

A Comprehensive Approach to the Stereochemical and Physical Factors in Nucleophilic Substitution on PVC in the Melt

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Synopsis

The nucleophilic substitution reaction of poly(vinyl chloride) (PVC) with sodium benzenethiolate (NaBT) has been studied in the melt with the aim of determining whether a conformational mechanism is applicable under conditions that would apply in the polymer processing. The evolution of unreacted syndio, hetero, and isotactic triads content, and of the apparent molecular weight has been followed by ^{13}C -NMR and GPC, respectively. The kinetic behavior was defined by choosing appropriate mixing conditions of temperature, shear stress, load, and amount of plasticizer. In all cases the kinetic curves attain a plateau after a rather fast reaction period has elapsed. The conversion at the plateau, that is, the reaction efficiency, proved to depend linearly on the amount of nucleophile and is hardly influenced by the mixing conditions for a given stoichiometric composition. The mixing conditions have been found to affect markedly the kinetics but to be quite inoperative on the evolution of both the content of unreacted tactic triads and the apparent molecular weight with degree of conversion. The results are discussed by taking into consideration those previously obtained in solution.

INTRODUCTION

There has been considerable attention paid to chemical modification of polymers in the melt.¹⁻³ First, this procedure allows for new structures, and hence improved materials, to be obtained during the polymer processing. Secondly, extrapolation of results obtained in analogous chemical reactions in solution to the melt conditions poses a number of fundamental problems, most of which are still to be solved. In particular, quantitative information as to the reaction mechanisms, the influence of microstructure, the reactant efficiency, and the distribution of modified units in chemical transformation in condensate state is scarcely given in the literature. However, no systematic correlation with data obtained in solution has been studied so far.

In earlier work,⁴⁻⁶ we have found that nucleophilic substitutions on PVC in cyclohexanone dilute solution proceed by a stereospecific mechanism that has been proposed to involve the occurrence of TT isotactic diad conformation.⁵ According to this mechanism, only the isotactic and the heterotactic triads should be reactive, since they are the only ones to contain the TT isotactic diad conformation either on their own, or as the result of conformational equilibria.

In agreement with these hypothesis, the content of isotactic and heterotactic triads was found to decrease with degree of substitution and to vanish completely when temperatures as high as 60°C were used. Furthermore, a

fraction of isotactic triads was demonstrated to be extremely reactive, very likely because they consist of GTTG⁻ conformations where TT fulfils all the S_N² substitution requirements, contrary to what happens for the same TT conformation located in heterotactic triads. An extensive survey of these studies on substitution in solution has been published elsewhere.^{5,7}

Controlled substitution appears to be an excellent way to obtain improved materials. As an example, when benzenethiolate groups are specifically substituted for the highly reactive isotactic triads in cyclohexanone solution, the modified polymer exhibits an enhanced thermal stability in terms of degradation rate and content of polyene sequences.⁸

Unfortunately, chemical modification of polymers in solution will not apply to technical procedures, so we thought it of fundamental interest to study the possible correlation between solution and condensate state conditions for a definite PVC substitution reaction that has been extensively examined in solution, i.e., that with benzene-thiolate group.⁴⁻⁶ The occurrence of such correlation would not only make the chemical transformation of the polymer operative during the technical processing of the polymer, but could provide new information as to the nature of the stereospecific mechanism. Actually, the fact that in the melt state there are shear stress, chain-chain interactions, higher temperatures, and especially, a system that consist of at least two phases, makes it likely for the isotactic diads to adopt the TT conformation in a different way than in solution. The close contact between the reactant species occurs at the interphase, contrary to what happens in solution. The above circumstances might make some structures other than isotactic TT conformation reactive and so cause the reaction to occur through some diads that were not reactive in solution. Consequently, the decrease of isotactic and heterotactic triads with degree of substitution ought to be different from that observed in solution. On the contrary, a similar behavior would support our belief that TT conformation of the isotactic diad is the only reactive species and that its occurrence is necessary for the reaction to occur.

Elucidating the above problems in order for our previous results in solution to apply to practical reaction conditions is the purpose of the present work.

