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Local chain configuration dependence of the mechanisms of analogous reactions of PVC-5. Novel results on substitution reaction with sodium 2-mercaptobenzothiazolate

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Abstract

The nucleophilic substitution reaction on poly(vinyl chloride) (PVC) with sodium 2-mercaptobenzothiazolate has been carried out in solution in cyclohexanone at different temperatures. The kinetic parameters indicate the occurrence of one process having an activation energy of 63 KJ.mol^{-1}. The evolution of unreacted iso, hetero and syndiotactic triad contents with degree of substitution has been followed by ^{13}C n.m.r. spectroscopy. By comparing quantitatively the microstructural changes with degree of substitution and taking into account that the reaction is of S_N2 type only the mechanisms of substitution through the **mm** triad of **mmr** tetrad and the **rm** of **rrmr** pentads are proved to react. On the contrary, owing to steric hindrance the reaction by the **mr** triad in the **mmr** tetrad is quite unlikely, thus enhancing the stereoselective nature of the reaction. This conclusion was confirmed on the basis of the *FT*i.r. results and is more feasible than using other nucleophiles to study the effect of the aforementioned structures on the polymer properties and therefore provides new approaches to better comprehension at the molecular level of the structure–property relationships. These novel contributions are an original approach to the prominent role of the microstructure-dependent local conformation in the mechanisms of analogous reactions of PVC. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl chloride); Stereoselective substitution; Local configurational mechanisms

1. Introduction

Owing to the great commercial importance of poly(vinyl chloride) (PVC) the modification of this polymer continues to attract the attention of many polymer researchers [1–3]. In some previous work [4–11] we have extensively pointed out that nucleophilic substitution in PVC with sodium benzenethiolate (NaBT) proceeds via a stereospecific S_N2 mechanism in that only isotactic and heterotactic triads participate in the reaction. As is easily observable with the help of atomic models the chain-reactive sites are the **mmr** tetrad and the **rrmr** pentad, exclusively, that is, the local configuration at the end of isotactic and syndiotactic sequences, respectively, regardless of their length.

The **mmr** structure may take either of the GTTG$^-$TT and GTGTTT conformations which contain respectively the highly reactive GTTG$^-$ isotactic triad and the less reactive GTTT heterotactic triad conformation. GTTG$^-$ can exist solely at **mmr** sequences whereas GTTT can be adopted by all the **mr** triads along the atactic parts. In addition, because GTTG$^-$ is very different to unreactive GTGT, the other likely isotactic triad conformation, the conformational change GTGTTT → GTTG$^-$TT at **mmr** sequences is necessary for the reaction to occur, preferably through the isotactic triads as long as they exist in the polymer, in accordance with experience [9].

The above results, taken together, led us to suggest first that the actual reactive species should be the **mmr** and the **rrmr** structures under the GTTG$^-$ or TTTG conformation, respectively; and secondly, that the reaction proceeds preferably through the former structure on condition that the above conformational change operates so as to ensure the presence of the highly reactive GTTG$^-$ triad conformation.

It is worth noting 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, it substantially alters the configuration and the related conformation of the adjacent triads, thereby bringing about a significant

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rearrangement of a definite chain segment. This consideration coupled with the aforementioned finding allowed us to propose the following stereospecific mechanisms: Mechanism A applies for the reaction of the **mm** triad of **mmr** and involves the simultaneous disappearance of one isotactic triad and one heterotactic triad by exchanging for one benzenethiolate centered triad and one co-syndiotactic triad, respectively. Mechanism B is that of substitution by the **rm** triad of **rrmr** and involves the elimination of a single heterotactic triad. Finally, mechanism C relates to a well defined fraction of **mmr** tetrads which react via the **mr** tetrad instead of the **mm** tetrad. This 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 mechanism B) [11].

Encouraged by these findings we became interested in exploring the influence on the proposed mechanisms of the nucleophile group which is substituted for chlorine atoms. Recently, we have studied the substitution reaction in PVC using sodium thiobenzoate [12], a similarly bulky nucleophile with a greater capability of interacting with hydrogen atoms than NaBT. Through the results obtained, the mechanisms of substitution as proposed in a previous study [11] have been confirmed. The aim of the present work is to analyse the hypothetical influence of the volume of the nucleophile in the aforementioned mechanisms of reaction of PVC. A bulky nucleophile without significant change in nucleophility, involves, in principle, a low reactivity owing to the strong steric hindrance making the less reactive mechanisms unlikely. For this study we have selected sodium 2-mercaptobenzothiazole (NaMBT) as nucleophile.

2-mercaptobenzothiazole and its derivatives which are available commercially because they are relatively inexpensive, have been used as vulcanization accelerators in the rubber industry [13] and also as photoinitiators of vinyl polymerizations [14–16]. Chemical modification of chloromethylated polystyrene with 2-mercaptobenzothiazole has recently been carried out by Ergozhin et al. [17] to use linear ion exchanges as analytical reagents for the detection and identification of transition and noble metals.

