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Influence of Tacticity on Some Reactions of PVC

J. Millàn[a]
[a] Instituto de Plasticos y Caucho Juan de la Cierva, Madrid, Spain

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Influence of Tacticity on Some Reactions of PVC

J. MILLÀN

Instituto de Plasticos y Caucho Juan de la Cierva
3 Madrid, 6 Spain

ABSTRACT

The influence of the tacticity on PVC reactivity is discussed on the basis of preliminary results obtained in ionic dehydrohalogenation and chlorination reactions. From the reaction of an atactic PVC and a 70% syndiotactic PVC with LiCl in dimethylformamide and hexamethylphosphortriamide as solvents, it follows that both the reaction rate and the polyene sequence distribution depend markedly on the syndiotacticity content. This effect is accounted for by the fact that the isotactic parts are preferred in dimethylformamide and the syndiotactic ones in hexamethylphosphoramide. On the other hand, the chlorination of PVC appears to be easier through the heterotactic parts than through the syndiotactic sequences as shown by ^{13}C-NMR.

The influence of tacticity on polymer reactivity has not been extensively studied for any polymer. However, some authors like Harwood [1] and Sakurada [2] found differences in kinetic features for the hydrolysis of polymethacrylates and poly(vinyl acetate) in relation to their microstructure. In the case of PVC, attempts are still more scarce, possibly because of the difficulties in preparing and characterizing samples with a well definite tacticity content.

As an example of this, I shall present some results obtained in two old reactions of PVC: ionic dehydrochlorination and chlorination.

Figure 1 shows the kinetic curves of dehydrochlorination with lithium chloride for an atactic sample and for a 70% syndiotactic

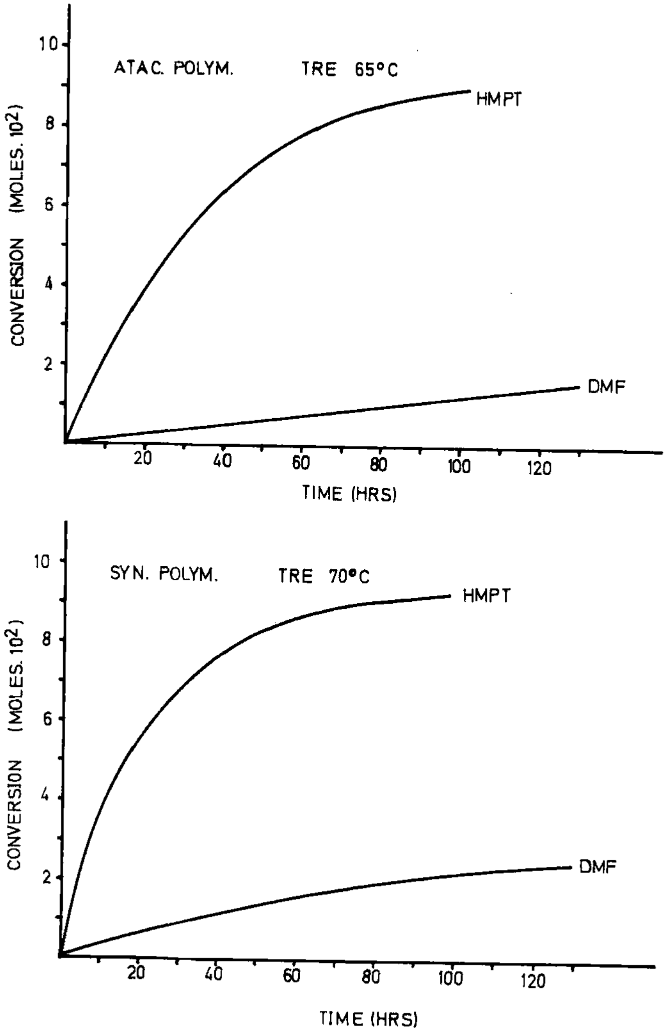

FIG. 1. Dehydrochlorination of atactic and 70% syndiotactic PVC with lithium chloride in dimethylformamide (DMF) and hexamethylphosphortriamide (HMPT).

sample in dimethylformamide (DMF) and hexamethylphosphortriamide (HMPT) as solvents. The reaction rate appeared to depend markedly on the tacticity content, as shown in Fig. 2. Here the reaction rate in DMF is seen to decrease with increasing syndiotacticity content, contrary to what happens in HMPT.

