

Stereoselective Modification of Poly(vinyl Chloride) in a Twin Screw Extruder

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SYNOPSIS

Continuous chemical modification of poly (vinyl chloride) (PVC) with sodium benzene thiolate (NaBT) in a counter-rotating twin screw extruder has been studied. The course of the reaction is analyzed, taking into account the physical changes of the polymer along the length of the screw. From the results, it is concluded that the modification reaction is associated with the fusion–gelation process. The reaction kinetics are determined as a function of the mean residence time with the aid of a UV tracer. Temperature profile, flow rate, and premixing are some of the processing parameters influencing the reaction kinetics. The continuous modified polymer is analyzed in terms of thermal behavior, molecular weight, and stereochemical structure, and the results are compared with those obtained by a discontinuous melt process (Haake–Rheocord). It is confirmed that the same stereoselective substitution mechanism occurs as that in discontinuous melt with no side reactions.

INTRODUCTION

Chemical modification of synthetic polymers during processing offers new possibilities for improving original polymer properties. For thermally sensitive or chemically reacting materials, extrusion processes can be considered an important tool for the continuous chemical modification reaction in polymers.

Where thermoplastics are concerned, by far the largest proportion of reactive processes employed during extrusion is devoted to the crosslinking and grafting of polyolefins by radical reactions^{1,2} and to the reactions of EVA with metal alkyls and metal alcoholates.^{1,3} However, in the case of PVC, only the grafting of plasticizing groups with the aid of sodium isooctylthiosalicylate has been carried out in a twin screw extruder,⁴ even though it possesses chemically reactive atoms attached to the chain backbone, as has been extensively reported in solution or discontinuous melt processes.^{4–13}

It has been demonstrated that PVC is able to react in a discontinuous melt process, by means of a Haake plasticorder and a rolling mill, with nucleophilic reactants, following a stereoselective mechanism, in a way identical to that found in the solution reaction.^{6–10} Nevertheless, the kinetics of the substitution reaction is markedly dependent on the reaction conditions.⁸

Although chemical modification of PVC can be carried out up to high degrees of conversion by choosing appropriate mixing conditions of temperature, shear stress, load, and amount of plasticizer,⁸ this procedure will not find industrial application if it does not occur by a continuous process. For this reason it is fundamentally important to transpose the discontinuous melt reaction conditions into a continuous environment, which is the objective of the present work. To achieve this aim, it is necessary to correlate the reaction with the extrusion process, and to establish the influence of the new processing factors which govern the course of the reaction, such as quality of mixing, distribution of the residence time, and temperature profile. An understanding of these relationships is indispensable for the generalization of chemical modification of PVC in industrial conditions.

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EXPERIMENTAL

Materials

Polymer

The poly(vinyl chloride) (PVC) sample used was a commercial suspension polymer S6502 kindly furnished by Limburgse Vinyl Maatschappij (L.V.M.). The value of number average molecular weight (M_n) determined by gel permeation chromatography is 48,600.

Sodium Benzene Thiolate

Sodium benzene thiolate (NaBT) was prepared from the reaction of benzene thiol acid and metallic sodium in the *p*-xylene at 150°C by a method published elsewhere.¹³ The precipitate was washed with a high excess of 1,2-dichloroethane under an inert atmosphere, and dried under vacuum over 48 h.

Solvents

Diethyl phthalate (DOP) was used without further purification. Tetrahydrofuran (THF) was distilled prior to use.

Substitution Reaction in the Extruder

Premixing of the reactants PVC, NaBT, and DOP was performed in a Henschel mixer at high speed (800 rpm). The mixture was blended for 15 min until a temperature of nearly 90°C was reached. For comparative reasons some mixtures were stopped at 40°C after 5 min of mixing.

The substitution reaction of PVC with NaBT was carried out in a LSM 30–34-mm Leistritz intermeshing counter-rotating twin screw extruder provided with a single hopper. Some experiments were also carried out with a corotating configuration. The screw length/diameter ratio, L/D , is 23 and 33.5 for the counter- and corotating configuration, respectively. The outlet of the extruder was equipped with a strip die, $L = 50$ mm, $H = 2$ mm, a pressure gauge, and a thermocouple measuring the melt temperature inside the die. The temperature profile was regulated by five heating controllers on the barrels, and one on the die. The screw speed of the extruder was fixed at 40 rpm for all experiments.

