Polymer Bulletin 13, 151-154 (1985)

Polymer Bulletin

Quantitative Determination of Non-Defect Unstable Structures in PVC Through Selective Nucleophilic Substitution with C_6H_5SNa

G. Martínez, C. Mijangos, and J. Millán

C.S.I.C., Instituto de Plásticos y Caucho, Juan de la Cierva 3, E-28006 Madrid, Spain

SUMMARY

The nucleophilic substitution with C_6H_5SNa, at -30°C, is compared for five PVC samples with various contents of isotactic triads. The conversion curves consist of a very fast stage followed by a steady one. All the samples are found to behave in the same way except for the content of the structures involved in the fast period. This content is estimated by extrapolating the straight lines of the steady stages to zero time. The obtained values are found to be a linear function of the content of isotactic triads. The results, together with some earlier ones, allow for the content of the labile non-defect structures in PVC to be determined.

INTRODUCTION

It is now widely accepted that the thermal instability of PVC is due to the presence of some labile structures which may be either defect structures arising from a number of events in the polymerization process (1) or non-defect isotactic conformations which were proposed to be the GTTG* triad (2-3). The extremely low content of the former defects makes it very difficult to measure them accurately. Nevertheless, some important approaches have been already done (4).

On the other hand, it has been recently shown that the latter labile isotactic triads are the only ones to react with C_6H_5SNa in cyclohexanone during the very fast initial stage which occurs in the nucleophilic substitution on PVC provided that the reaction temperature is sufficiently low (< 5°C) (3). Thus, this specific substitution reaction should be, in principle, an appropriate method to determine the content of such non-defect isotactic structures which cause instability in PVC. In this connection, we thought it interesting to compare the above substitution reaction at -30°C, for five PVC samples with different content of isotactic triads in order to investigate whether the reaction is sensitive enough for analytical purposes. If so, the work would provide with a useful approach to the important problem of predicting quantitatively the thermal instability of PVC in relation to the polymerization conditions. Actually, most of the difficulties in studying the mechanisms of degradation of PVC have arisen from the lack of accurate measurements of the various types of labile structures in the polymer.

EXPERIMENTAL

Preparation of Polymers

Samples 1 and 3 were prepared by bulk polymerization at 90 and 60°C respectively, using 2-2′-azodiisobutyronitrile as initiator. Samples 4 and 5 were prepared by the same method but using UV radiation to initiate polymerization at 30 and 0°C respectively. The full details have already been published (5). Sample 2 is a commercial polymer without any additive, obtained by bulk polymerization.

Characterization of Polymers

The osmometric measurements were carried out at 34°C with solution in cyclohexanone using a Knauer membrane osmometer. Data are shown in Table I.

The tacticities were measured by means of the ^{13}C-NMR spectra obtained at 75.5 MHz and 80°C using a XL-300 Varian spectrometer. The polymers were examined as a 10% solution in a 1:4 mixture of deuterated dimethylsulphoxide and O-dichlorobenzene. 10 mm sample tubes were used. The calculations were carried out by measuring the areas with a compensating polar planimeter as well as by means of the built-in electronic integrator (Table I).

Substitution Reactions

Substitution reactions with sodium thiophenate at -30°C in purified cyclohexanone were performed according to the experimental conditions described previously (2-3). However, it should be emphasized that all the reactions were carried out simultaneously and using the same freshly prepared thiophenate so that the occasional risks either of hydrolysis or of oxydation should be avoided.

The degree of substitution was determined by measuring the absorbance at 256 nm in the UV-Visible spectrum. A calibration curve was previously obtained from the absorbance at 256 nm for samples modified to well defined extents as measured by microanalysis of the content of Cl and S. Some of these values were checked by ^{1}H-NMR spectroscopy, which accounts for the accuracy of the calibration curve.

Table I
Characterization of Polymers

Sample	$\overline{M_n}.10^{-3}$	P(II)	P(SI&IS)	P(SS)
1	21.5	0.214	0.505	0.281
2	44.0	0.208	0.495	0.297
3	38.9	0.193	0.508	0.299
4	46.0	0.168	0.502	0.330
5	85.0	0.154	0.468	0.378

RESULTS

The kinetic curves for the five polymers are shown in Figure 1. They demonstrate that the very fast stage of the reaction, preceding the slow and steady one, strongly depends on the type of polymer.