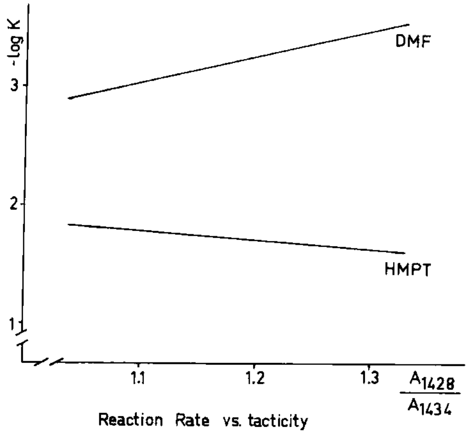

FIG. 2. Reaction rate for dehydrochlorination vs. tacticity of PVC.

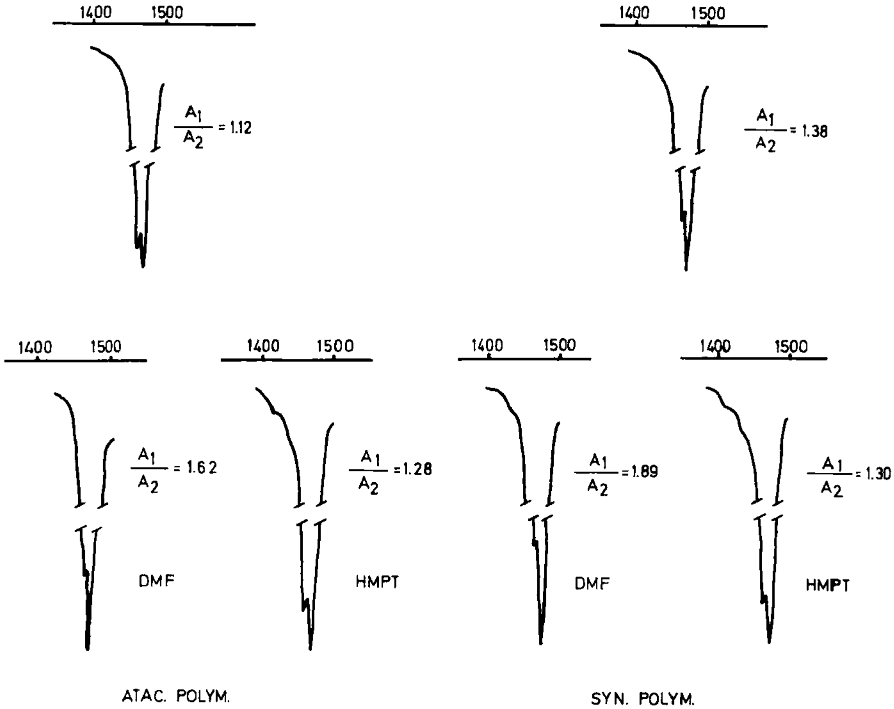

FIG. 3. Selective dehydrochlorination of PVC depending on the solvent and tacticity.

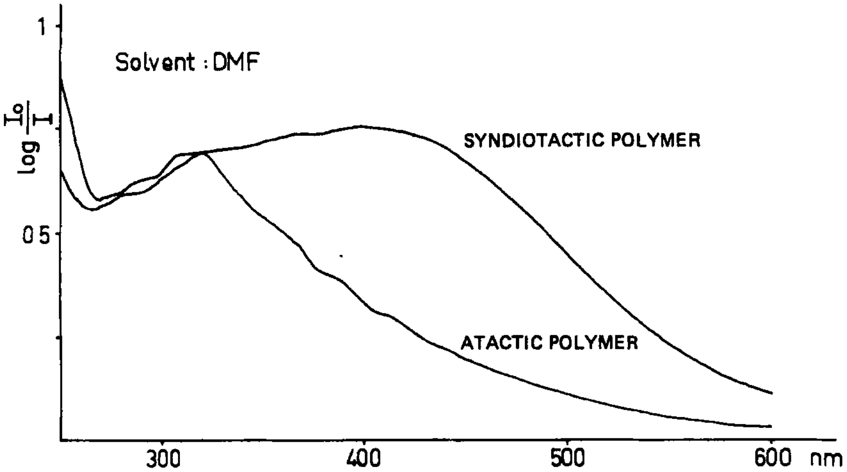

FIG. 4. Polyene sequence distribution after dehydrochlorination in DMF.

