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STEREOSELECTIVITY IN SUBSTITUTION REACTIONS OF PVC WITH SODIUM ISOOCTYLTHIOGLYCOLATE AND SODIUM ISOOCTYLTHIOSALICYLATE

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Abstract—The nucleophilic substitution reactions of a commercial poly(vinylchloride) with sodium isooctylthioglycolate and sodium isooctylthiosalicylate have been studied in solutions in cyclohexanone. The kinetic results show that only a fraction of polymer is capable of reacting even if severe experimental conditions such as high temperature and concentration of nucleophile are used. The reactive parts, as quantitatively estimated according to earlier results, is shown to be higher for sodium isooctylthiosalicylate than for sodium isooctylthioglycolate probably because of the higher nucleophility of the former species despite its higher steric hindrance. ^{13}C-NMR measurements for all the modified samples demonstrate the content of unreacted isotactic and heterotactic triads to be lower as the degree of substitution increases, this effect being more important for triads of the former type during the first stages of the reaction. It is inferred that the stereoselectivity of substitution on PVC is independent of the nucleophile, while both the total reactive parts and the rate of substitution depend on the type of nucleophile. Degrees of substitution of 1 1.3% enhance the thermal stability of the polymer and cause pronounced changes in the u.v.-visible spectrum of the polymer after degradation. Both features are explained on the basis of earlier results with sodium thiophenate. The results indicate a useful pathway for controlled grafting of suitable functions on PVC.

INTRODUCTION

Substitution reactions are an appropriate way to attach chemical functions to polymeric chains for improving properties of the polymers whether special or widely used commercial materials [1]. In the case of PVC, the number of uses is steadily increasing but, despite the large amount of research on this polymer, many problems (due to migration of additives) remain unsolved. This migration results in a loss of mechanical properties and may cause toxicity hazards in certain uses as packing of drugs, foods, biological products, etc.

In previous work [2-4] we demonstrated that the SN 2 reaction of PVC with sodium thiophenate proceeds selectively at the isotactic TT diads which can only exist either in the GTTG* isotactic or in the TTTG heterotactic triads, the former being much more reactive than the latter. On the other hand, it was also concluded that the selective substitution of the central chlorine atom in GTTG* isotactic triads enhanced the thermal stability of the polymer, i.e. it involves the elimination of a type of labile structure in PVC [3, 5]. A detailed survey of these features has been recently given [4]. An attempt to carry out the same reaction in the condensed state has been also made [6].

In order to see whether the nucleophilic substitution on PVC is stereospecific in character regardless of the type of nucleophile, we have now studied the reaction of PVC with nucleophiles of different structure such as sodium isooctylthioglycolate and sodium isooctylthiosalicylate in solution in cyclohexanone. Because these reactants are of a plasticizer nature, the stereospecific substitution affords a useful way to plasticize PVC by attaching appropriate functions to the labile structures which are stabilized as the result of substitution. Parallel work in the condensed state has been made [7].

EXPERIMENTAL

Polymer preparation

The poly(vinyl chloride) sample used was a commercial polymer RB8010 (ATOCHEM). The molecular weight measurements were carried out by gel permeation chromatography at room temperature with solution in tetrahydrofuran. The tacticity was determined by measuring the A_{1428} cm^{-1}/A_{1434} cm^{-1} absorbance ratio in the i.r. spectrum; the value of this ratio was 1.08. The values of $\bar{M}_n$ and $\bar{M}_w$ for the polymer were 48.0×10^3 and 116.0×10^3 respectively.

Synthesis of sodium isooctylthiosalicylate

The isooctylthiosalicylic acid was prepared from diethylhexanol (high degree of purity) and thiosalicylic acid (Merck). For 10 g of acid, 8.44 g of alcohol and 0.3 g of *p*-toluensulphonic acid as catalyst were added in toluene.

After heating at 80 for 3 hr, the esterification was performed by refluxing at 130 . Water was removed continuously by means of a Dean Stark until 90% yield was reached. Then, the non-reacted products were eliminated by centrifugation and vacuum distillation.