2. Experimental

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 cyclohexanone (CH) using the osmometric method. Tetrahydrofuran (THF) was distilled under nitrogen with aluminium lithium hydride to remove peroxides. CH was purified by fractional distillation. 2-Mercaptobenzothiazole (Fluka) (MBT) 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 dispersed (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

2.0 g (32.0 mmol, based on monomer unit) of PVC was dissolved in 125 ml of CH and 6.24 g (33.1 mmol) of NaMBT in 125 ml of CH was added to the polymer solution. The mixture was stirred and heated at 40, 50, 60 and 70°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 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 was 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 n.m.r. spectroscopy, which accounts for the accuracy of the calibration curve [18]. The UV spectra were determined in a Perkin Elmer 554 UV-Vis spectrophotometer at room temperature with a 1 cm^{-1} path length cell.IR(film): 3080 (NH); 1456, 1427 (CH, CN, NH stretching); 1250, 1240 (–N = C–S stretching); 757, 727 cm^{-1} (CH, CN, CS stretching).^{1}H n.m.r. (200 MHz): $\delta = 2.5$ (CH_2); 4.6 (CH Cl); 7.5, 7.6, 7.9 and 8.0 (CH of benzene ring).

2.4. Infrared measurements

An *FT*i.r. Nicolet 520 spectrometer equipped with a DTGS detector was used for the IR measurements. Thirty-two scans were signal averaged at a resolution of 2 cm^{-1}. The peak absorbances were determined from a tangent baseline.

2.5. ^{13}C n.m.r. spectroscopy

The tacticity of both the starting and modified polymers were measured by means of ^{13}C n.m.r. 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 16 K data points were used. The relative peak intensities were measured from the integrated peaks area, calculated by means of an electronic integrator.

3. Results and discussion

The incorporation of 2-mercaptobenzothiazolate group into the polymer is proved by UV spectroscopy, as shown in Fig. 1. Moreover, the change in the UV spectra with reaction time enables the kinetic features to be easily studied after a calibration curve has been determined [18].

Fig. 2 shows the evolution of the degree of substitution of PVC with NaMBT as a function of time for the indicated reaction temperatures. As can be seen, the kinetic curves exhibit a steep period followed by a slower one. The gap between the two periods is markedly smoother than that obtained when the substitution reaction is achieved with other nucleophiles, e.g. NaBT, probably as a consequence of the lower nucleophility of the 2-mercaptobenzothiazolate group. This result is in accordance with the observation that the degree of conversion after a moderate time (Fig. 2) is also lower than that got with NaBT at an analogous range of temperatures. The tangent at the outset of reaction to obtain the initial rates could be easily drawn. The rates as obtained from the slopes in Fig. 2 are collected in Table 1. The plot in Fig. 3 makes clear that the above rates fit into the Arrhenius diagram, the corresponding activation energy being 63 kJ mol^{-1}. This value is in good agreement with that obtained for substitution with NaBT at the same range of temperatures [19]. As inferred from the lower rates (Table 1) NaMBT is of lesser reactivity than NaBT, certainly because of its much higher bulkiness which is known to hinder greatly any nucleophilic attack. Thus, owing to the great superiority of the **mm** triad relative to the **mr** triad of **mmr** in reacting [9], NaMBT unlike NaBT, should be expected to react only through the former triad, thereby making the mechanism C of substitution inoperative in practice. As a result NaMBT ought to yield a more

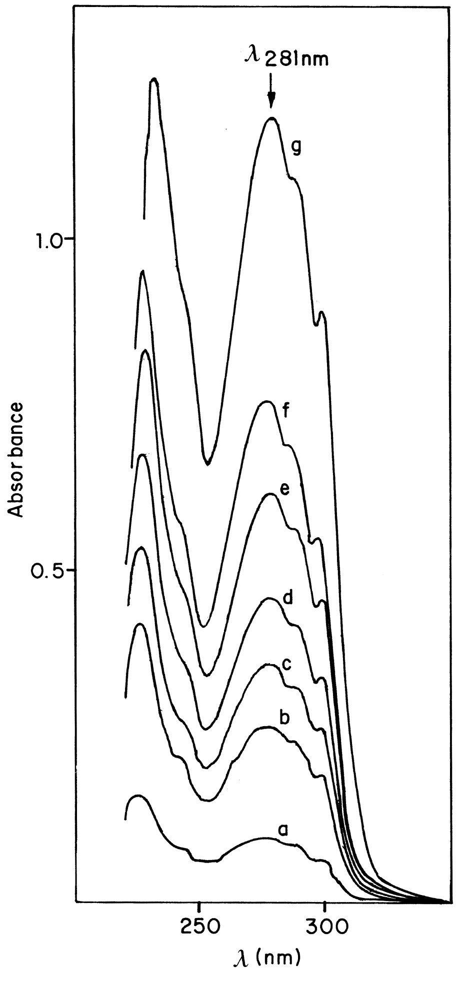

Fig. 1. UV spectra of modified PVC with NaMBT at different conversions. (a) 1.1%; (b) 2.6%; (c) 3.8%; (d) 5.1%; (e) 6.7%; (f) 8.9%; (g) 16.2% conc = 0.048 g/l.