EXPERIMENTAL

Materials

The two PVC samples used were kindly supplied by Rio Ródano Industries, Spain. Their main characteristics are shown in Table I, where $A_{1428\text{cm}^{-1}}/A_{1434\text{cm}^{-1}}$

TABLE I
Characteristics of Polymers

Sample	IR		$\bar{M}_n \times 10^{-3}$	¹³ C-NMR			h^a
	$A_{1428\text{cm}^{-1}}/A_{1434\text{cm}^{-1}}$			P_{mm}	P_{mr}	P_{rr}	
A	1.19		45.5	0.197	0.499	0.303	0.6
B	1.14		33.0	0.212	0.499	0.288	0.8

^a Content of highly reactive structures

$A_{1434 \text{ cm}^{-1}}$ refers to the tacticity measured by IR absorbance ratio. The number-average molecular weight was determined by gel permeation chromatography (GPC) and h refers to the content of highly reactive structures in PVC as determined by substitution reaction with sodium benzenethiolate (NaBT) in cyclohexanone at -30°C .⁹

The NaBT was a commercial product from Fluka. Dioctyl phthalate (DOP) and tetrahydrofuran (THF) were distilled prior to use.

Substitution Reaction with NaBT

The substitution reaction of PVC with NaBT has been carried out in a Haake Rheocord System 40 and a Brabender Pasticorder both fitted with a mixing head Rheomix 600.

Mixing of the reactants has been performed in a butcher where the NaBT was first stirred in DOP and then PVC was added. The PVC mixture was charged into the chamber at the reaction conditions and closed by a 5 kg loading ram.

To establish the best conditions for the melt substitution reaction, a preliminary study of the PVC rheology was carried out at different temperatures (from 160 to 190°C) and shear rates (from 40 to 80 rpm). As PVC shows a rapid fusion process at high temperature and shear, we found 160°C and 40 rpm as the appropriate conditions to follow the incorporation of nucleophile in the PVC chain during the fusion process.

A load of 62 g appeared to be the most appropriate for rigid processing conditions. Nevertheless, when NaBT and DOP are added, PVC mass must be decreased to keep the same load. Since DOP is required for the substitution reaction to take place, we maintained a constant PVC/DOP ratio for all the reaction runs, but the no contribution of NaBT to the shear stress made it necessary to increase the whole mass of the reaction. The conditions of substitution reaction are given in Table II, where other conditions for different kind of studies are also shown.

Because stopping the fusion process and withdrawing samples does not change the shape of the rheogram,¹⁰ the substitution reaction could be followed by removing small samples of about 0.5 g each from the reaction chamber at different stages of the rheogram.

GPC

Degree of Substitution

The degree of conversion of PVC modified with NaBT in the melt was determined directly from the melt mixture, using a Waters Model 510 GPC with a series of UltraStyragel columns: 1×10^3 , 1×10^4 , 1×10^5 . The samples were continuously monitored by a Waters 401 differential refractometer and a Pye Unicam PU 4025 variable wavelength UV photometer, using THF as mobile phase at a flow rate of 1 mL/min at room temperature. About 30–70 mg of reaction mixture, depending on the degree of conversion attainable, was dissolved in 10 mL of THF, for the injection samples.

The degree of conversion of benzenethiolate grafted in the PVC chain was evaluated from the ratio of the UV photometer maximum peak height at

TABLE II
Experimental Conditions for Substitution Reactions in the Melt

Run	Polymer (g)	NaBT (g)	DOP (g)	T (°C)	Final Conversion (%)
0	57	—	5	160	—
1	59	3	0	160	0.7
2	57	5	0	160	0.7
3	59	3	0	190	0.7
4 ^a	59	3	0	160	0.9
5	54	5	3	160	3.5
6	52	5	5	160	2.8
7	47	5	10	160	3.6
8	44	8	10	160	5.6
9	40	12	10	160	9.3
10	40	12	10	190	8.5
11	32	20	10	160	17.6
12	43	27	13.5	160	22.7
13	48	34	15	160	23.6
14	37	40	11.6	160	39.0
15	30	55	9.5	160	49.8

^aSample B.