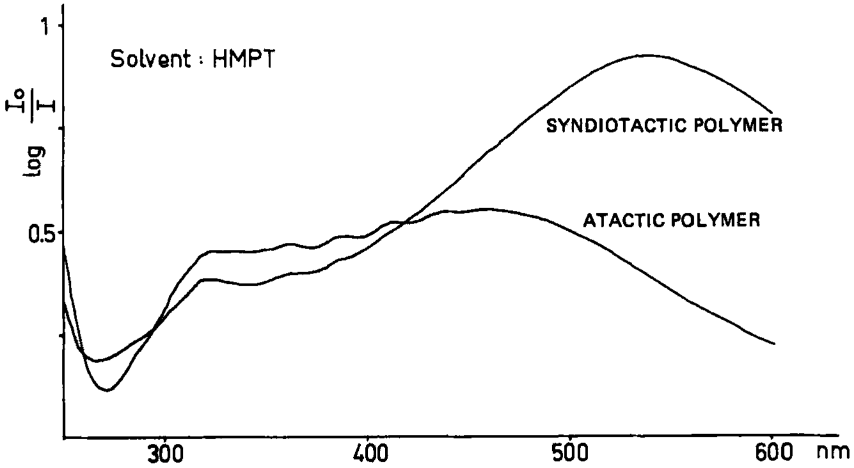

FIG. 5. Polyene sequence distribution after dehydrochlorination in HMPT.

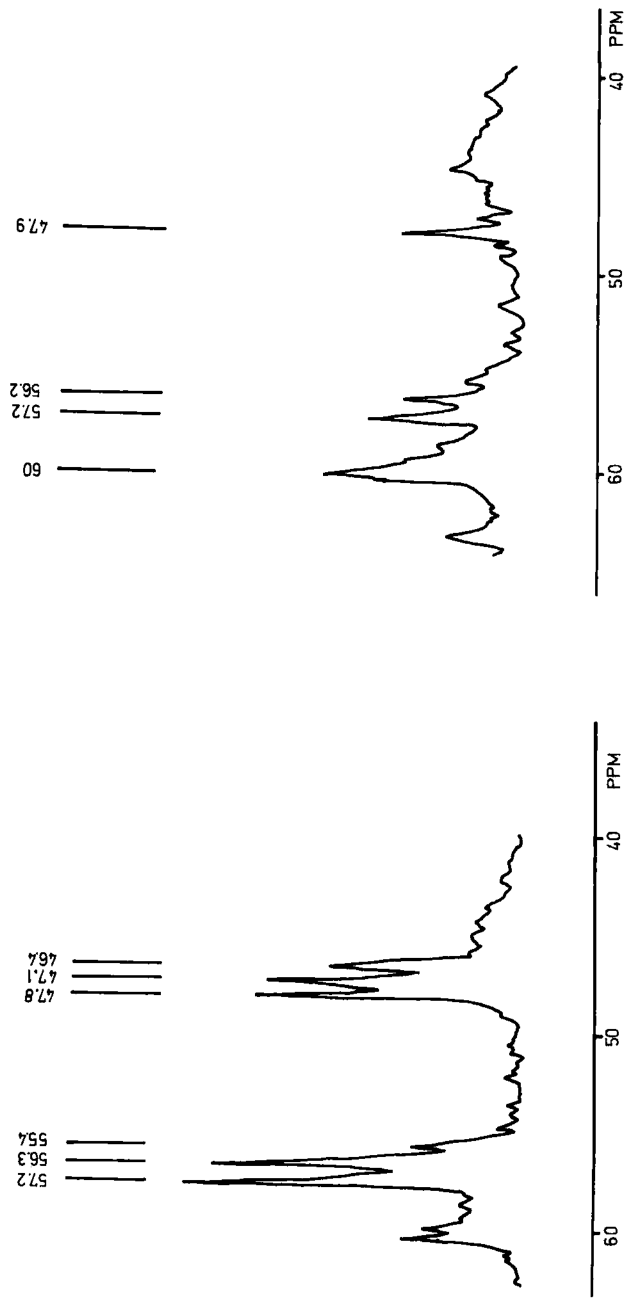

FIG. 6. ^{13}C-NMR spectra of 60% syndiotactic PVC chlorinated at 59 and 65%.