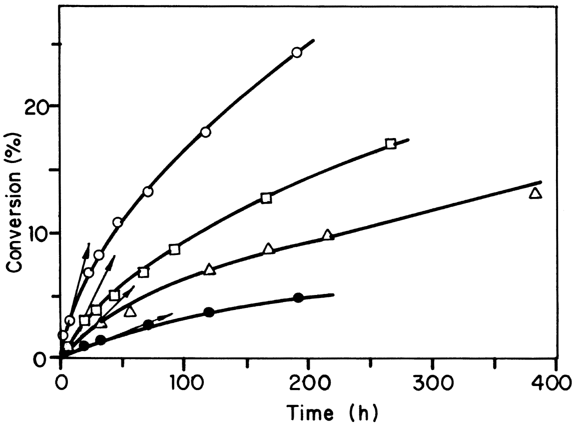

Fig. 2. Nucleophilic substitution on PVC with NaMBT at different temperatures. (●) 40°C; (△) 50°C; (□) 60°C; (○) 70°C. [PVC] = 1.28 × 10^{-1} mol/l; [NaMBT] = 1.32 × 10^{-1} mol/l.

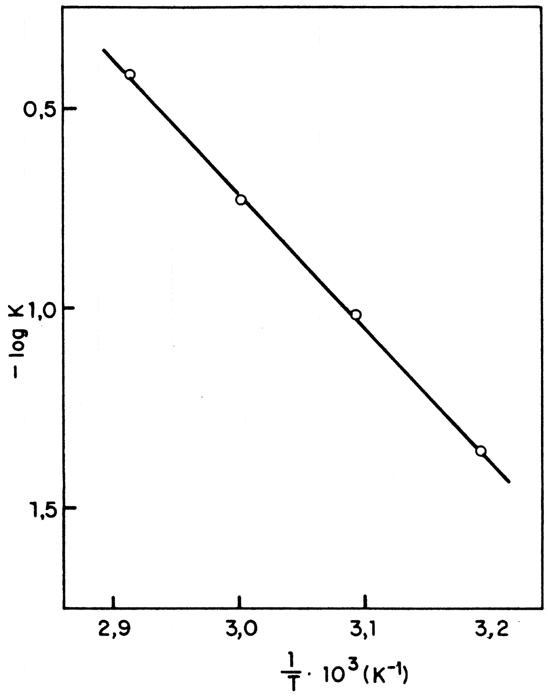

Fig. 3. Arrhenius plot for the initial steps on substitution reaction of PVC with NaMBT (K in % min^{-1}, Table 1).

Table 1
Initial rates of nucleophilic substitution on PVC with NaMBT at different temperatures

Temp. (°C)	10^3.K (% min^{-1})
40	0.7
50	1.6
60	3.1
70	6.4

stereoselective nucleophilic substitution than NaBT. In fact, this mechanism as found for NaBT has a significant effect on the local microstructure and thus on properties [20]. Instead, its frequency of occurrence is low compared with mechanism A [9].

The evolution of tacticity with the conversion can be followed by high resolution ^{13}C n.m.r. spectroscopy. The content of unreacted iso, hetero and syndiotactic triad at any degree of conversion can be determined from the set of signals centered around 57.5, 58.5 and 59.2 ppm, respectively, provided that they be separated enough for their areas to be measured accurately. As shown by Fig. 4, this is the case for the spectra in this study. Furthermore, such a resolution makes it possible to follow, at least to some extent, the changes in **rmmmrx** and **mmmmrx** (x = **m** or **r**) isotactic heptad content as the degree of substitution increases. On the other hand, it may be observed that substitution brings about the appearance of new bands at 59.9–60.2 ppm, very close to the syndiotactic triads of unmodified PVC. In addition, some minor bands at 58.7 and 58.9 ppm can be observed. No appreciable change in position of the bands of pure PVC is observed though some broadening of syndiotactic triads is noticed.

In light of the present work [9], we assume that the bands at 59.9–60.2 ppm are due to the polymer unit after modification. In contrast, the small bands at 58.7 and 58.9 ppm might be due to long-range steric effects on the ^{13}C n.m.r. 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 results. From the overall surface areas of each type of pentad, the contents of syndio, hetero and isotactic triads may be calculated easily. The values found for the studied PVC prior to and after modification to various degrees, are shown in Table 2.