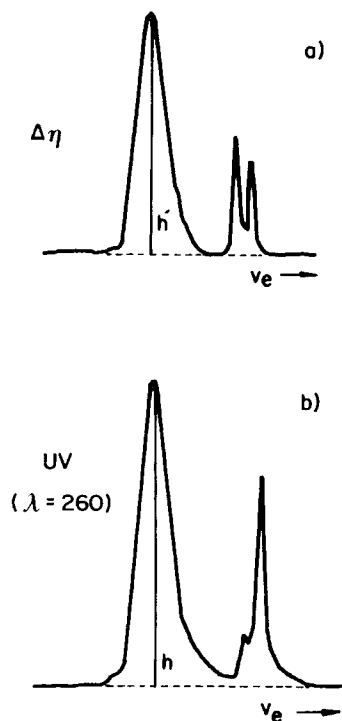


Fig. 1. Chromatograms of PVC modified with NaBT: (a) refractometer detector; (b) ultraviolet detector.

260 nm and the refractometer maximum peak height (see Fig. 1). The two values are needed because the PVC exact concentration is not known. In this case a previous calibration curve of well-characterized PVC modified samples was necessary.

The method was quantitative as determined by UV spectroscopy by measuring the purified samples.

Molecular Weight

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

Ultraviolet-Visible Spectroscopy

The degree of substitution of several modified samples in the melt was determined by a 554 Perkin-Elmer UV-Vis spectrometer from the benzenethiolate band intensity at 256 nm with the aid of a calibration curve.⁵

¹³C-NMR Spectroscopy

The tacticities for both starting and modified polymers were measured by ¹³C-NMR spectroscopy at 75.5 MHz and 100°C using an XL 300 Varian spectrometer. Polymer samples after purification were examined in a 10–15% (w/v) solution, depending on the degree of modification of the polymer, in a mixture of deuterated dimethyl sulfoxide–1,2-dichlorobenzene (volume ratio 1/4), using 10 mm sample tubes. To ensure integral accuracy, a flip angle of 80°, a pulse repetition rate of 4 s, and broad-band proton decoupling were used. The spectral width was 2000 Hz and 16 K data points were used. In PVC samples 30,000 scans gave a very satisfactory signal-to-noise ratio but high modified polymer were recorded using 30,000–75,000 scans.

The resonance we used are those of methine carbons of the backbone ranging from 55 to 58 ppm. The calculations were carried out by measuring

TABLE III
Conversion and Probability of Iso, Hetero, and Syndiotactic Triad Content

Run and number of sample	Conv. (%)	P_{mm}	P_{mr}	P_{rr}
0	—	19.7	49.9	30.3
1—3	0.6	19.8	49.7	30.3
4 ^a —4	0.9	21.1	49.7	28.8
11—1	3.9	18.2	49.2	31.1
11—4	7.8	14.5	44.9	36.4
11—6	10.2	13.1	42.9	37.8
11—9	17.0	9.1	37.5	41.4
13—7	21.8	8.1	35.4	41.9
14—6	27.8	5.8	28.6	44.9
14—7	30.0	4.7	27.3	43.8
14—13	38.7	2.8	20.0	42.7
15—17	49.6	1.4	12.2	26.0

^aSample B.

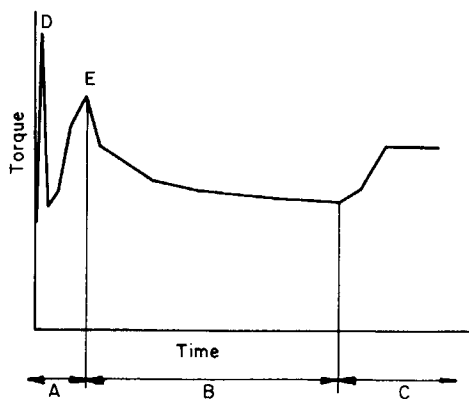


Fig. 2. Typical rheogram of PVC: 160°C; 40 rpm; (A) fusion period; (B) flow period; (C) reaction period; (D) charge peak; (E) gelification-fusion peak.

the areas with a compensating polar planimeter. The obtained values are summarized in Table III, where P_{mm} , P_{mr} , and P_{rr} refer to the probability of iso, hetero, and syndiotactic triads, respectively.