Since DOP is necessary for the substitution reaction of PVC with NaBT to take place, as previously found,⁸ we maintained a constant PVC/DOP ratio for all of the runs. The chemical reactions were carried out in the presence of 1% of stearic acid as lubricant under a range of conditions, varying the

concentration of nucleophile, flow rate, and temperature (see Table I).

Residence Time Distribution

The residence time distribution (RTD) of the reaction mass is used to characterize the kinetics of the chemical reaction. Residence time distribution may be described quantitatively using one function $E(t)$, which gives the response of an extruder to a pulse. This function represents the age distribution of the polymer leaving the extruder. From this function the mean residence time (t_m) can be calculated, which is the first moment about the origin of RTD. To determine RTD, a pulse of a tracer material was supplied at the inlet of the extruder, after the extruder had reached a steady state, and the concentration of the tracer was measured by UV spectroscopy. The tracer consisted of 1 g of anthracene (Fluka). Samples taken from the outlet at several time intervals were analyzed by a method described elsewhere.¹⁴

Characterization

Degree of Substitution

The extent of the reaction was measured directly from the strip at the outlet of the screw by gel per-

Table I Counter-Rotating Twin Screw Extruder

Run	NaBT ^a (g)	Flow Rate (kg/h)	T^b (°C)	Conv (%)
1	320	1.5	172	9.7
2	157	4.0	172	4.6
3	132	2.1	172	4.8
4	132	4.1	172	4.2
5	132	5.7	172	3.9
6	274	1.5	172	7.9
7	274	3.7	172	5.7
8	274	4.9	172	5.0
9	368	2.45	172	9.8
10	368	4.2	172	9.4
11	368	4.2	178	9.4
12	426	2.5	145	5.7
13	71	3.8	172	2.6
14	274	4.2	160	6.8
15	274	4.2	172	7.3
16	270	4.2	178	7.3
17	413	0.78	172	6.9
18	413	1.5	172	5.3
19	413	3.9	172	4.0

^a PVC/DOP/lubricant = 1000/300/10 g.

^b Barrel temperature in the fusion-gelation zone.

meation chromatography, using a Waters Model 510 GPC chromatograph provided with a series of Ultrastiragel columns 10^3 , 10^4 , 10^5 , and double detection: differential refractometer and variable wavelength UV photometer. The degree of conversion was evaluated with the aid of a calibration curve in the same way as for the discontinuous melt process.⁸

RMN

The tacticities of the starting and modified polymers were examined in a 10% (w/v) solution in a mixture of ortho-dichlorobenzene and deuterated dimethyl sulfoxide. The ^{13}C -NMR spectra were recorded at 100°C using a XL 300 Varian Instrument (75.5 MHz for ^{13}C). Typical accumulation conditions were: flip angle of 80°, spectral width 200 Hz, a pulse repetition of 4 s, and about 30,000 scans. The resonances used are those of the methinic carbons in the backbone. The relative areas of the different peaks corresponding to the probability of iso-, hetero-, and syndiotactic triads were determined with a compensating polar planimeter.

Polymer Degradation

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

Molecular Weight

Apparent molecular weights were measured by GPC in THF at 25°C using a polystyrene calibration.

RESULTS AND DISCUSSION

Previous papers^{8,9} concerning the chemical modification of PVC with sodium benzene thiolate in a Haake Rheocord system and in a rolling mill already demonstrated the feasibility of reacting PVC by nucleophilic substitution. Very recently⁸ it has been reported that although the presence of DOP is necessary for the mechanism of substitution to operate, the chemical reaction is dependent on the PVC processing conditions.

Since the processing of PVC in the extruder is different from that of the Rheocord, first, it was tested whether the polymer is able to react with sodium benzene thiolate under the normal processing conditions for both rigid PVC and for plasticized PVC.

