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Stereospecificity of substitution on PVC

Kinetic results at low temperatures

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SUMMARY

The kinetics of substitution reaction on PVC with sodium benzenethiolate at temperatures from -30°C to 5°C is studied and compared to that of earlier work at temperatures from 5°C to 70°C. The kinetic parameters indicate the occurrence of two overlapping processes having activation energy of 10 and 17 Kcal/mol. Their attribution to the isotactic GTTG⁻ and the heterotactic GTTT triad conformations respectively, is argued on the basis of recent results. A few of substitution experiments were repeated in the presence of diglyme or crown ether. They clearly demonstrate that kinetic features are only dependant on the microstructure of the polymer.

INTRODUCTION

In a series of works we have shown that the nucleophilic substitution reaction on poly (vinyl chloride) (PVC) with sodium benzenethiolate (NaBT) proceeds by the isotactic TT diad conformation as the only reactive species. This diad is only possible at the isotactic GTTG⁻ and the heterotactic TTTG triad conformations, the former being much more reactive than the latter (1-3). Thus, these conformations should be formed either during the polymerization or through conformational equilibria for the reaction to occur (2-3). The concentration of GTTG⁻ which is a rather unlikely conformation, is very low and was associated to the small fraction of PVC isotactic triads that are capable of reacting at very low temperatures. Values ranging between 0.2 and 0.8% depending on the overall isotactic content are usually found by this method (4). In contrast, TTTG conformation is known to be very common (2-3). As a result both substitution processes could not be discriminated at the usual reaction temperatures.

To overcome this problem we have studied the kinetics of substitution at temperatures between -30°C and 5°C and compared the results with those obtained elsewhere at temperatures between 5°C and 70°C (5). On the other hand,

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*To whom offprint request should be sent interactions between the nucleophile ions and the cyclohexanone could be invoked to influence the extent of the reaction. In fact, we attributed the plateau obtained at temperatures higher than 60°C to the absence of reactivity in the syndiotactic configuration. No effect of the nucleophile was considered. We would expect such an effect to be enhanced at low temperatures, then we also studied the kinetics in the presence of diglyme or crown ether for some of the temperatures utilized. The results of these attempts are presented in this paper.

EXPERIMENTAL

Materials

The PVC sample studied was prepared by bulk polymerization process at 60°C with 2,2'-azoisobutyronitrile (AIBN) as initiator. Reagent grade of NaBT (Fluka, purity ~97%), diethylene glycoldimethyl ether (diglyme) (Fluka, purity > 99%) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown- 6) (Fluka, purity 98%) were used without further purification. Cyclohexanone (CH) was distilled twice prior to use. Tetrahydrofuran (THF) was freed from peroxides using lithium aluminium hydride.

Substitution reactions

18-crown-6 (0.467 g, 1.77 mmol) or diglyme (17.5 cc, 0.123 mol) were dissolved in CH (50 cc). NaBT (3.125 g, 23.67 mmol) was added to the solution thermostated at the chosen reaction temperature (-30, -15, -5 and 5°C) and stirred under inert atmosphere for 1 h. PVC (1.25 g, 20.0 mmol based on monomer unit) dissolved in CH (110 cc) was added. At appropriate reaction times, samples were withdrawn, then precipitated with methanol and dried. The precipitate was collected by filtration washed with methanol and dried. The product was reprecipitated from THF into methanol, washed and finally dried under vacuum at 40°C. The degree of substitution was determined by UV spectroscopy (2). The above conditions save the quantity of diglyme or 18-crown-6, were utilized for the standard reactions in the absence of dissociation agent.

RESULTS AND DISCUSSION

Fig.1 shows the conversion curves for the indicated temperatures. They consist in a very steep period followed by a slower one. Note that the rate during the latter period is lower as the temperature increases. Moreover, it becomes a plateau at temperatures equal to or higher than 60°C (5).

Using a very large scale for each temperature the tangent at the outset of reaction to obtain the initial rates could be easily drawn. They are reproduced in Fig.2. The rates at temperatures from -30°C to 5°C as obtained from the slopes in Fig.2 are collected in Table 1 together with those at 5°C to 60°C from earlier work (5).

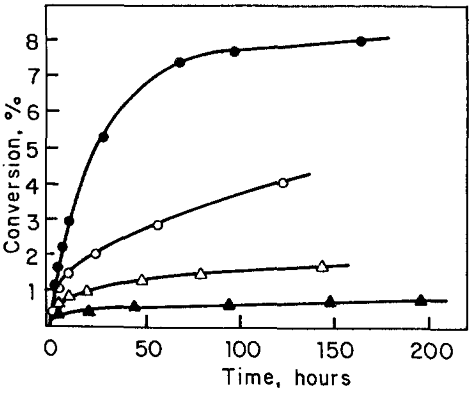


Fig.1. Nucleophilic substitution on PVC with NaBT at different temperatures. (●) 5°C; (○) -5°C; (△) -15°C; (▲) -30°C.

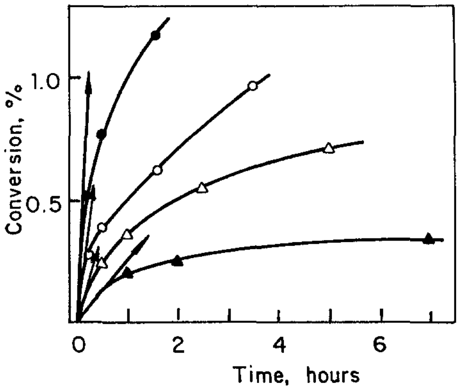


Fig.2. Initial steps of nucleophilic substitution on PVC with NaBT at different temperatures (see Fig.1).

