaction conditions, we carried out experiments at two different concentrations of TBAB as PTC to provide modified samples with degrees of substitution not higher than 15% (range used before in solution). The conversion curves are shown in Fig. 8. They exhibit a steep period followed by a slower one. Interestingly, the initial rates are higher than those in solution and they could influence the reaction mechanisms.

The contents of unreacted iso-, hetero- and syndiotactic triads are shown in Fig. 9, where the evolution of the content of the tactic triads with conversion for reaction in CH is also included (type 1, Fig. 3). The most salient result from this plot is that the evolution of heterotactic triads is independent of the experimental conditions. In fact, comparing this behaviour with that obtained in solution (Fig. 3), it is apparent that the substitution is, in both cases, of the same nature. Nevertheless, as inferred from the lower slope of both the depletion of isotactic triads and the augmentation of syndiotactic triads, the discrimination between the two reactive structures, namely the mmr tetrad and the rrmr pentad, is more like that found for solvents of type 2 than of type 1, and is large enough for the relative contents of mmr and rrmr structures to be changed in a controlled manner. This can be more accurately observed in Fig. 10, showing that the removal percentage of mm triads against conversion approximates to those obtained using DMF and MP as solvents, included for comparison.

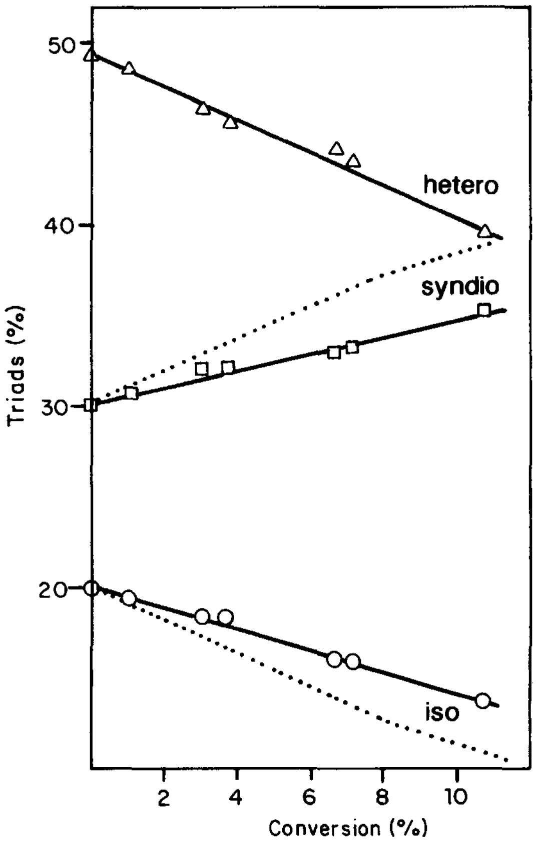


Fig. 9. Evolution of the content of tactic triads with conversion of PVC after the substitution reaction in aqueous suspension in the presence of TBAB. Dotted lines represent the behaviour of the substitution reaction in solution with solvent of type 1.

It is worth noting that every act of substitution involves not only the disappearance of one mmr or rrmr structure, but also, owing to the inversion of the configuration of the carbon, characteristic of the S_N2 mechanism, substantially

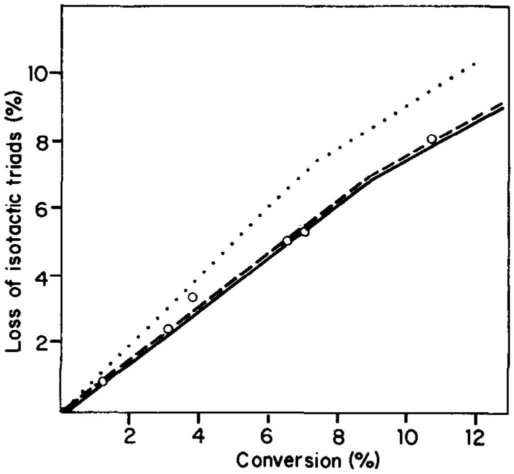


Fig. 10. Evolution of loss of isotactic triads with conversion of PVC after the substitution reaction in aqueous suspension in the presence of TBAB. Dotted and dashed lines represent the behaviour of the substitution reaction in solution with solvents of type 1 and type 2, respectively.

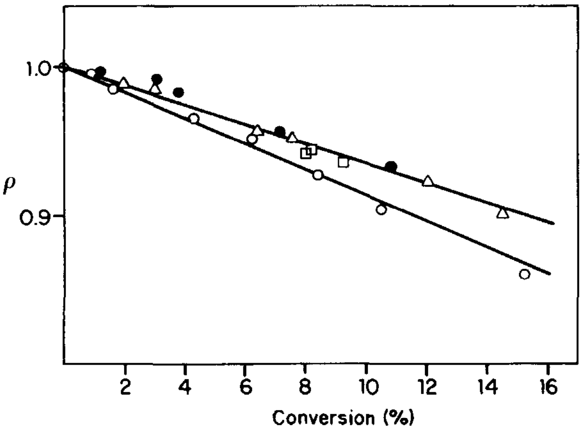


Fig. 11. Evolution of persistence ratio (ρ) with conversion in different reaction media: (○) CH; (△) DMF; (□) MP; (●) aqueous suspension in the presence of TBAB.

alters the configuration and the related conformation of the adjacent triads, thereby bringing about a significant rearrangement of a definite chain segment. With the purpose of illustrating the variation of these configurational rearrangements, we calculated the persitence ratio ρ (as defined by Reinmöller and Fox [13], $\rho = P(S)/P(S/I)$), for all the experiments performed in this work. ρ was thus found to decrease linearly with conversion (Fig. 11), which implies that the modified samples depart gradually from bernoullian behaviour ($\rho = 1$).

However, what is important for the purpose of the present research is to realize that there are two well-defined straight lines, the slope of which changes with the reaction conditions. The behaviour depends on whether the reaction is carried out in CH (type 1) or in solvents of type 2 or in aqueous suspension in the presence of PTC. Furthermore, the slope of the plot in the former case is higher than in the latter. This indicates that, for the same conversion, there is a more severe rearrangement in CH than in the other reaction media, which is consistent with the aforementioned finding that the reaction occurs exclusively through mmr in solvents of type 1 and then with the higher stereoselectivity in these solvents. Finally, the lack of appreciable difference observed when the reaction is accomplished either in solvents of type 2 or in aqueous suspension is in accordance with the analogous performance achieved in both kinds of experiment, as inferred from the elimination of mm triads with conversion (Figs 4 and 10).

4. Conclusions

1. The nucleophilic substitution of PVC with NaTB has been proven to proceed through the local configuration-driven mechanism found for NaBT as nucleophile in previous work.
2. This mechanism is consistent with the superiority of the mmr configuration terminal of isotactic sequences, relative to rrmr configuration terminal of syndiotactic sequences, in reacting, and has been shown to be operative in two distinct types of solvent and in aqueous suspension in the presence of a PTC. However, these conditions are able to vary the relative contribution of each reactive species, thereby enabling one to prepare polymers with controlled microstructure.
3. The results provide some novel basic concepts in the field of chemical modification of polymers.

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