Table II The Influence of the Plasticizer on the Reaction

PVC (g)	NaBT (g)	DOP (g)	Conv (%)
1000	131	0	0.7
1000	132	300	4.8

Table II shows the degree of conversion, expressed in % mol, of chlorine atom substitution with sodium benzene thiolate for PVC processed at 170°C in the absence, and in the presence, of DOP. Other conditions are given in the table. When no plasticizer is added, the reaction does not proceed, except for 0.7% of chlorine substitution. This result is quantitatively the same as that obtained in the Rheocord system.⁸ As in that previous work, where more direct evidence was provided, these results are interpreted on the basis of chain interactions, which will be more extensively discussed later. In rigid PVC, agglomerates remain and chain interactions are not destroyed, so that the nucleophile will not be accessible to the attack point (besides this, PVC and NaBT are totally incompatible). This 0.7% of substituted chlorine might be attributed to the GTTG⁻ isotactic conformation as discussed by Del Val et al.¹⁵

DOP is known to be a good plasticizer for PVC and for that reason the penetration inside the chain and consequently the interruption of the PVC interactions is easy to understand. This makes Cl atoms available for the substitution reaction which occurs during the short time of continuous plasticized PVC processing. The degree of conversion thus obtained is 4.8% and corresponds to an efficiency of 80%, which is the same as that found in the discontinuous melt process over a longer time period.

Analysis of the PVC after extrusion has revealed that the composition is uniform inside the strip (along the *x*- and *y*-axes, width and length, respectively); that is, no distribution of conversion or reactant segregation was found. This fact may be important for the quality of the final product.

Processing and Reaction

One of the aims of the present work is to correlate processing of PVC and its chemical reactivity. PVC reactivity can be highly dependent on extruder configuration. Accordingly, the course of PVC reaction was analyzed, taking into account the different physical changes that can arise in the polymer along the length of the screw (compression, densification,

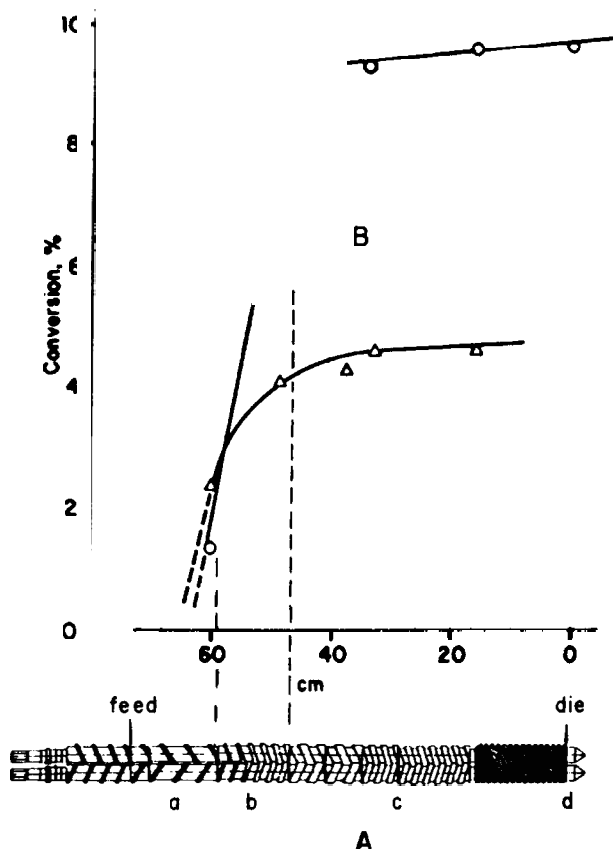


Figure 1 (A) Counter-rotating screw configuration from hopper to die (cm): (a) solid transport zone; (b) fusion-gelation zone; (c) conveying zone; (d) discharge. (B) Evolution of the degree of conversion for PVC reaction with sodium benzene thiolate along the screw. PVC = 1000 g, DOP = 300 g, NaBT = (O) 320 g; (Δ) 157 g.

and fusion of PVC grains), in the following way: As the reaction mass passed through the extruder, the screws were withdrawn at the same time that the flow was stopped. The reaction was cooled very rapidly and several samples were taken from the different zones of the screw and analyzed. To verify the results, another run of experiments was repeated.