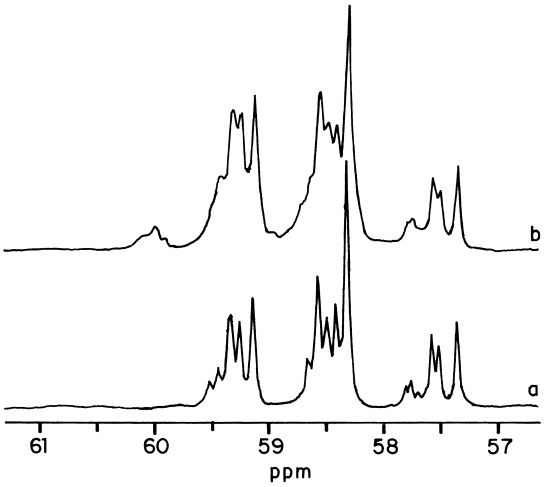

Fig. 4. ^{13}C n.m.r. spectra of (a) virgin PVC; (b) PVC after 6.7% substitution.

The nucleophilic substitution is expected to involve necessarily important changes in the tacticity of the unreacted parts of the polymer. In fact, the configuration inversion resulting from the S_N2 substitution [8] not only makes one PVC triad disappear by exchanging it for one nucleophilic group centered triad, but also alters the tacticity of the triads on either side of the modified one, thereby producing a new local tacticity order along the polymer chain. Whether, and to what extent, this change disturbs the overall balance of the isotactic and syndiotactic configurations will depend on the specific reactivity they have in S_N2 substitution.

As shown in Table 2, both the heterotactic and the isotactic triad contents decrease as the substitution increases, but the latter triad does so at a much higher rate than the former. On the other hand, the ratio of **r** to **m** diads is drastically higher as the degree of substitution increases. Clearly **m** diads are, as a whole, more reactive than **r** diads. This point is better illustrated by Fig. 5, which refers to the evolution of the content of each triad with the degree of substitution. As can be observed, the isotactic triad content decreases up to conversion of roughly 8%; then, that

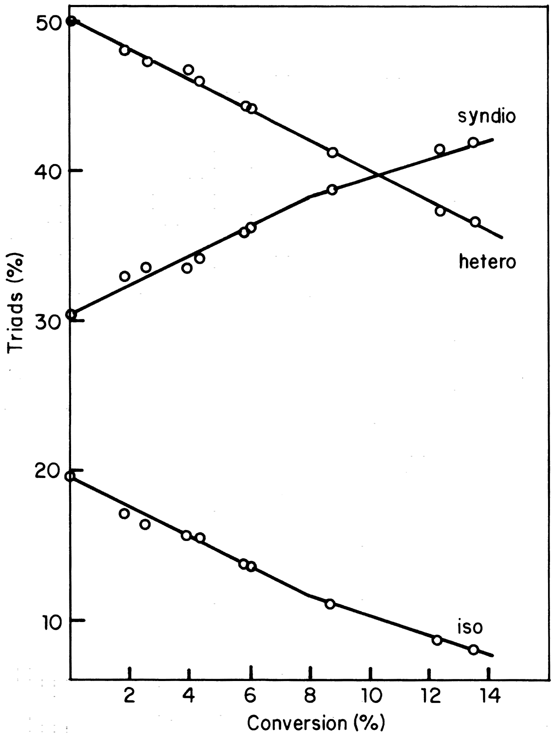

Fig. 5. Evolution of relative contents of triads with conversion.

Table 2
Triad and diad probabilities of unmodified and modified PVC samples

		^{13}C NMR						
Sample	$\bar{n}$M.10^3	Conv.	P^a_{rr}	$P_{mr} + P^a_{rm}$	P^a_{mm}	P^b_r	P^b_m	P_r/P_m
		(%)						
0	45.0	—	0.304	0.499	0.197	0.553	0.446	1.24
1	44.0	1.9	0.326	0.481	0.174	0.566	0.414	1.37
2	—	2.5	0.335	0.474	0.166	0.572	0.403	1.42
3	46.9	3.9	0.336	0.468	0.157	0.570	0.391	1.46
4	—	4.3	0.342	0.460	0.155	0.572	0.385	1.49
5	48.0	5.8	0.358	0.444	0.140	0.580	0.362	1.60
6	—	6.0	0.363	0.440	0.137	0.583	0.357	1.63
7	47.1	8.7	0.388	0.413	0.112	0.594	0.318	1.87
8	—	12.3	0.415	0.374	0.088	0.602	0.275	2.19
9	46.6	13.5	0.420	0.363	0.082	0.601	0.263	2.28

[a] Probability of Syndio (P_{rr}), hetero ($P_{rm} + P_{mr}$) and isotactic (P_{mm}) triads
[b] Probability of Syndio (P_r) and isotactic (P_m) diads

decrease becomes slower. On the other hand, that decrease clearly occurs in an almost symmetrical way to the increase of syndiotactic triad content which accounts for both changes concomitantly. As for the heterotactic triad content, this was found to decrease linearly throughout the substitution in agreement with prior work [9,12].

It is noteworthy that these effects are somewhat more marked than those obtained for the reactions accomplished with other nucleophiles [9,12]. This might relate to the abovementioned implications of the high bulkiness of NaMBT, especially the inoperativeness of mechanism C. Giving that this mechanism is operative in the reaction with the other nucleophiles, as studied so far [9,12], and has important effects on properties such T_g [20], we thought it exciting, scientifically, to investigate whether, and to what extent, it occurs with NaMBT as nucleophile.