RESULTS AND DISCUSSION

Figure 2 presents a typical torque-time diagram for the reaction of PVC with NaBT under definite conditions of load, temperature, and shear stress as indicated. It exhibits three different stages and two peaks, which are characteristic for the flow behavior of PVC. The periods are known as fusion, flow, and reaction periods (reaction period means side reactions such as degradation, crosslinking, etc.). Since substitution occurs before the reaction period, at least under the experimental conditions mostly used in this work, this period will not be taken into consideration. The peaks are the charge and the gelation-fusion peak.

One initial aim was to determine which of the above periods are suitable for the reaction to take place. The different stages were experimentally controlled so as to make possible both the detection of reaction and the kinetic measurements. According to the literature the flow behavior of PVC depends on temperature, shear stress, plasticizer, and load. After choosing 62 g of polymer as the most convenient chamber load, we analyzed the influence of shear stress and temperature on a torque diagram. As expected, the fusion zone was found to be shorter with increasing either temperature or shear stress. As to the influence of plasticizers, it is also known that they cause decreased fusion time and the torque values. The results obtained for DOP agree with these predictions.

Substitution in the Absence of Plasticizer

Figure 3 shows the evolution of degree of substitution with time as well as the corresponding torque diagram. Two important data are worth emphasizing: (i) only degrees of conversion as low as 0.7% are obtained; (ii) the reaction takes place only within a short and definite period that corresponds to the fusion process. In fact, the reaction is accomplished during the initial part of flow period. Afterward, substitution extent remains constant.

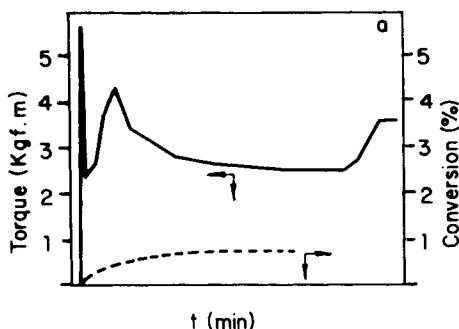


Fig. 3. Evolution of torque (—) and kinetics (---) for PVC modified with NaBT (run 1).

This behavior may be tentatively explained on the basis of some recent results in our laboratory. The fact that only a small amount of polymer reacts clearly indicates that polymer mobility is restricted to only a few local sites that thus become accessible to nucleophile attack. T_g decreases linearly with increasing content of a fraction of isotactic triads that are capable of reacting with NaBT in cyclohexanone solution at temperatures as low as -30°C .¹¹ These triads, which were proposed to be the GTTG^- isotactic conformation,⁴ are then to be viewed as both locally mobile and extremely reactive structures. Since their content was determined to range between 0.3 and 0.9%, depending on the overall tacticity of the polymer,⁹ it seems reasonable to assume them to be the structures that react in the melt without plasticizer.

In support of this assumption are the results obtained using either greater amount of nucleophile (run 2) or higher temperatures (run 3). As illustrated by Table II, no higher conversions than 0.7% were obtained, which indicates that the extent of reaction is determined by the content of reactive structures in the polymer. Moreover, substitution under the same conditions of a PVC sample with higher isotactic content gave 0.9% conversion (run 4).

Substitution in the Presence of Plasticizer

Figure 4 presents the torque diagrams for two reactions in the presence of different amounts of DOP and the corresponding conversion curves [data without DOP (Fig. 3) are also shown for comparison]. Obviously, these results

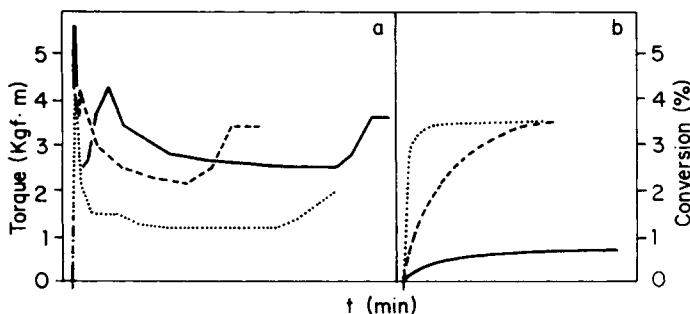


Fig. 4. DOP dependence on the evolution of both the torque (a) and the kinetics (b) in PVC modification with NaBT: (—) 0 g; (---) 3 g; (···) 10 g.