Figure 1(A) shows the profile of the counter-rotating screw from the hopper to the die (cm). Three different zones can be distinguished: a solid transport zone, a fusion-gelation zone, a conveying zone and discharge. Figure 1(B) shows the evolution of Cl substitution with the length of the screw for two reactions with the same processing conditions. The

only difference is the amount of NaBT used. From kinetic results, the same behavior is obtained in both cases, shown by the upper and lower curves. That is, the majority of PVC chlorine is substituted in a very narrow zone of the screw (between the dotted lines), which corresponds to the fusion-gelation zone of the screw, as can be appreciated from the part A of the figure. These results clearly imply that chemical reaction on PVC is associated with its fusion-gelation step, which favors the polymer's motion and the dispersion of the nucleophile at the molecular level. This finding is in agreement with our previous⁸ results obtained in a discontinuous process, where fusion-gelation process can be isolated from other processes and controlled by torque measurement as a function of time. There it was demonstrated that substitution on the polymer only occurred during its fusion-gelation in such a way that if fusion-gelation process of PVC is controlled by temperature or plasticizer amount, kinetics is also modified.

A confirmation of the results from the extrusion work is obtained when the reaction of PVC with the nucleophile is carried out in the corotating screw extruder, where for the various runs studied, the degree of conversion is appreciably lower than that found in a counterrotating configuration. This phenomenon can be explained by a comparison of the two screw geometries Figures 1(A) and 2. In the second case, there are no compression elements where fusion-gelation can take place sharply, as in the first case, and fusion of PVC must presumably take place in a continuous, although incomplete, manner along the screw. As fusion-gelation is incomplete, the reaction cannot be completed, as is found (Table III).

Aside from the important fundamental conclusion that has arisen from this study, another important conclusion must be drawn. This is the fact that any extrusion equipment used for the chemical modification of PVC requires a compression zone to favor the fusion-gelation process and then in consequence the dispersion of reagents and the chemical attack. Other factors such as length do not seem so important.

Kinetics of the Substitution

The minimum information required to characterize a reacting system in an extruder reactor is the res-

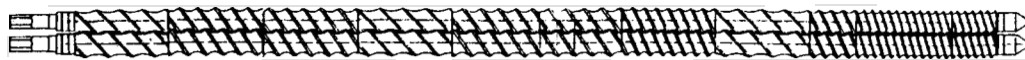


Figure 2 Corotating screw configuration.

Table III The Influence of the Screw Configuration on the Mean Residence Time

Run	Configuration	PVC ^a (g)	NaBT (g)	Flow Rate (kg/h)	t_m (min)	Conv (%)
a	Corotating	1000	132	1.3	4.25	3.5
b		1000	132	3.1	2.79	3.3
c		1000	206	3.0	2.64	4.7
d		1000	206	1.8	4.45	5.2
e	Counter-rotating	1000	368	2.4	3.52	9.8
f		1000	132	2.1	5.23	4.8
g		1000	132	4.0	2.54	4.2
h		1000	132	5.7	2.13	3.9

^a DOP = 300 g.

idence time function $E(t)$. The mean residence time of the reactional mass in the extruder can be considered, to a first approximation, as the reaction time (the reaction is stopped at the outlet of the die by passing the strip through a bath at room temperature). The description of the method has been given in experimental section of the present work, and more exhaustively in Ref. 14.

There are two possible ways of varying residence time in an extruder, change in the flow rate and change in the screw design. The first was employed in this work, and the second will be mentioned later.

In Figure 3 are given the residence time distribution functions, determined by UV tracer, for the PVC reactions with NaBT in the same proportion of reactants and same conditions at 5.7, 4.0, and 2.1 kg/h flow rate. Table III reports the corresponding values of the mean residence time (t_m) together with those of several other runs. It is observed that, first, the mean residence time is longer for the counter-rotating than for the corotating screw (see, for instance, a and f runs), because, as shown in Figure 2, the corotating screws are filled only with conveying elements. Second, the higher the concentration of nucleophile for the same flow rate, the smaller is t_m (see, for instance, b and c or e and f).

Considering t_m as the reaction time, Figure 4 plots the degree of conversion as a function of time for three different compositions, where the amount of nucleophile is varied. It must be emphasized that the influence of the reagent concentration is the only effect studied since the screw speed and the barrel temperature profile are the same in all cases. The shape of the curves clearly correspond to typical conversion-time curves, where increasing the amount of reactants gives increasing conversion. This figure also shows that the larger part of nucleophiles are grafted in a very few minutes. The

solid line corresponds to the experimental points and the dotted line corresponds to what would be expected, from the nucleophile efficiency point of view, if the reaction was allowed to continue.