The ester so obtained was converted into the corresponding sodium isooctylthiosalicylate through reaction with an equimolecular concentration of sodium hydride in tetrahydrofuran at room temperature and then purified by vacuum distillation.

Table 1. Substitution conditions of reactions A–H (Fig. 1): [polymer] = 1.28×10^{-1} mol/l; [nucleophile] = 1.47×10^{-1} mol/l; [$HSCH_2COOC_8H_{17}$] = [K_2CO_3] = 1.47×10^{-1} mol/l

Run	Nucleophile	*T* (°C)
A	$NaSC_6H_4COOC_8H_{17}$	60
B	$NaSCH_2COOC_8H_{17}$	60
C	$HSCH_2COOC_6H_{17} + K_2CO_3$	60
D	$HSCH_2COOC_6H_{17} + K_2CO_3$	50
E	$HSCH_2COOC_6H_{17} + K_2CO_3$	40
F	$HSCH_2COOC_6H_{17} + K_2CO_3$	25
G	$NaSCH_2COOC_8H_{17}$	25
H	$HSCH_2COOC_6H_{17} + K_2CO_3$	0

Synthesis of sodium isooctylthioglycolate

The isooctyl ester of thioglycolic acid was reacted with an equimolecular concentration of sodium hydride in tetrahydrofuran to obtain the corresponding sodium isooctylthioglycolate.

Substitution reaction

For the substitution reactions, an appropriate amount of nucleophile was dissolved in a part of the purified cyclohexanone. The polymer was dissolved in the other part of the solvent. Both solutions, independently thermostated at the temperature of the reaction, were poured into the reaction vessel which was also kept at the same temperature. All the experiments were carried out under an inert atmosphere. At appropriate reaction times, samples were drawn out and at once precipitated with methanol, purified in tetrahydrofuran/methanol and dried at 45° under vacuum. The reaction conditions for these reactions are given in Table 1.

Another set of experiments was carried out at various temperatures from 0 to 60° with a mixture of equimolecular amounts of isooctylthioglycolic acid and potassium carbonate, to form isooctylthioglycolate anion "*in situ*", in cyclohexanone. At appropriate times, samples were withdrawn and at once precipitated with methanol–water mixture, purified in tetrahydrofuran–methanol–water as solvent/precipitant system and dried at 45° under vacuum. The reaction conditions are summarized in Table 1.

The substituted PVC samples so obtained were characterized by i.r. spectroscopy, following the ester absorption band, and elemental analysis.

^{13}C-NMR spectroscopy

The tacticities of all the samples were determined by ^{13}C-NMR spectroscopy using an external locked field (hexadeuterated dimethylsulphoxide, DMSO) at 20.1 MHz with a Bruker WP80 Spectrometer. The spectra were recorded at 100° using a 10 mm tube and about 10–15 (w/v)% solution in *o*-dichlorobenzene. The calculations were carried out by measuring the areas with the compensating polar planimeter as well as by means of the built-in electronic integrator. The results are shown in Table 2 and Figs 4–6.

Polymer degradation

All the samples were degraded up to 0.3% in the solid state at 180°. The HCl evolved was followed by conductivity measurements and the slope of the linear part of isotherms is taken as the degradation rate.

Table 2. Evolution of iso, hetero and syndiotactic triad content (^{13}C-NMR) for modified polymers for reactions A and B (Table 1)

Sample	Conversion (%)	P(II)	P(SI + IS)	P(SS)
RB 8010	0.0	21.6	48.6	29.7
A-2	10.0	11.3	41.4	36.6
A-3	16.1	7.9	34.3	42.2
A-6	34.6	—	20.9	49.0
B-2	6.0	16.3	47.6	33.2
B-4	15.5	7.9	36.4	38.7