make it clear that substitution occurs only during the fusion period, since the conversion curve levels off at the outset of the flow period. It is also apparent that the degree of conversion at the plateau is independent of the amount of DOP. This conversion value agrees with that expected from the nucleophile efficiency; that is, it does not depend on the amount of plasticizer even if, as clearly demonstrated by results in Figure 4(b), some plasticizer is required for conversions that should agree with nucleophile efficiency, to be likely. In contrast, as it follows from the comparison of curves a and b, the reaction rate appears to be higher and the fusion period shorter as the amount of plasticizer increases. Aside from some fundamental features, this behavior is particularly important for industrial applications, not only because it allows for the reaction to be controlled, but also because it makes the separation of substitution and degradation processes possible. Actually, curves in Figure 4(a) show how a decrease in DOP proportion involves a higher torque value during the flow period and therefore the appearance of the reaction period, where degradation takes place, before the plateau is completely attained.

Because the presence of DOP is necessary for the efficiency of the reaction to run, even though the latter is independent of the amount of DOP, the major effect of plasticizer is that of making the local motion of chain reactive sites sufficient for the close contact with nucleophile particules to be ensured. From previous results on substitution in DOP heterogeneous medium where the polymer and the NaBT are soluble and insoluble, respectively,¹² the efficiency of the reaction depends on the amount of nucleophile while the chemical mechanism of substitution is controlled by the stereochemistry of the polymer, that is, when both the polymer and the nucleophile are soluble.⁵ Whether or not DOP is associated with interactions with some definite conformations of the polymer remains to be clarified at present. Some of the current studies in our laboratory are dealing with this problem.

The importance of the influence of mass and temperature on both the torque diagram and the conversion-time curves derive from the fact that they both affect the shear stress operating on the system. It is known that shear stress increases with increasing mass or decreasing temperature.¹³ Figure 5 shows the conversion curves for two reactions with different mass but equal for all other conditions, including the mass molar composition. Both reactions will lead to the same plateau but they behave differently in that decreasing of mass causes a drastic reduction of reaction rate throughout the process. The most likely interpretation of these results is that increasing of shear stress gives rise to an enhanced number of local motions in the polymer chain and, consequently, to a greater probability of chemical attacks. Note that shear stress favors the nucleophile diffusion, too.

In a similar way decreasing shear stress by increasing the temperature from 160 to 190°C has been shown to result in decreasing reaction rate while the same plateau is obtained. But, contrary to what happens for changes in mass, the former effect is appreciable only after conversion of 5% is exceeded (Fig. 6).

The lower number of local motions due to the decrease of shear stress may be compensated by the higher number of reactive sites that reach the activation energy on increasing temperature. This seems likely for the first stages of the reaction where the concentration of the reactive sites is higher. Then, insofar as the reaction advances, the kinetic effect of temperature should vanish while that of shear stress remains constant.

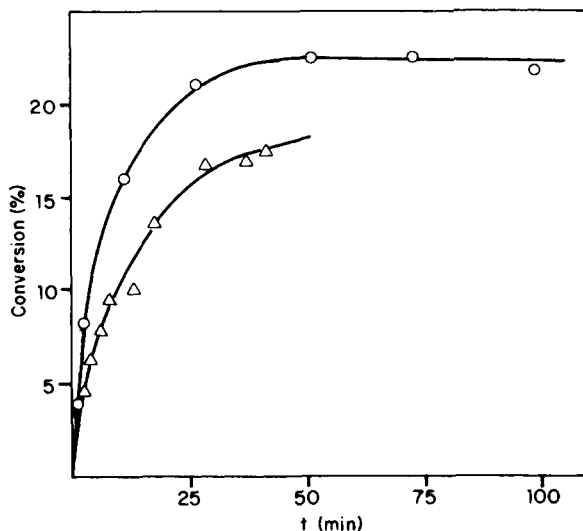


Fig. 5. Influence of total mass on the kinetics of the reaction (runs 11, 12; Table II).