Apart from these results being illustrative for a general study of the kinetics for the continuous reactions on polymers, some comments regarding Figure 4 can also be made. When a low level of modification is enough to improve the polymer properties, such as thermal or mechanical properties, the above working conditions are, in principle, suitable. If a higher level of grafting is desired, a longer residence

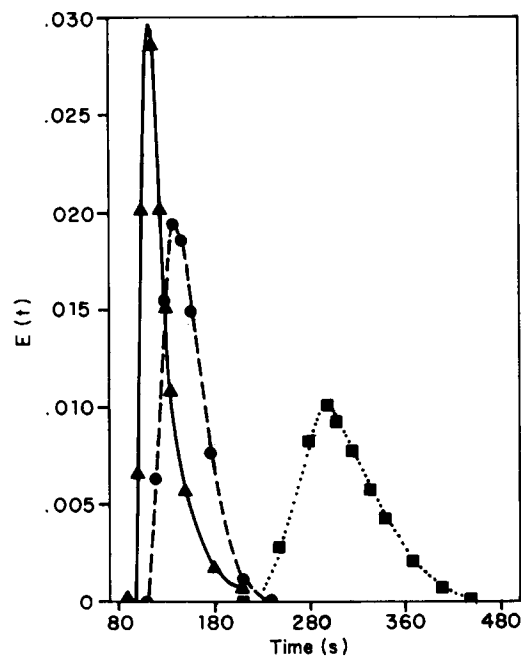


Figure 3 Residence time distribution for PVC reaction with sodium benzene thiolate, PVC = 1000 g, NaBT = 155 g, DOP = 300 g; (\blacktriangle) 5.7; (\circ) 3.9; (\blacksquare) 2.1 kg/h.

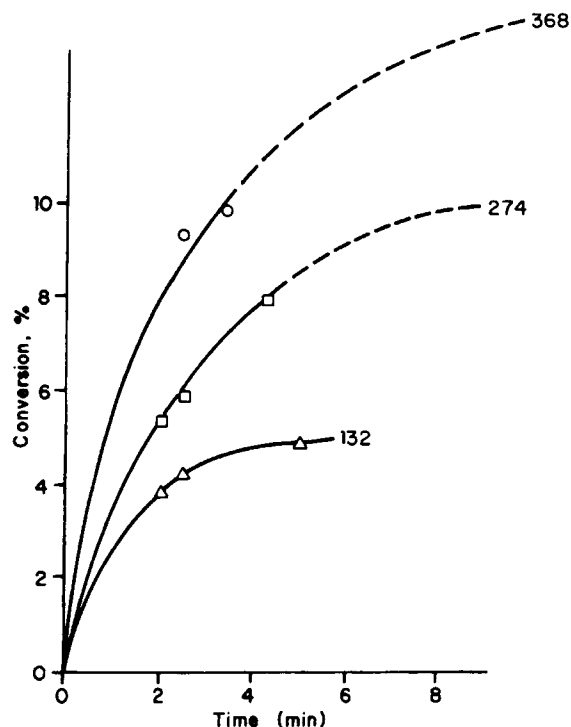


Figure 4 Conversion time curves for PVC substitution PVC = 1000 g, DOP = 300 g, NaBT: (Δ) 132 g; (\square) 274 g; (\circ) 368 g. RMP = 40; T_{barrel} in the fusion-gelation zone = 172°C.

time can only be achieved by an appropriate selection of screw elements, i.e., channel depth, length, and flight thickness. Current developments in twin screw design open new possibilities for chemical reactions on polymers.¹⁶

Processing Parameters

The influence of the processing parameters, such as shear stress, plasticizer, load, and temperature, has been well established in the reaction of PVC with NaBT in a Rheocord system.⁸ The effect of the extruder processing parameters on the reaction has been examined.