Table 1

Initial Rates of Nucleophilic Substitution on PVC at Different Temperatures

Temp. (°C)	10^2.K (%.min^{-1})
-30	0.4
-15	1.2
- 5	2.7
5	5.6
25	16.9
40	66.7
60	303.0

As indicated in Fig.3 all the above rates fit into the Arrhenius diagram; yet two well discriminated slopes are observed. They concern the -30°C to 25°C and 25°C to 60°C ranges of temperature respectively. Thus, there appear to exist two different initial processes depending on the reaction temperature. The corresponding activation energies are 10 and 17 Kcal/mol respectively.

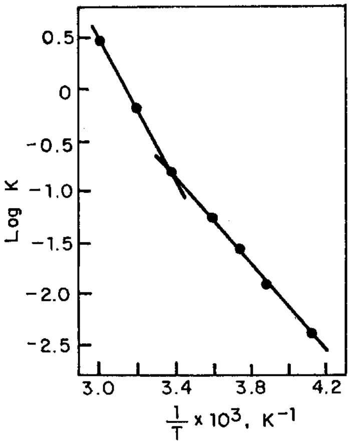
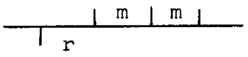


Fig.3. Arrhenius plot for the initial steps on substitution reaction on PVC with NaBT (k in %.min^{-1}, Table 1).

Obviously, both processes are to be assumed to overlap at any reaction temperature but as the temperature is lowered the contribution of the process with lower activation energy will increase at the expense of the other. As shown by curve at -30°C in Fig. 1 and stated elsewhere (4), the portion of polymer involved in the fast period is very low (no higher than 1%). This prevents this period from being observable as the reaction temperature increases, that is, as the species of higher activation energy are reacting. These results clearly support our proposal above as the conformational mechanism of substitution. According to this mechanism the substitution can occur whenever an isotactic sequence starts regardless of its length, that is at the sequence **...rmm...** in which there may be the following conformational equilibrium:

$\mathrm{GTTG^{-}TT} \rightleftharpoons \mathrm{GTGTTT}$



scheme 1

Given that GTTG isotactic conformation is at the same time very reactive by S_N2 substitution (2) and very scarce in the polymer (2-3) the fast period in Fig.1 may be reasonably attributed to this structure at least to a great extent. Because $GTTG^-$ conformation is little favoured its formation through the conformational equilibrium $GTTG^- \rightleftharpoons GTGT$ should be highly slow. As a result, once all the initial $GTTG^-$ structures derived from the polymerization process have reacted the GTTT heterotactic conformations keep being the main reactive species. It may either exist by its own or be easily formed as the result of the equilibrium

TGTT ⇄ GTTT in the heterotactic sequences. Accordingly, all the heterotactic triads will react as the process advances. Moreover, its reaction will involve the disappearance of the isotactic sequences. Actually, whenever the chlorine at the central carbon atom of the GTTT heterotactic triad is replaced by the nucleophile through a S_N2 mechanism, the neighbouring isotactic triad (scheme 1) will become a coheterotactic one (2-3). Hence, the main substitution process at temperature sufficiently high, is that of the GTTT heterotactic conformation and the slow period observed at low temperatures may be associated to this structure.

On the basis of our mechanism the syndiotactic structure should be quite unreactive (1-3). In this connection, the reaction at temperatures equal to or higher than 60°C exhibits a plateau, that is, a portion, which roughly agrees with the syndiotactic content, happens to be unreactive (1-3). Yet, such limitation would be also observed if a part of the nucleophile was involved in complexes with the solvent. Obviously this phenomenum could be particularly intense at low temperatures. So, we carried out the reaction at -30°C and 60°C in the presence of diglyme to ascertain the whole dissociation of the benzenethiolate. The results, as compared with those obtained in the absence of diglyme, are shown by Fig.4 which also includes a reaction at -30°C in the presence of 18-crown-6 as dissociation agent.

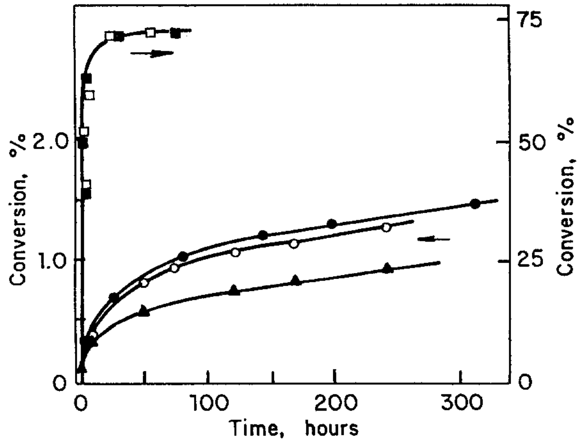


Fig.4. Influence of dissociation agent on kinetics of substitution on PVC. a) at 60°C: (□) standard conditions; (■) with diglyme. b) at -30°C: (▲) standard conditions; (●) with diglyme; (○) with 18-crown-6.

As can be seen, no difference is observed at 60°C. As to the experiments at -30°C the observed effect of dissociation agents is not great enough for the conclusions above as to the conformational mechanism of substitution to be altered.

Acknowledgement

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