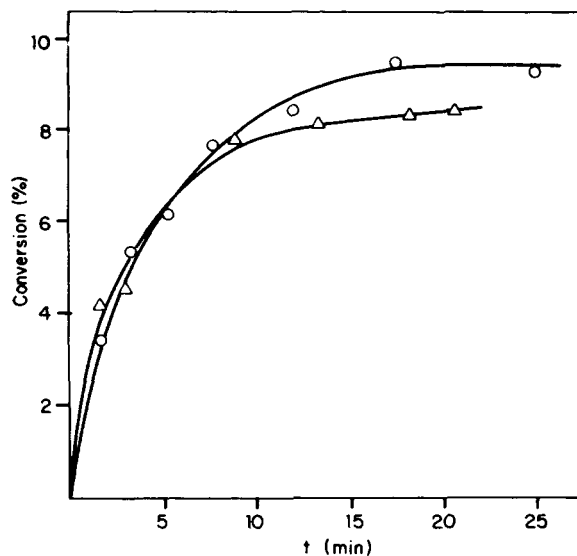


Fig. 6. Influence of temperature on the kinetic of the reaction: (O) 160°C; (Δ) 190°C; (runs 9, 10; Table II).

Efficiency of the Reaction

Figure 7 displays a set of conversion curves for reactions carried out under the same conditions of temperature and shear rate. Increasing amounts of nucleophile within a very large range (Table II) were used. On the contrary, PVC/DOP ratio was kept rather constant and their total amount was changed so that the torque could vary as little as possible. In all cases the curve levels off after a rather quick period during which most of the reaction takes place. This period corresponds to that of fusion in torque diagram.

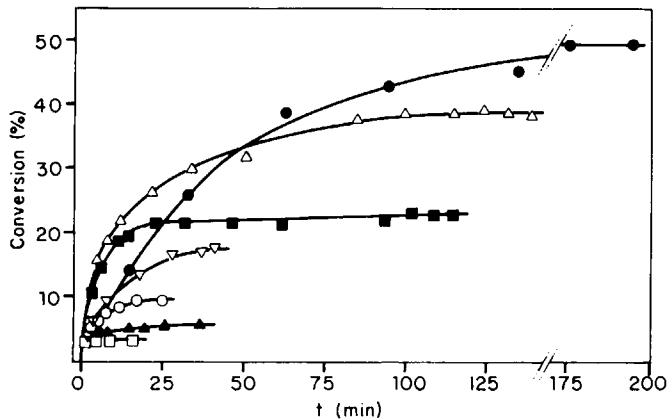


Fig. 7. Conversion-time curves for various reaction conditions: (\square) run 7; (\blacktriangle) run 8; (\circ) run 9; (∇) run 11; (\blacksquare) run 12; (\triangle) run 14; (\bullet) run 15 (Table II).

Within experimental error, all the conversion curves are similar in shape, even if changes are made both in mass and in the nucleophile/DOP ratio (Table II). This means that the overall shear stress conditions are similar and that the PVC/DOP ratio is, at least to a certain extent, a major kinetic-determining factor. Nevertheless, the most outstanding implication is that final conversion is found to be higher as the amount of nucleophile increases. Furthermore, this relationship is linear with experimental errors, as clearly demonstrated by Figure 8. The latter finding is of great interest in that it allows the reaction efficiency to be determined by the amount of nucleophile no matter which experimental conditions are used (except for the plasticizer presence requirement). This assertion, besides the fact that kinetic features

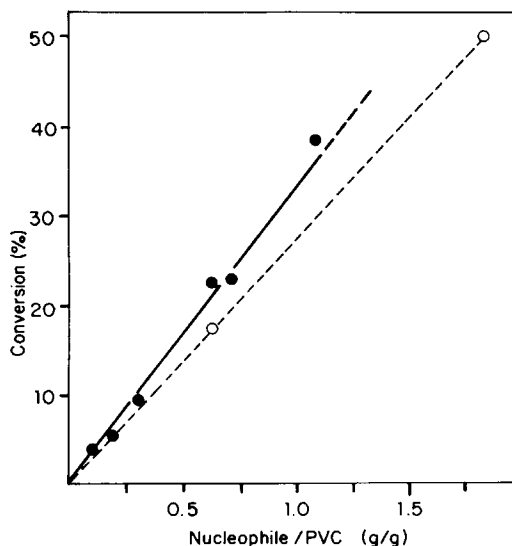


Fig. 8. Reaction yield as a function of nucleophile/PVC ratio: (\bullet) high shear stress; (\circ) lower shear stress.

depend markedly on any factor related to local motions in the polymer chain, accounts for the occurrence of a single mechanism of reaction as expected.