Figure 5 shows the influence of the barrel temperature on the reaction conversion for two different compositions. The temperature plotted corresponds to the controller nearer the fusion-gelation zone. In both cases, upper and lower curves, two different behaviors are found. As the temperature increases from 150 to 160°C, the substitution of chlorine atoms increases from about 5% up to about 8.5% for the highest concentration. This result may be explained by both a better fusion-gelation of the polymer and a better dispersion of the nucleophile at

160°C because it is well known that the extrudates show unagglomerated particles in the samples corresponding to extrusion at low temperatures. At temperatures higher than 160°C, the conversion of chlorine atoms is constant whatever the conversion of nucleophile is. These results confirm that the substitution reaction takes place at the same time as the fusion gelation of PVC.

Another obvious parameter controlling the reaction conversion is the flow rate. In Figure 6, the degree of conversion as a function of nucleophile amount for two different flow rates is plotted. The figure clearly shows that a decrease in the flow rate of about 23% is not a determinant parameter with respect to the substitution of chlorine atoms. This conclusion is also in good agreement with the fact that the reaction takes place mainly during the fusion-gelation zone, as discussed previously.

Quality of mixing appears to be the most outstanding parameter controlling the reaction kinetics. Several authors have reported quality of mixing effects on the polymer properties of the final product.¹⁷ However, the formulations of the mixtures have not been reported and there is no evidence as to how mixing can affect the reaction kinetics. In the case of PVC, the diffusion of DOP into the polymer chain is highly dependent on the temperature¹⁸ and the PVC-DOP interactions are responsible for the substitution reaction mechanism to operate.⁸ For that reason, the degree of mixing might have a great influence on the kinetics results of reactive extrusion. In this work the effect of premixing of reactants and

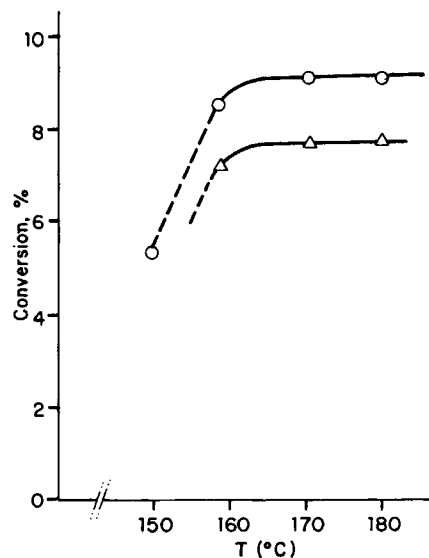


Figure 5 Influence of temperature on conversion PVC = 1000, DOP = 300 g; NaBT: (\circ) 368 g; (\blacktriangle) 274 g.

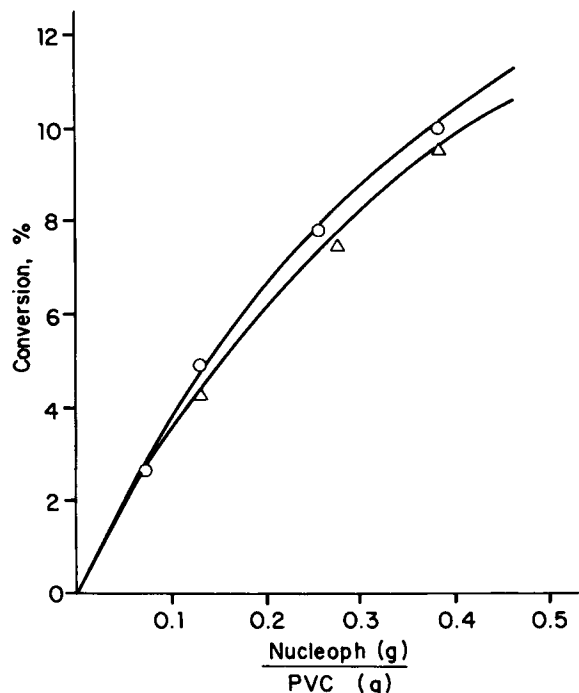


Figure 6 Influence of the flow rate on the conversion for the same conditions but different flow rate: (O) 3 kg/h; (Δ) 4 kg/h.

DOP in a Henschel mixer prior to the extrusion process has been examined.