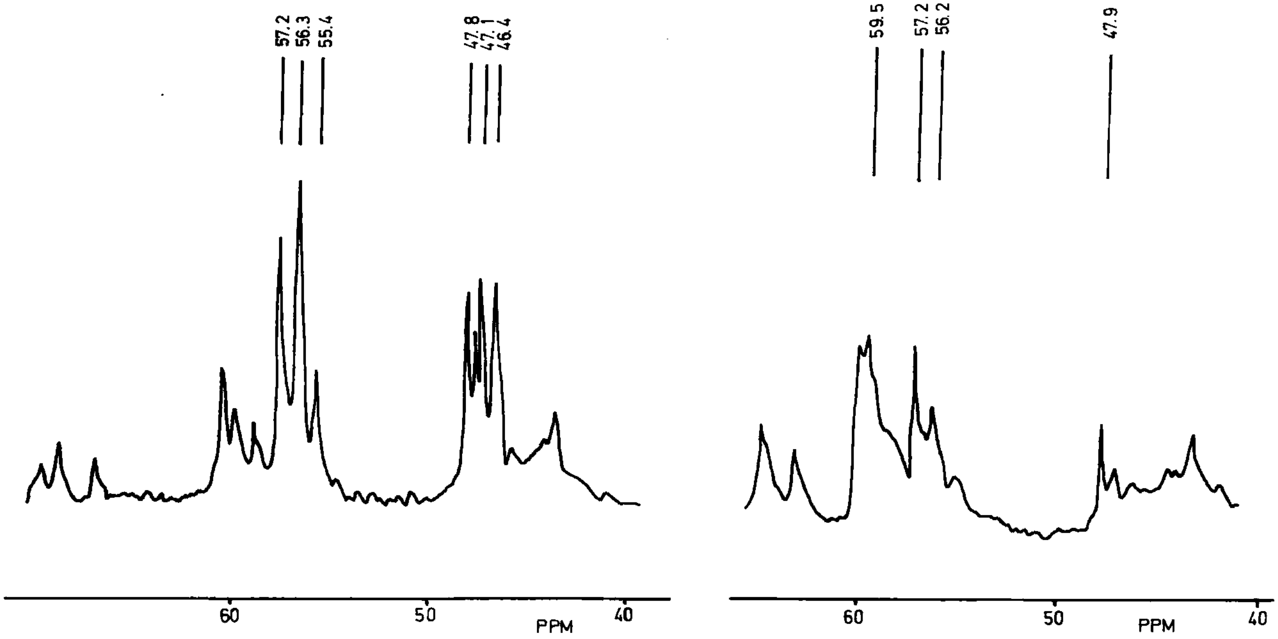

FIG. 7. ^{13}C-NMR spectra of an atactic PVC chlorinated at 59 and 65%.

From Fig. 3 it follows that isotactic portion is preferred in DMF and the syndiotactic in HMPT. Indeed, the ratio syndio diads/iso diads as measured through the infrared absorbancy ratio$A_{1428\ cm^{-1}}/A_{1434\ cm^{-1}}$ increases in DMF, while in HMPT it increases only slightly in the atactic polymer and even decreases in the more syndiotactic sample.

These kinetic features are reflected in the polyene sequence distribution in the transformed polymers. Figure 4 shows that in DMF, the syndiotactic sample after elimination contains more long polyene sequences than atactic polymer, and this effect is enhanced in HMPT, as shown in Fig. 5.

It is apparent also that both polymers give rise to longer polyene sequences than in DMF, which accounts for the effect of solvent. These results are even more significant as the absorbance scale used for syndiotactic polymer in UV-VIS spectra (Figs. 4 and 5) is twice that used for the atactic sample (0-2 and 0-1, respectively).

As for the chlorination reaction, the possible influence of the tacticity on the mechanism has not been yet clarified in spite of some interesting approaches such as those of Allen [3] and Kolinsky [4]. Some recent results we obtained by chlorination in carbon tetrachloride in the presence of o-dichlorobenzene, may be summarized by saying the order of chlorination to be: first TTG'T, TTGT, and TTTG, which are heterotactic triads, and second TTTT, which are syndiotactic triads.

This is shown in Figs. 6 and 7. Figure 6 shows the ^{13}C-NMR spectra of an about 60% syndiotactic PVC chlorinated at 59 and 65%.

It is evident that the content of unchlorinated syndiotactic triads and even tetrads is higher than that of heterotactic triads which have almost disappeared.

Figure 7 shows the same spectra for an atactic sample chlorinated to the same extent (59 and 65%). We observe here the same effect, which is the more significant as the initial content of syndiotactic sequences is lower than in the previous sample.

The infrared spectral data led us to the same conclusions.

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