The effect of physical factors affecting the diffusion of nucleophile and its specific surface should not be ruled out. Actually, Figure 8 shows how run 11 and 15 deviate somewhat from linear behavior. These effects could very well be due to small changes in nucleophile efficiency arising from differences in the overall shear stress, the nucleophile preparation, etc., that might affect the mixing of reactants. Such effects are in good agreement with some prior results on substitution in DOP heterogeneous medium, where the conversion was found to increase on decreasing the amount of DOP for a given stoichiometric condition.¹² This was suggested to be due to an enhanced probability of chain reactive sites on the surface of nucleophile particles. The conversion at the plateau is assumed to depend on the amount of nucleophile. In other words, the nucleophile efficiency is assumed to obey a linear behavior with respect to the amount of nucleophile, but the slope of the straight line, that is, the overall reaction efficiency, may be optimized by changing the shear stress conditions.

Stereoselectivity of Substitution

Figure 9 shows the ¹³C-NMR spectra of substituted samples for a number of degrees of conversion. Clearly, the bands of both the isotactic and heterotactic triads decrease with increasing conversion. The band of syndiotactic triads seems not to vary during all the process.

The quantitative evolution of the content of unreacted syndio, hetero, and isotactic triads, as calculated by measuring the areas of the respective ¹³C-NMR bands (Fig. 9) with the degree of substitution, is indicated in Figure 10. The most salient feature is that isotactic and heterotactic triads decrease linearly throughout the process. However, the fall in isotactic triad content exhibits two well-distinguished slopes: one faster slope until a conversion as high as 10% is reached and one slower slope afterward. For the heterotactic triads, a single straight line is found. The apparent increase in syndiotactic triad content may be easily explained because substitution at the central unit of a heterotactic triad that is flanked by another heterotactic triad results necessarily in the formation of a new β -substituted syndiotactic triad. Note that this increase vanishes at about 25% conversion. Information concerning ¹³C-NMR signals of the polymer after substitution in solution has been previously given. It must be noticed that the appearance of 57.7 ppm is due to benzenethiolate group centered triads.⁴⁻⁶ It should be emphasized that results in Figure 10 agree quantitatively with those obtained in dilute solution.^{5,7}

Variation of Molecular Weight with Substitution

Figure 11 illustrates the evolution of average molecular weight with degree of substitution whether in the melt or in solution. Taking into account that the structure of the polymer changes as the reaction progresses, many interpretations as to the physical significance of the values obtained might be given and need to be studied separately. Molecular weight evolution is similar for both reaction conditions. This indicates that the structure of modified polymer, that is, the distribution of modified units along the chain for a given

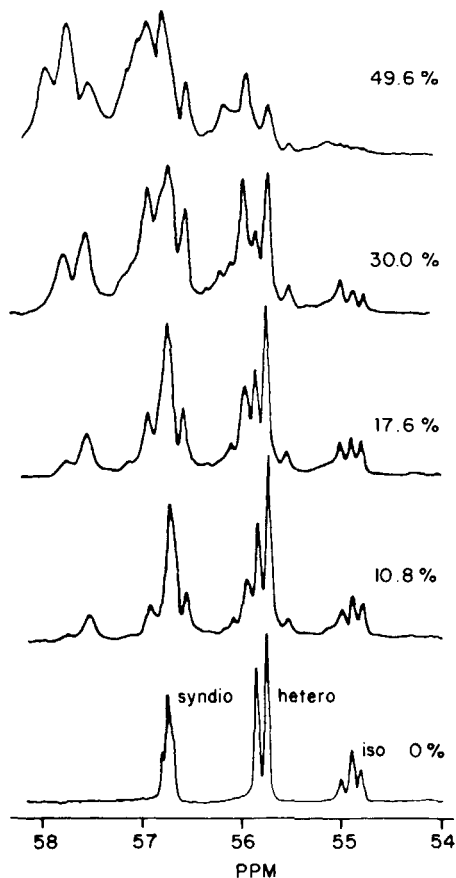


Fig. 9. ^{13}C -NMR bands of the methine carbons of modified samples at various conversions.

conversion, is independent of the reaction conditions, which supports the conclusion that substitution occurs by a single mechanism.