In Figure 7 is shown the conversion of substituted chlorine as a function of mean residence time for two different premix conditions. The conditions for the two runs are identical; in the upper curve the NaBT amount is even smaller than in the lower curve. The only difference comes from the fact that in the first case the mixture was allowed to stir until 90°C was reached. In the second the mixture was stopped at 40°C and the time of mixing is about two times shorter than case 1. It has been verified that in case 1 no reaction took place in the Henschel mixer. The results of the Figure 7 show clearly the influence of the conditions of premixing on the substitution of chlorine atoms. In these experiments the residence time is controlled by the flow rate, and for that reason the comparison of the results must be made only for the same flow rate to be compared at the same thermomechanical history. For instance, for a mean residence time of about 3 min when the mixing is carried out in the presence of DOP at 90°C the chlorine conversion increases about 100% with respect to the mixing carried out at 40°C. On the other hand, it is well known that DOP diffuses rapidly inside PVC grains at temperatures higher than T_g . Furthermore, the NaBT is insoluble in DOP.

Thus the difference in the conversion rate between the two previous conditions of premixing can be explained by differences of state of DOP diffusion and also by differences of initial state of nucleophile dispersion. The curve 2 shows that the chlorine conversion increases with respect to the residence time, that is, as the flow rate decreases, and this result tends to confirm that the extruder contributes to improve the dispersion of the nucleophile inside the extruder. A verification of this "mixing" parameter influence was carried out for other reaction conditions in which temperature or amount of nucleophile was changed, and the same qualitative results were obtained.

As a general example of the influence of processing conditions on the reaction, Figure 8 compares the kinetics of two substitution reactions, one carried out in the extruder and the other in the Rheocord system. The difference can only be analyzed in terms of the physical factors influencing the performance of the physical (fusion-gelation) process, since the chemical factors are the same: PVC, NaBT, DOP concentrations, and temperature.

In this study some of the relevant factors that affect the kinetics have been identified. Nevertheless, some other parameters, such as shear and special screw configuration, also need to be investigated.

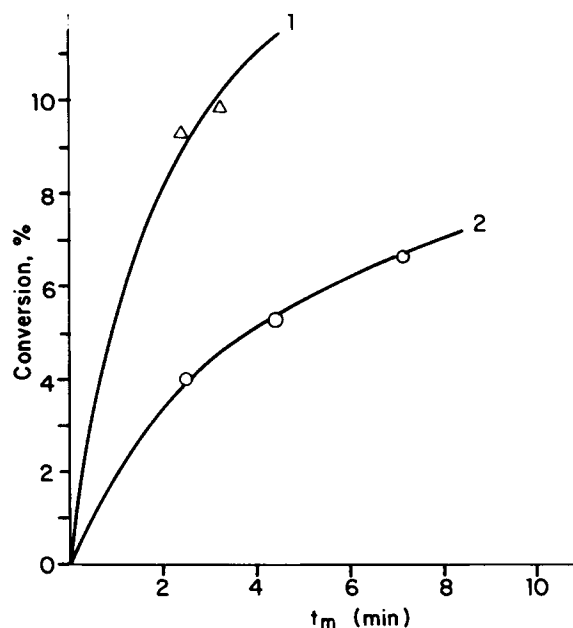


Figure 7 Effect of the premixing on the final conversion. T_{barrel} near fusion-gelation zone = 172°C; RMP = 40; PVC = 1000 g, DOP = 300 g; NaBT: (1) 368 g, premixing at 90°C; (2) 413 g, premixing at 40°C.

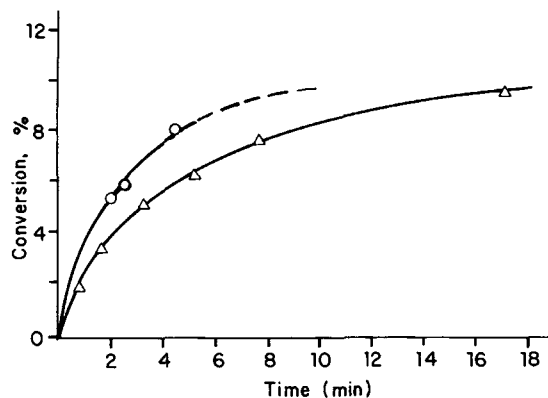


Figure 8 Comparison of kinetics of PVC substitution with benzene thiolate in the melt for near the same conditions PVC = 1000; DOP = 300; (O) NaBT = 274 g, extrusion process, this work; (Δ) NaBT = 300 g, Rheocord process.⁸