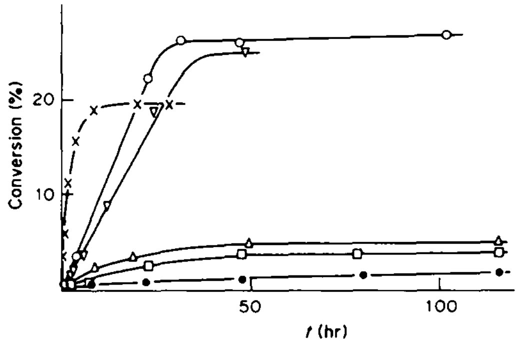

Fig. 1. Nucleophilic substitution of PVC. (×) Reaction B, (○) reaction C, (▽) reaction D, (□) reaction E, (●) reaction F, (△) reaction G (see Table 1).

The u.v.-visible spectra of degraded samples were recorded with 4 g/l solutions in hexamethylenphosphortriamide using a Perkin–Elmer 554 spectrophotometer.

RESULTS AND DISCUSSION

As shown in Fig. 1 the conversion curves for sodium isooctylthioglycolate (NaSR) at stoichiometric concentration exhibit a plateau which, as expected, increases with increasing temperature. When equimolecular concentrations of isooctylthioglycolic acid (HSR) and K_2CO_3 are used instead of a similar concentration of NaSR (Table 1) higher conversions are obtained at 60° even if the reactions are slower (Fig. 1). This indicates that a higher concentration of effective nucleophile RS^- is present in the latter reaction probably because of the excess of K^+ ion relative to the stoichiometric conditions. Hence, only a fraction of PVC units appear to be capable of reacting. The size of this fraction may be reasonably assumed to be that of the reaction with HSR + K_2CO_3 because the high concentration of K^+ ion should ensure a concentration of RS^- high enough for all the PVC units to react provided that they are reactive (Table 1). On the other hand, it has been shown that no further conversion is obtained by increasing the reaction temperature in this type of reaction [4]. In Fig. 2 the reactivities of NaSR and

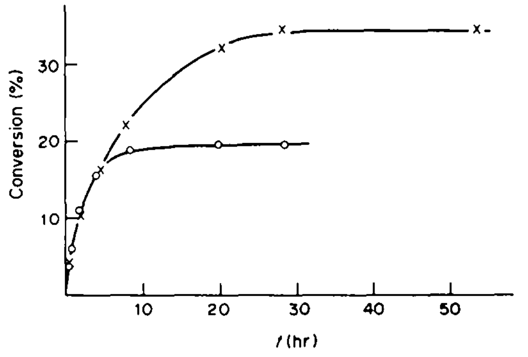

Fig. 2. Nucleophilic substitution of PVC. (×) Reaction A, (○) reaction B (see Table 1).

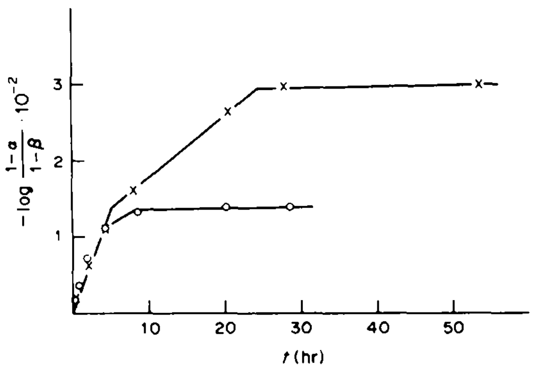

Fig. 3. Kinetic plots of nucleophilic substitution of PVC. (×) Reaction A, (○) reaction B.

sodium isooctylthiosalicylate ($NaSC_6H_4R'$) are compared. The higher reactivity of the latter is apparent and may be attributed to its expected higher nucleophility, despite its greater steric hindrance (the ester group is in the *ortho* position). This result, together with that previously obtained with sodium thiophenate [2–4], demonstrates how the reactive fraction in PVC depends on the type of nucleophile regardless of the kinetic features.