Fig. 6 shows the disappearance of **mm** triads with degree of substitution. As can be seen, two well differentiated steps are apparent. Their respective slopes are unity and between 0.5 and unity, thus indicating that up to roughly 7% only isotactic triads, i.e. **mmr** structures are reacting; then, the competing reaction by **rrmr** pentad starts working. Overall, this is essentially the behaviour found for the other nucleophiles where the isotactic **mmr** that are the only ones to react during the early period were demonstrated to be those at the end of isotactic sequences at least one heptad in length [6,9]. That this holds true for NaMBT can be confirmed by comparing the ^{13}C n.m.r. spectra of PVC prior to and after substitution up to 6.7% (Fig. 4). As can be seen, the decrease of the 57.51 ppm signal corresponding to **mmmmrx** (x = **r** or **m**) is more pronounced than that of the 57.58 ppm signal for **rmmmrx** (x = **r** or **m**).

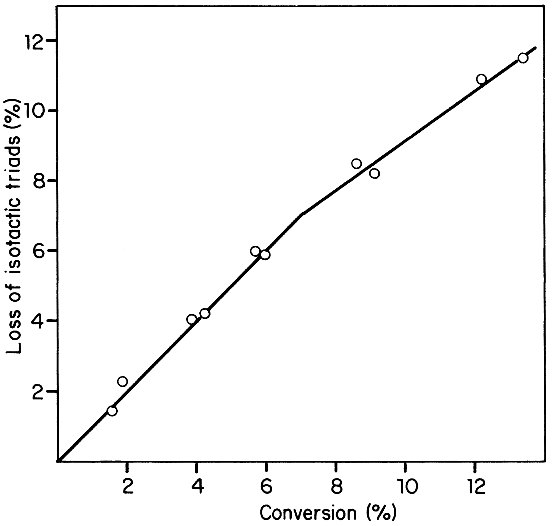

Fig. 6. Loss of isotactic triad content vs conversion of PVC after the substitution reaction with NaMBT.

With respect to the heterotactic triad **mr** the situation is somewhat different. On the grounds of the above quoted recent results [9,12] the change of the linear behaviour (second step in Fig. 6) is the result of the competing reaction through **GTTT** conformation in the **rrmr** heterotactic parts, indicating that the highly reactive **mmr** segments (first step) start to disappear. However, the corresponding slope is higher than that obtained in the reactions with other nucleophiles [9,12]. This is consistent with the lower reactivity of NaMBT as a result of its high bulkiness, which as already indicated, ought to restrict the capability of **rrmr** to react by mechanism B, compared with **mmr** (mechanism A). In addition, the higher slope for the second period (Fig. 6) compared with the nucleophiles formerly studied gives support to the assumption, to a first approximation, that mechanisms A and B should be the unique operatives, so indicating the enhanced stereoselectivity of NaMBT.

As argued in earlier work [9], the results of Fig. 6 are an indication that the substitution involves either the **mmr** tetrad or the **rrmr** pentad, but no conclusion can be drawn as to whether all the **mmr** structures react by mechanism A or whether a small fraction of them is able to react by mechanism C, as is the case for other nucleophiles [9,12]. The reason for this is that mechanisms A and C involve both

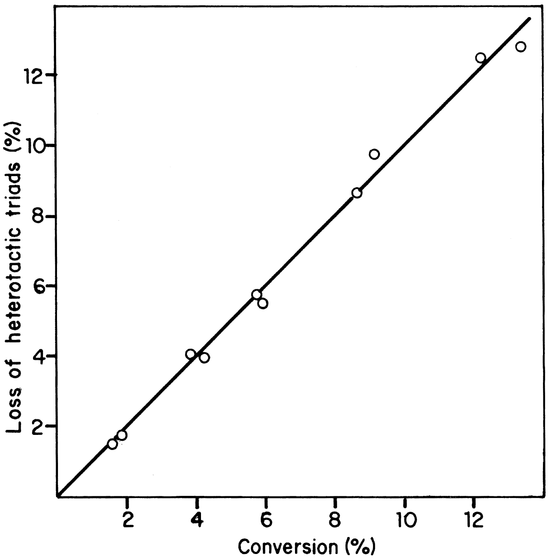

Fig. 7. Loss of heterotactic triad content vs conversion of PVC after the substitution reaction with NaMBT.

the same change in content of **mm** triads. Now, if mechanisms A and B were the only ones operative, then, the evolution of the heterotactic triad loss versus conversion and of the isotactic triad loss versus the syndiotactic triad increase ought both to be linear with a slope of unity. Conversely, any departure from that behaviour, indicating that some of the **mmr** disappear without yielding either the appearance of syndiotactic triads or the disappearance of heterotactic triads, reveals unambiguously the occurrence of mechanism C [9]. The results obtained for NaMBT are given in Fig. 7 and Fig. 8. As can be seen, any mechanism other than mechanisms A or B are to be discarded in NaMBT contrary to what occurs with the nucleophiles studied previously.