CONCLUSIONS

i. The presence of some plasticizer is required for the reaction to occur, but the final conversion is independent of the amount of plasticizer. In the absence of plasticizer only a small fraction of isotactic triads is reactive. This fraction agrees with that found to be reactive at very low temperatures in solution (Ref. 9 and Table I).

ii. The reaction efficiency depends linearly on the amount of nucleophile. Minor variations in the slope are observed when the mixing conditions are changed.

iii. Mixing conditions (shear stress, temperature, amount of plasticizer, load, etc.) are found to affect the kinetics and, to a lesser extent, the nucleophile efficiency. In contrast, the evolution of the type of triads and apparent molecular weight with conversion is quite insensitive to such conditions.

iv. Surprisingly, the evolution of both the tactic triads content and the apparent molecular weight with conversion agrees thoroughly with that found in solution.

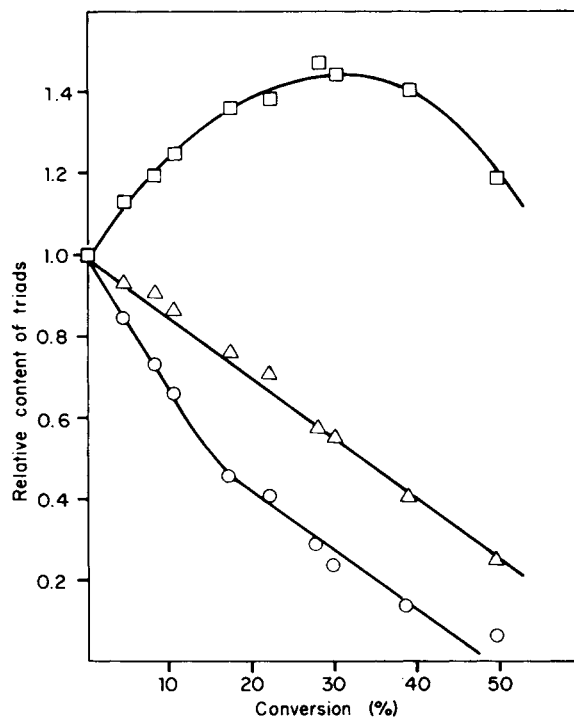


Fig. 10. Evolution of the relative content of triads with the degree of substitution: (□) syndiotactic triads; (Δ) heterotactic triads; (○) isotactic triads.

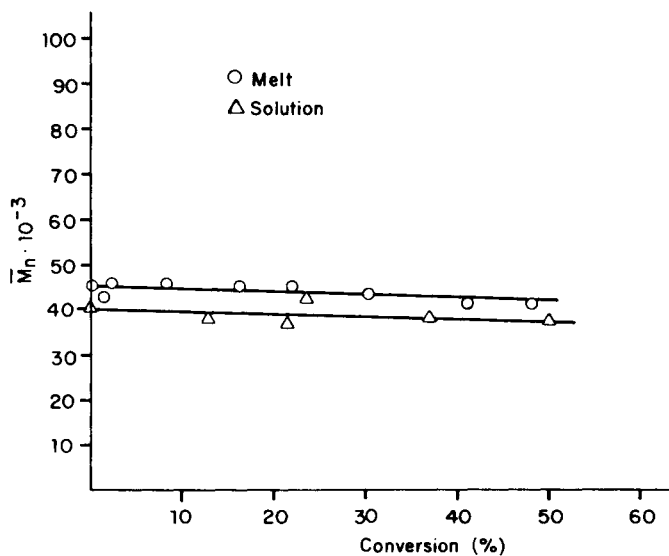


Fig. 11. Evolution of apparent average molecular weight with the degree of substitution: (Δ) solution; (○) melt.

In summary, the reaction occurs specifically through a definite type of reactive sites in the polymer, no matter which mixing conditions are used. These conditions prove useful for the optimization of the reaction efficiency. The fact that the reactive sites are iso and heterotactic triads and that their relative reactivity is similar to that found in dilute solution, accounts for a conformational mechanism, as proposed previously,^{5,7} to operate in a condensed state as it does in solution. Such correlation allows for some basic features in polymer modification close to those of polymer processing to be understood. Further detailed results about this matter will be published in the near future.

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