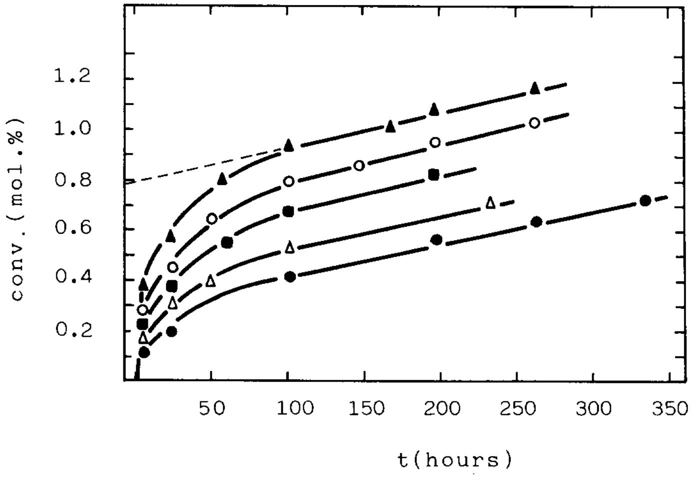

Fig.1 Nucleophilic substitution on PVC with sodium thiophenate at -30°C for:(▲) Sample 1;(○) Sample 2;(■) Sample 3;(△) Sample 4;(●) Sample 5.

Since the straight lines of the steady stage are quite similar in slope for all the polymers, the amount of highly reactive chlorine atoms can be determined accurately by extrapolating the straight lines to zero time (Figure 1). The values so obtained are found to increase linearly with increasing content of isotactic triads, as illustrated by Figure 2.

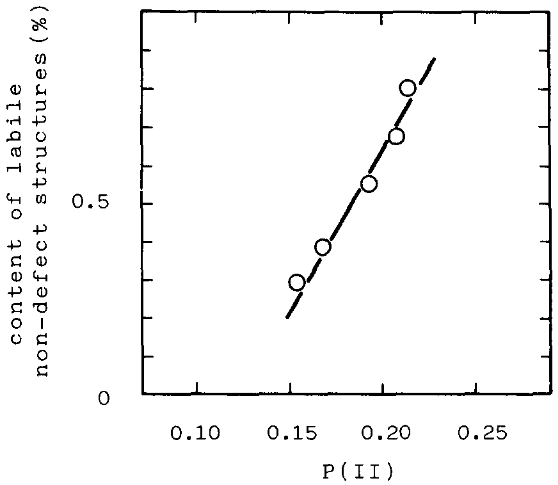

Fig.2. Content of labile non-defect structures vs. probability of isotactic placement from ^{13}C-NMR.

In the light of the above quoted earlier results on the lability of the very reactive isotactic fractions (2-3), the substitution reaction, as proposed in this work, provides with an appropriate method to evaluate the content of labile non-defect structures in PVC, which has been recently shown to be much higher than that of defect structures (6).

ACKNOWLEDGMENTS

The authors are grateful to the COMISION ASESORA DE INVESTIGACION CIENTIFICA Y TECNICA (CAICYT) for its financial support.

REFERENCES

1. W.H.Starnes,Jr., Dev.Polym.Degradation,3, 135 (1981) and references cited therein.
2. G.Martínez, C.Mijangos and J.Millán, J.Macromol.Sci.Chem., A17, 1129 (1982).
3. J.Millán, G.Martínez and C.Mijangos, accepted for publication in J.Polym.Sci.
4. T.Hertberg and E.M.Sörvik, J.Macromol.Sci.Chem.,A17, 983 (1982).
5. J.Millán, G.Martínez and C.Mijangos, J.Polym.Sci.Polym. Chem.Ed.,18, 505 (1980).
6. G.Martínez, C.Mijangos and J.Millán, accepted for publication in Eur.Polym.J.

Accepted January 23, 1985