These results confirm the tacticity driven microstructure dependence of the nucleophilic substitution mechanisms, and, coupled with those obtained formerly, allow us to prepare model polymers with various local and sequential well differentiated molecular arrangements. This enables new approaches to a better comprehension at molecular level of the structure–property relationships [20].

Within the framework of the substitution reaction of PVC with NaBT the evolution of the C–Cl bands of the *FT*i.r. spectrum was studied [12]. It is well known that the mechanisms of reaction cause the involved local configurations and the respective local conformations to be altered so that the conformationally sensitive C–Cl vibration bands should be expected to change with substitution. In fact, the experimental changes in the bands, in particular those at 615 and 637 cm^{-1} prior to and after substitution, were found to be in close agreement with theoretical expectations. Consequently, on the basis of the above *FT*i.r. results, the local configurational nature of the mechanisms of analogous reactions of PVC was strongly supported [12].

The specific details of *FT*i.r. band assignments for PVC have been extensively argued elsewhere [11]. Based on

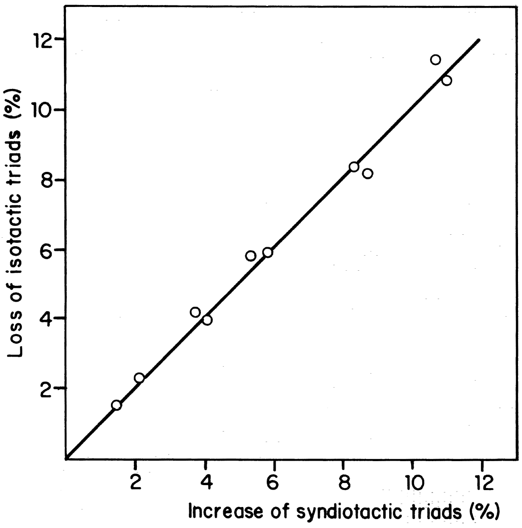

Fig. 8. Loss of isotactic triad content vs increase of syndiotactic triad content of PVC after the substitution reaction with NaMBT.

them and taking into account the changes in local configuration and conformation which each of the substitution mechanisms produces, the variations of C–Cl bonds and their respective vicinities, as expected from substitution, were analysed from a theoretical point of view. Accordingly, mechanism A gives rise to the appearance of $(S_{HH})_b$ 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) [11]. In contrast, in the second period of reaction (after 8%) when the reaction takes place by **mr** triad (mechanisms B and C) the disappearance of the $(S_{HH})_a$ modes occurs, and hence, a decrease of the band at 637 cm^{-1} would have to arise [11].

With the aim of checking whether the above improved stereoselectivity with NaMBT agrees with the *FT*i.r. results, Fig. 9 shows the evolution of the spectrum with nucleophilic substitution. By inspection, the following changes may be noted: (i) the absorption of the bands at 727 and 757 cm^{-1} relevant to the 2-mercaptobenzothiazolate group in the modified polymer increases progressively from spectrum **a** to spectrum **f**; (ii) the intensity of the band at 615 cm^{-1} compared with that of the 637 cm^{-1} increases; furthermore, it becomes narrower and more symmetrical. The band at 637 cm^{-1} seems to decrease in a parallel, although slower, way to the increase of the 615 cm^{-1} band. In addition, the shoulder at approx. 602 cm^{-1} which is observable in the spectrum of unmodified PVC disappears as the 637 cm^{-1} band decreases. Since $(S_{HH})_a$ chlorine is responsible for the 637 and 602 cm^{-1} pair of bands [11], the decrease of 637 cm^{-1} with substitution must be assumed to be concomitant with that of the 602 cm^{-1} shoulder.

These peculiarities happen to be similar to those found in the substitution reaction with NaBT [11]. However, our current interest is focused on analysing the possible differences of the ratio $A_{615\,\mathrm{cm}^{-1}}/A_{637\,\mathrm{cm}^{-1}}$ compared with the results

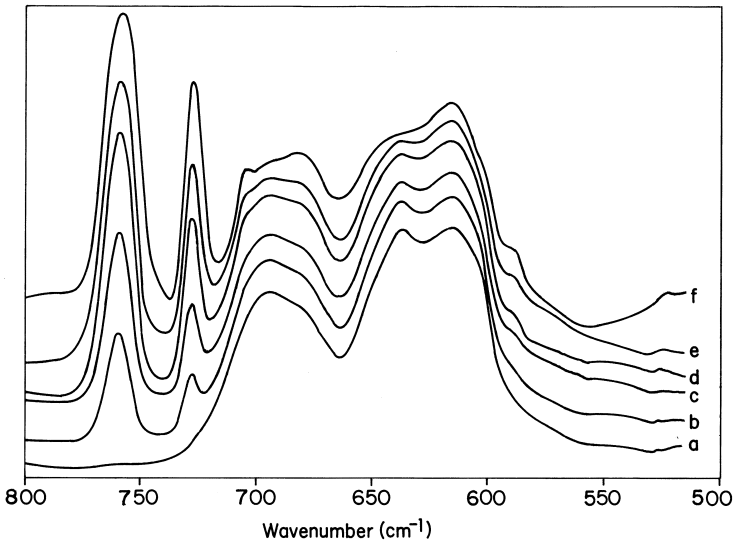

Fig. 9. Evolution of infrared spectra with conversion: (a) 0%; (b) 1.8%; (c) 2.9%; (d) 5.7%; (e) 7.4%; (f) 14.5%.