The reactive fractions are easily evaluated by applying a second-order kinetic treatment which consists in plotting $-\lg[(1-\alpha)/(1-\beta)]$ vs time, where α and β are respectively the PVC and nucleophile molar fractions that have reacted at time t [2–4]. The results for both nucleophiles are shown in Fig. 3. They quantitatively confirm the results quoted above.

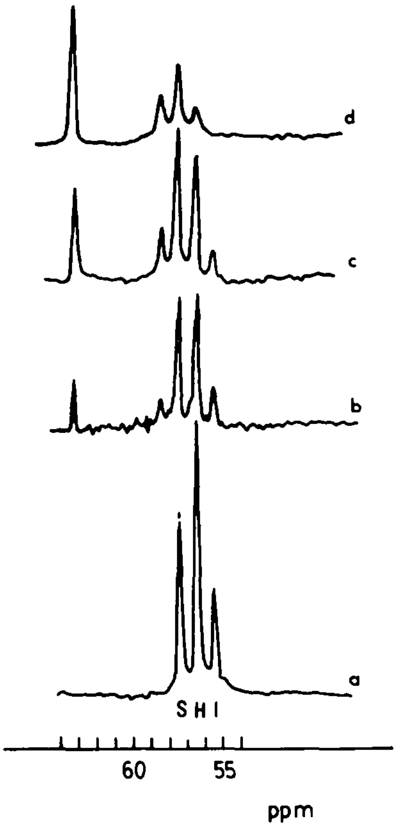

Fig. 4. ^{13}C-NMR spectra of samples modified with $NaSC_6H_4R'$ at various conversions: (a) 0.0%; (b) 10.0%; (c) 16.1%; (d) 34.6%.

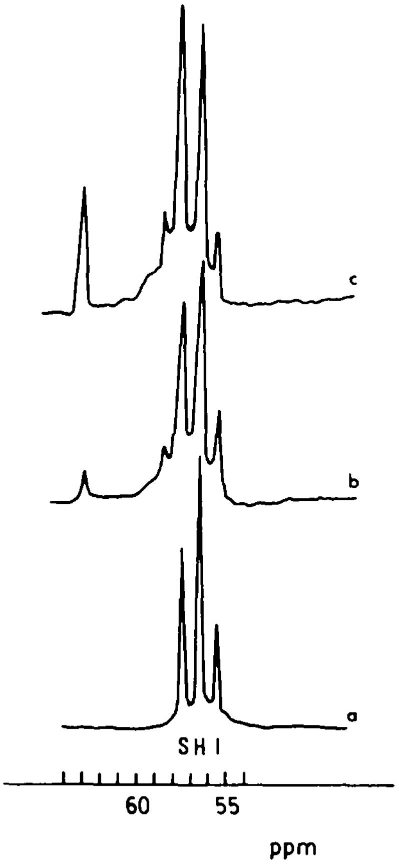

Fig. 5. ^{13}C-NMR spectra of samples modified with NaSR at various conversions: (a) 0.0%; (b) 6.0%; (c) 15.5%.

Whether or not the reactive units are the ... TT ... isotactic diad conformations, as found for sodium thiophenate [3], remains to be decided. Because the TT isotactic diad can only exist in isotactic GTTG* and heterotactic TTTG triads, the stereospecificity of the reaction can be concluded by measuring by high resolution ^{13}C-NMR spectroscopy the changes in the content of isotactic and hetero-

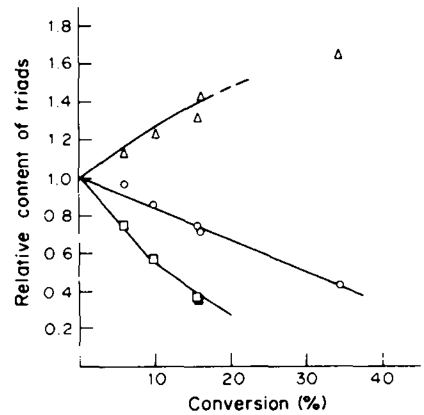

Fig. 6. Evolution of the relative content of triads with the degree of conversion. (△) Syndiotactic triads, (○) heterotactic triads and (□) isotactic triads.

