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Nucleophilic Substitution on PVC Effect of the Tacticity

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Summary

The substitution reaction with $NaSC_6H_5$ is studied for two samples of PVC having very different tacticities. From both the kinetic results and the thermal degradation of the modified polymers it is concluded that the observed very fast initial period of the reaction involves selectively a small fraction of isotactic and heterotactic triads, and that such triads are likely to be considered as labile structures in PVC. The results are therefore a contribution to the understanding of the thermal instability of PVC.

Introduction

The first results on the reaction of $NaSC_6H_5$ with PVC, as published recently (MARTINEZ et al. 1980) pointed out that, during its fast period, the reaction occurs selectively through the isotactic GTTG and heterotactic TTTG triads. Moreover, the substitution of these triads was proved to result in an enhanced stability of the polymer, which suggests them to be taken as normal labile structures in PVC.

Since a quite atactic polymer was then used and taking into account that the fraction of triads involved during the fast period of the reaction was very low (between 0, 7 and 1, 5% depending on the overall tacticity of the polymer), it seems interesting to compare the behaviour of two PVC samples with different tacticities. Actually, the higher the overall syndiotacticity the lower is the content of isotactic GTTG and heterotactic TTTG triads, and, hence, the lower is expected to be the fraction of units involved in the fast period of the reaction. This paper deals with the preliminary results obtained using a rather Bernoullian polymer (sample A) and a non-Bernoullian syndiotactic polymer (sample B) (Table II).

Experimental

The PVC samples were prepared and characterized as described elsewhere (MILLAN et al. 1973). The tacticity data are

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given in Table II. The substitution conditions are those displayed in Table I which also contains the values found for the reaction constants of the three reaction periods.

TABLE I. Substitution conditions for samples A and B (Figure 1) and rate constant values (Figure 2)

Sample	$[PVC].10^2$ (mole/liter)	$[NaSC_6H_5].10^2$ (mole/liter)	Rate constant. 10^3 (liter/mole. hour)		
			k_1	k_2	k_3
A	6, 4	7, 6	52, 5	3, 2	0, 8
B	6, 4	7, 6	52, 5	2, 2	0, 4

The second order kinetic treatment employed consists in plotting $\log[(1-\alpha)/(1-\beta)]$ versus $((a-b)kt)/2,3$ (MARTINEZ et al. 1980) where α and β are respectively the PVC fraction and the thiophenate fraction reacted at time t; and a and b are the initial concentration of PVC and of thiophenate respectively. The time conversion curves and the kinetic plots are shown in Figures 1 and 2 respectively.

TABLE II. ^{13}C-NMR Tacticity Data

Sample	conversion (%mole)	P(SS)	P(SI&IS)	P(II)	P(S)	P(I)
A	--	0, 327	0, 475	0, 198	0, 565	0, 435
B	--	0, 450	0, 474	0, 076	0, 678	0, 322
A_1	0, 26	0, 330	0, 474	0, 196	0, 568	0, 432
A_2	0, 31	0, 331	0, 474	0, 195	0, 569	0, 431
A_3	0, 50	0, 335	0, 473	0, 192	0, 572	0, 428
A_{11}	2, 26	0, 359	0, 468	0, 173	0, 593	0, 407

The tacticity of all the samples (Table II) was determined by ^{13}C-NMR (PHAM et al. 1974).

The samples were thermally degraded using both a conductimetric method (MILLAN et al. 1973) and a thermobalance.

The values for degradation rate are given in Table III.

Results and Discussion

The time conversion curves (Figure 1) show that the reaction involves a very fast initial period and a steady one; both are separated by a transition period. The conversion at which the fast period ends is much higher for sample A than for sample B.

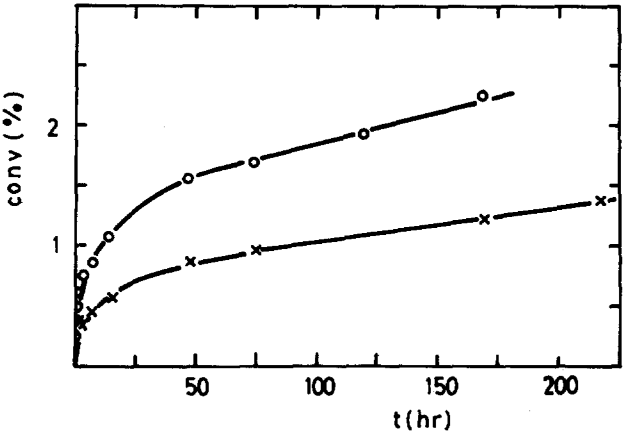

Fig. 1. Nucleophilic substitution on PVC with sodium thiophenate. (o) sample A; (x) sample B.