described previously [11]. In this respect Fig. 10 illustrates the evolution of the absorbance ratio $A_{615\,\mathrm{cm}^{-1}}/A_{637\,\mathrm{cm}^{-1}}$ with conversion. As can be observed this ratio increases progressively in all ranges of conversions studied. This trend clearly indicates that only a mechanism prevails in contrast to what happens in the reaction with NaBT, where a trend towards a stabilization of $A_{615\,\mathrm{cm}^{-1}}/A_{637\,\mathrm{cm}^{-1}}$ takes place at the end of a well defined reaction period which corresponds to the disappearance of the **mmr** reactive species (after 6–9%) [11].

The evolution of the absorbance ratios $A_{757\,\mathrm{cm}^{-1}}/A_{615\,\mathrm{cm}^{-1}}$, $A_{757\,\mathrm{cm}^{-1}}/A_{637\,\mathrm{cm}^{-1}}$, $A_{727\,\mathrm{cm}^{-1}}/A_{615\,\mathrm{cm}^{-1}}$ and $A_{727\,\mathrm{cm}^{-1}}/A_{637\,\mathrm{cm}^{-1}}$ with conversion (Fig. 11 and Fig. 12) show the behaviour of the 2-mercaptobenzothiazolate 757 and 727 cm^{-1} bands with respect to the C–Cl 615 and 637 cm^{-1} bands. Once again, linear relationships are simply obtained, unlike in the reaction with NaBT where the relations between 615 cm^{-1} and 637 cm^{-1} and the bands characteristic of the benzenethiolate anion were not linear [11]. This clearly agrees with the above quoted conclusion that NaMBT, unlike NaBT and other nucleophiles, is not able to react by mechanism C. As a whole the results in Figs 10–12 are consistent with the highly stereospecific nature found in the evolution of the molecular microstructure with substitution (Figs. 6–8).

Finally, as recently shown [12] and previously evoked, every act of substitution, owing to the inversion of the configuration of the carbon, alters the configuration and the related conformation of the adjacent triads thereby bringing about a significant rearrangement of a definite chain segment. By means of the variation of these configurational rearrangements we tried to confirm the influence of the nucleophile nature on the substitution mechanisms, as shown by the results obtained herein compared with earlier results [9,12]. Fig. 13 depicts the variation of the persistence ratio (ρ) (as defined by Reinmöller by the ratio between the normalized intensity of isotactic diads and the conditional probability of a syndiotactic placement on an isotactic chain end [21]) against the conversion of the studied samples. Such a plot reveals that ρ decreases linearly with conversion denoting that the substitution reaction brings about a progressive deflection from the bernoullian character ($\rho = 1$). As a whole, this behaviour happens to be similar to that found in the substitution reaction with NaTB [12] but the slope in Fig. 13 is higher compared with that reaction under the same experimental conditions. This indicates that for the present reaction a harsher rearrangement takes place which is in accordance with the aforementioned higher stereospecificity of NaMBT and the inoperativeness of mechanism C.

What is worth emphasizing here is that the stereospecific nature of the nucleophilic substitution reaction in PVC can be enhanced by increasing the bulk of the nucleophile which

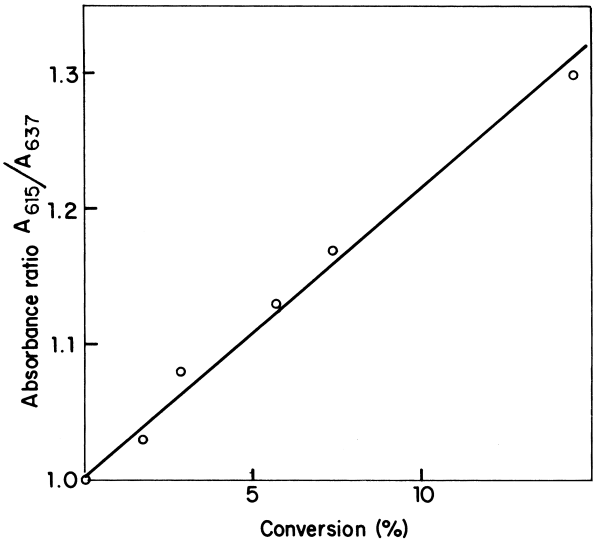

Fig. 10. Evolution of the i.r. absorbance ratio $A_{615\,\mathrm{cm}^{-1}}/A_{637\,\mathrm{cm}^{-1}}$ with degree of substitution.