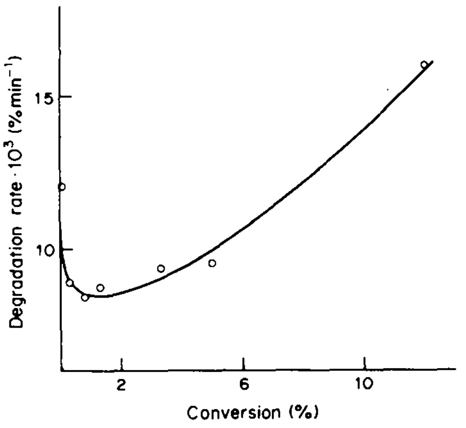

Fig. 7. Dependence of degradation rate of modified samples on degree of substitution for the solid state at 180°. Reactions B and G (Table 1).

tactic triads with the degree of substitution. The results are given in Table 2 and Figs 4 and 5. They demonstrate that signals at 54.20 and 55.10 ppm, i.e. the content of isotactic and heterotactic triads, decrease with increasing conversion and that this effect is more pronounced for the isotactic triads, particularly during the first stages of the reaction. These features are confirmed by Fig. 6 which indicates the evolution of the relative content normalized to initial polymer of each triad, as calculated by measuring the areas of the respective bands, with the degree of conversion.

It is worthy of note that the curves in Fig. 6 are quite similar to those obtained for the reaction with sodium thiophenate [4], which is surprising since the reactants are quite different in reactivity. Hence, the substitution reaction on PVC is demonstrated to be stereoselective no matter what type of nucleophile is used. Needless to say that, according to the above results, the total fraction of iso and heterotactic triads able to undergo substitution strongly depends on the reactivity of the nucleophile.

Because a small fraction of isotactic triads was found to be labile [5], the quoted stereoselective substitution with nucleophiles of a plasticizer nature, was expected to involve a concomitant stabilizing effect. As illustrated by Fig. 7 the degradation rates at 180° for the polymers modified with NaSR, markedly decrease up to degrees of substitution of about 1–1.3% and then increase steadily. Both effects are those obtained for sodium thiophenate, which were proved to obey respectively a decrease of concentration of labile site as the result of specific substitutions by GTTG* isotactic triads, and a favoured propagation once the labile structures have disappeared [3–5].

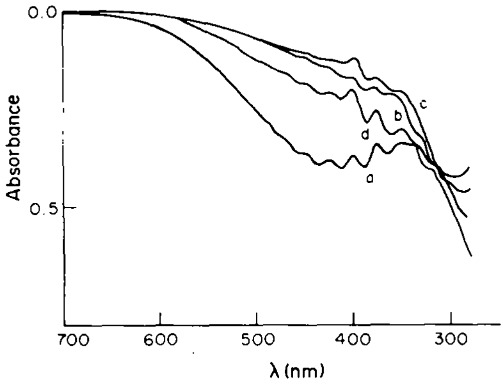

Fig. 8. u.v.-Visible absorption spectra of modified samples with NaSR at 25° degraded to 0.3% at 180° for the solid state. (a) 0%; (b) 0.3%; (c) 3.3%; (d) 11.0%.

These conclusions were supported by the observed influence of substitution on the shape of the u.v.-visible spectrum of equally degraded polymer [5]. As illustrated by Fig. 8 the same results are obtained for the nucleophiles used in this work. Actually, the substitution with NaSR brings about a strong decrease of the absorptions between 390 and 440 nm, i.e. of polyenes of 7–9 double bands, which were proved to be related to the concentration of labile GTTG* isotactic triads in the polymer [5–8].

The present results make it evident that the previously found stereoselectivity of the substitution reaction on PVC [2–4] can be regarded as a general behaviour, even if the type of nucleophile is proved to be a determining factor on both the kinetics of the reaction and the total fraction of polymer which is capable of reacting. They provide a new route for grafting suitable functions to PVC, specifically through its labile structures.

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