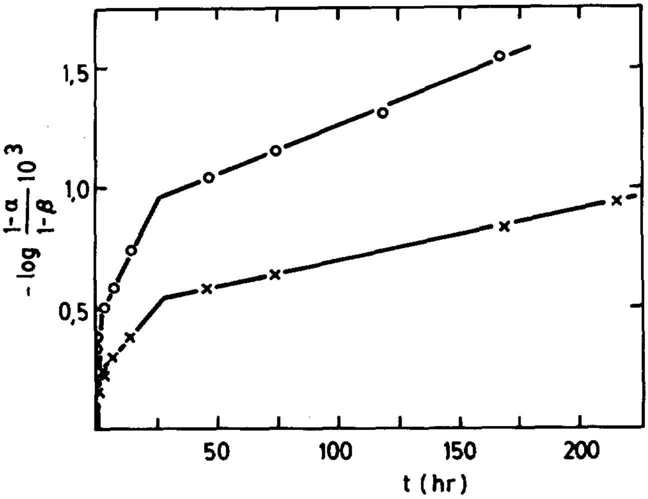

Fig. 2. Kinetic plots of nucleophilic substitution on PVC with sodium thiophenate. (o) sample A; (x) sample B.

The kinetic curves (Figure 2) make it clear that a three-steps reaction takes place and that all the processes are second-order, which accounts for a S_N2 mechanism. It is worth noting that only the reaction constant k_1 (fast period) is independent of the tacticity of the samples and that k_2 and k_3 are the lower as the isotactic placement content is low. These results may be accounted for by assuming that the fast period involves a single type of chlorine atoms which are obviously much more reactive than the other. Conversely, k_2 and k_3 steps might be thought to obey overall processes in which the substitution occurs simultaneously through at least two types of chlorine atoms of reactivities not different enough for their substitution to occur separately in time. Actually, the relative content of these types of chlorine atoms is likely to differ from sample A to sample B.

^{13}C-NMR data (Table II) for modified sample A, make it reasonable to conclude that, within the conversions studied so far, isotactic and heterotactic triads react preferably relative to syndiotactic triads.

Although more ^{13}C-NMR work is under way in order to get further information about the very type of conformations that have reacted during the initial period, the above data, besides the fact that k_1 process for sample B involves a much lower fraction of chlorine atoms than it does for sample A (Figure 2), clearly support our prior assertion (MARTINEZ et al. 1980) that the k_1 step is to be related to some of the isotactic and, to a lesser extent, of the heterotactic triads in the polymer. As previously discussed (MARTINEZ et al. 1980), the more reactive triads would be the GTTG isotactic and the TTTG heterotactic.

TABLE III. Thermal Degradation Values

Sample	Degradation Rate. 10^3	
	Conductimetric Method ($[ClH]/[ClH]_o$. min^{-1})	Thermobalance (%wt. loss. min^{-1})
A	3, 45	4, 7
A_1	2, 93	4, 0
A_2	2, 78	2, 8
A_3	3, 28	3, 2
A_{11}	6, 04	10, 7

Degradation data in Table III demonstrate that substitution during the k_1 period gives rise to a markedly enhanced stability, while further conversions result in decreasing stability. The former result would indicate that some chlorine atoms at the reacted triads are labile; the latter result is easy to explain if the influence of syndiotactic sequences on the building-up of polyenes, as demonstrated previously (MILLAN et al. 1980), is taken into consideration. Nevertheless, a complete study of polyene distribution in the degraded samples, now under way, becomes necessary to draw more definitive conclusions.

Preliminary though they are, the above results enable for the fast period of substitution and the resulting stabilization effect, to be related to a few of isotactic and heterotactic triads in PVC. Therefore some normal structures are to be taken into account, beside the extensively studied abnormal defects, to understand thoroughly the degradation process of PVC.

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