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The Chain Transfer to Polymer in Vinyl Chloride Bulk Polymerization

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SUMMARY

Self grafting of PVC has been studied by introducing a 36-chlorine labelled low molecular PVC fraction in the polymerization mixture of vinyl chloride. The fractionation of the polymer obtained follows the same pattern as a synthetic mixture of the polymer with the same fraction. It is concluded that, under those working conditions, chain transfer to the polymer with grafting has not taken place, at least in a considerable extent.

Although the majority of branchings in PVC are of $>CH-CH_2Cl$ type there is a small number of longer branches, which may bear chlorine atoms at tertiary carbons (CARACULACU, 1981b; BURUIANA et al. 1980). But there are few data regarding the way they are formed.

There are also evidences indicating that a chain transfer to polymer during vinyl chloride polymerization may produce isolated double bonds on the polymer chain (CARACULACU et al. 1981a).

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In this paper we have tried to find whether a certain amount of the radicals resulted from a radicalic attack on PVC chain are able to continue the polymerization process with formation of long branches.

The occurence of a single graft of this type on the macromolecule could lead to a considerable increase of the molecular weight.

With this purpose in mind a low molecular PVC fraction was prepared, isotopically labelled with 36-chlorine and introduced in a polymerization mixture of vinyl chloride and initiator. The polymer obtained was fractionated and there was followed the shift of the radioactive fraction towards higher molecular weights as a result of a self-grafting process.

EXPERIMENTAL PART

As a preliminary, blanks were run on unlabelled PVC samples.

The preparation of low molecular PVC fraction-was performed by extracting PVC with benzene (100 g PVC:1000 ml benzene) (MICHEL and BURILLE, 1978), under stirring for 24 hrs., at room temperature. The insoluble polymer was removed by filtration. The benzene soluble fraction was recovered by distilation of the solvent at reduced pressure and purified by precipitation from tetrahydrofuran (THF)-methanol (MeOH) system.

Labeling of PVC fraction-$Al^{36}Cl_3$ was introduced in a solution of PVC fraction in 1,1,2,2-tetrachloroethane (the solvent was dried on $CaCl_2$ and distiled at low pressure). The mixture was stirred 18 hrs. at room temperature. The polymer was precipitated from solution with MeOH (solvent-unsolvent ratio was 1:10), filtrated and washed with water.

Some reprecipitation runs were carried out: two from THF/MeOH system, one from THF/petroleum ether (PE) system (followed by distilation of THF and PE) and finally again from THF/MeOH system.

In order to obtain a very fine powder of polymer the last precipitation was performed by pouring MeOH in THF containing 1% PVC fraction.

In the table I there is presented radioactivity of filtrated and dried PVC fractions.

The labelled fraction (F^*) was divided in two parts: one part was introduced in the vinyl chloride polymerization system and the other one was mixed with a control polymer.

TABLE I

The characteristics of soluble fraction

Polymer	Introduced quantity, g	Specific activity, imp/g min	Total activity, imp/min
F_T^*	1.4	183,487	256,881
F_A^*	1.3	183,487	238,533

F_T^* = fraction introduced in polymerization medium

F_A^* = fraction mixed with a control polymer

<u>Polymerization of vinyl chloride in the presence of labelled fraction</u> Vinyl chloride was bulk polymerised under argon, with azobisizobutironitrile (AIBN) as initiator.

0.6 g AIBN, 60 ml liquid vinyl chloride and 1.4 g fine powder of F^* were introduced in a glass vial under argon. The polymerization was carried out for 4 hrs., at 50°C, under strong shaking, in order to ensure an as fine possible PVC fraction dispersion in monomer. After interrupting the polymerization and removing the monomer excess the polymer was purified by precipitation with MeOH from a 4% solution in THF (1 volume of THF:4 volume of MeOH), then it was washed and dried.

Preparation of a synthetic mixture of PVC and F^* Vinyl chloride was polymerised as described above, except for the labelled fraction being introduced in system. The obtained polymer was solved in THF, and mixed with a solution of F^* in THF in such a way that the same ratio polymer: F^* as in the case of polymerization carried out in the presence of F^*, should result. The PVC-F^*, mixture was precipitated from this homogeneous solution with MeOH (THF:MeOH=1:4).

Fractionation of PVC obtained in presence of F^*(P_T) and of synthetic mixture PVC-F^* (P_A) To recover F^*, P_T and P_A were successively extracted with benzene, under the same conditions as for obtaining F^*, and then precipitated from the THF:benzene system. After evaporating the solvent, the fractions were dried under vacuum.

The measurements of radioactivity were performed using a particles counter with circulation of gases, VAM 160.

RESULTS AND DISCUSSIONS

As can be seen from table II, it was not possible to recover the whole radioactivity after extraction with benzene both for P_T and for P_A. This was attributed to an incomplete extraction of F^*.

That is why the integral recovering of radioactivity was tried by precipitation of polymers with benzene from THF. The polymer insoluble in benzene remain radioactive even after this treatment (table II).

TABLE II

The radioactivity of fractions obtained from P_T and P_A

Polymer	Fraction	Quantity		Total activity,		Specific activity,
		g	%	imp/min	%	imp/g min
P_T	F_{TSB}	3.63	19.8	110,765	41.9	30,513
	F_{TIB}	14.70	80.2	153,486	58.1	10,441
P_A	F_{ASB}	1.94	12.0	97,875	45.3	50,451
	F_{AIB}	16.10	88.0	117,984	54.7	7,328

F_{TSB} = fraction obtained from P_T, soluble in benzene

F_{TIB} = fraction obtained from P_T, insoluble in benzene

F_{ASB} = fraction obtained from P_A, soluble in benzene

F_{AIB} = fraction obtained from P_A, insoluble in benzene.

From the results presented in tables I and II, it comes out that there are not perceptible diferences of distribution of radioactivity between the fractions obtained from P_T and those obtained from P_A. This has indicated that chain transfer to polymer during vinyl chloride polymerization doesn't lead to self-grafting with appearance of long branchings in a perceptible degree.

It is probable that structure with tertiary chlorine previously determinated are bound at branchings formed another way, for example by an cyclic intramolecular transfer (ROEDEL, 1955)

However it should be useful to verify if a chain transfer with self-grafting could take place in the first steps of polyvinylchloride formation, when the particles are very small, presenting very large area and a small grade of coacervation. It is necessary to consider this problem because the value of chain transfer constant to polymer for model compounds with small molecule (LIM and KOLINSKY, 1961) has aproximately the same order of magnitude as the content of long branches with tertiary chlorine.

The polymerization conditions used in this paper have meant to ensure as favourable as possible an access to PVC molecule; the used fraction swells considerably with monomer, but we don t know if can exactly reproduce the conditions of PVC molecules formed during the polymerization process.

Another interesting observation was that even in the case of synthetic mixture a marked skattering of radioactivity in all fractions was produced, although the same conditions were used as for the obtaining of initial fraction.

This fact could represent a direct evidence for the existence of some associations between large and small molecules, the last ones being strongly bound satellites of the first species. The fractionation method on the basis of solubility diference can not separate these satellites. The shift of radioactivity towards higher molecular weight fractions in the case of P_A (synthetic mixture) would take place as a result of an exchange between small satellites of long PVC molecules. If this fact will be confirmed, there could be possible a quantitative estimation of association degree of PVC molecules in solution and during the fractionation process by using radioactive isotopes.

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