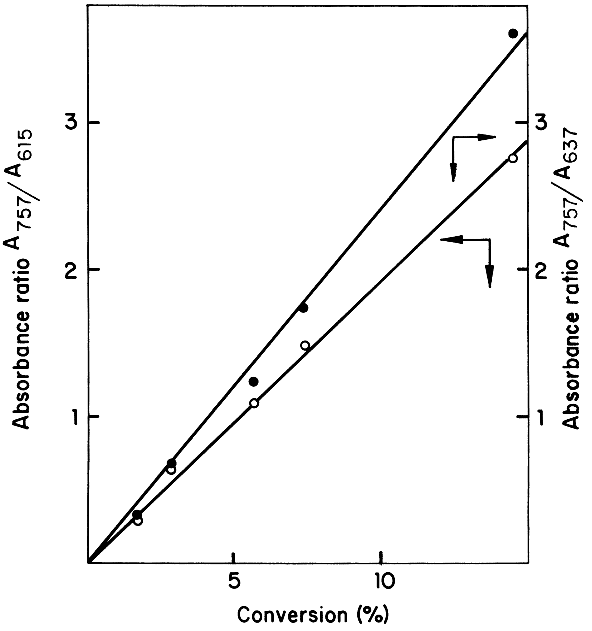

Fig. 11. Evolution of the i.r. absorbance ratio $A_{757\ \mathrm{cm}^{-1}}/A_{615\ \mathrm{cm}^{-1}}$ and $A_{757\ \mathrm{cm}^{-1}}/A_{637\ \mathrm{cm}^{-1}}$ with degree of substitution.

provides the appearance of steric hindrance, thereby either preventing the attack by the heterotactic triad **mr** of the **mmr** tetrad (mechanism C) or rendering more difficult the attack by the **mr** triad in the **rrmr** pentad (mechanism B), respectively.

In conclusion, the results presented in this work demonstrate the outstanding role of the nucleophile in enhancing the sensitivity of the stereocontrol of the reaction, which improves the significance of the previously proposed influence of local configurations in the mechanisms of reaction of PVC.

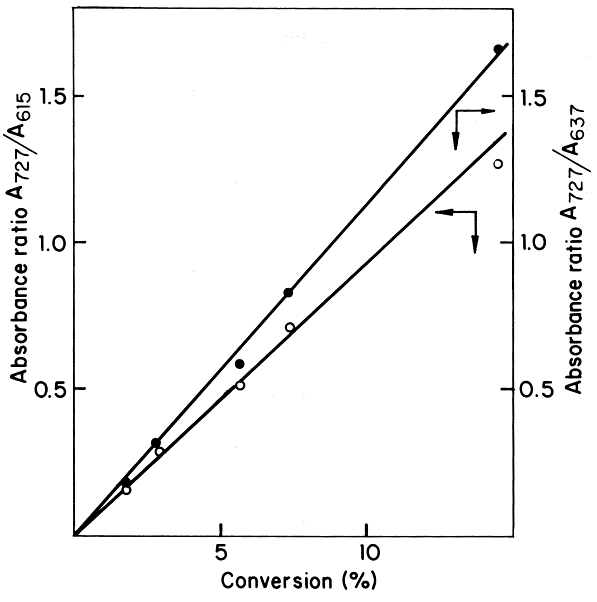

Fig. 12. Evolution of the i.r. absorbance ratio $A_{727\,\mathrm{cm}^{-1}}/A_{615\,\mathrm{cm}^{-1}}$ and $A_{727\,\mathrm{cm}^{-1}}/A_{637\,\mathrm{cm}^{-1}}$ with degree of substitution.

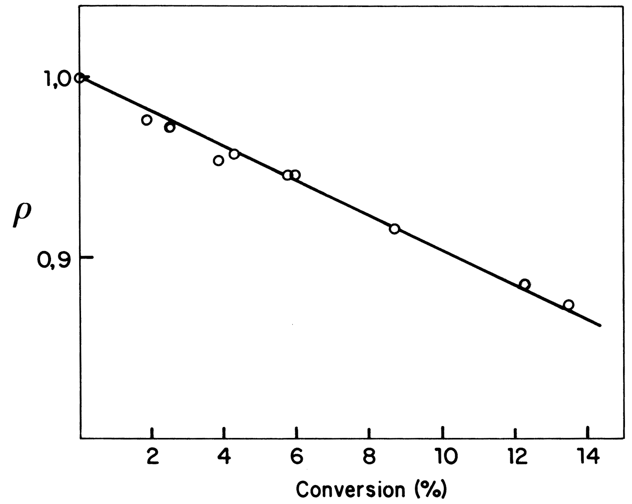

Fig. 13. Evolution of the persistence ratio (ρ) with conversion of PVC after the substitution reaction with NaMBT.

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