Mechanism of Substitution

It has been extensively reported by Millán et al. that nucleophilic substitution of PVC with sodium benzene thiolate and other nucleophiles in solution,

aqueous suspension, and discontinuous melt is a stereospecific reaction.⁸⁻¹³ In fact, only Cl from iso- or heterotactic triads is able to react. Whatever the reagent or the medium, the resulting modified structure is the same, and so it was expected for the continuously modified polymer. To verify whether changes in the reaction process could affect the stereochemical structure and polymer properties of the so-obtained polymer, a comparison of the thermal behavior, molecular weight, and stereostructure of the both continuous and discontinuous modified polymers was carried out. The reason for this study is because these properties are very sensitive to any change in chemical structure, and RMN allows the identification of the very nature of the reacted chlorine.

In Figures 9(A), (B), and (C), the evolution of the apparent molecular weight, dehydrochlorination rate, and relative content of isotactic, heterotactic, and syndiotactic triads with degree of conversion are plotted. Looking very closely for any changes in the respective plots, no qualitative or quantitative changes are observed. These results confirm that the same process is obtained in both cases, no side

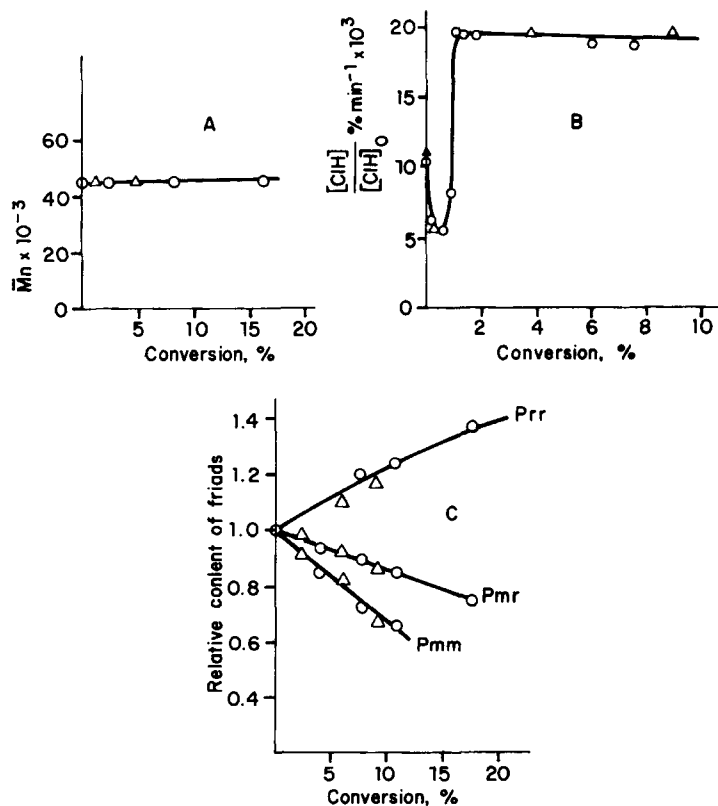


Figure 9 Evolution of apparent molecular weight (a), dehydrochlorination rate (b), and relative content of methinic carbons (c) with degree of conversion: (x) Extrusion process, this work; (O) Rheocord process.⁸

reactions such as crosslinking or degradation have occurred, and the same stereospecific substitution reaction mechanism to that previously found⁸⁻¹³ has been followed.

CONCLUSIONS

In this paper we have shown that the continuous chemical modification of PVC in a twin screw extruder process for grafting nucleophile reactants onto PVC is a feasible process, where the efficiency of the reaction can be > 75%, and the composition of the newly obtained polymer, is homogeneous. The substitution reaction on PVC is associated with the fusion-gelation process. Flow rate, premixing of reactants and plasticizer and temperature (studied to a lesser extent) are some of the parameters influencing the reaction kinetics.

The comparison of continuous and discontinuous melt processes confirm the same mechanism with no side reaction such as crosslinking or degradation, and the same stereospecific mechanism for the nucleophilic substitution on PVC. The differences can only be explained in terms of physical changes affecting the degree of gelation process of PVC.

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