POLYMERIZATION OF VINYL CHLORIDE BY ORGANOMETALLIC COMPOUNDS. EFFECT OF MOISTURE IN THE MONOMER

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

The effect of moisture in vinyl chloride (VC) on its polymerization initiated with *tert*-butyllithium was investigated. The conversion curves thus obtained and the dependences of molecular weights of isolated products show that within the range 6.5 – 80 ppm vol. water in vinyl chloride and the mole ratio *t*-BuLi/VC 0.0004 – 0.03 the conversion of vinyl chloride decreases, while the molecular weight of PVC increases. The distribution curves of molecular weights become broader with increasing water content in the monomer, and their maxima are shifted to higher molecular weights. The water content up to 40 ppm vol. in vinyl chloride does not affect the heat stability of PVC. At higher water contents the stability decreases.

In connection with the development of new special types of poly(vinyl chloride) (PVC), the polymerization of vinyl chloride initiated with organolithium compounds can be regarded as a possibility of preparing high-molecular-weight PVC (refs[1,2]). The polymers thus obtained differ markedly in their properties from all types of PVC known so far; along with high molecular weights (M_w up to 500 000), their characteristic features are, in particular, linearity of polymer chains and a low content of structural defects, such as branching, terminal and inner double bonds (allylic structures)[3,4]. Compared with the usual PVC types, these polymers have heat stability higher by as much as 30 °C, and their thermal degradation proceeds with an important induction period of dehydrochlorination. This study deals with the effect of moisture in the monomer on the conversion of polymerization and on the molecular weight of the polymer thus obtained. Also, the results allow us to estimate to what degree the monomer should be dried in technological process in order to make the results of polymerization economically advantageous.

EXPERIMENTAL

Materials

Commercial vinyl chloride (Spolana Neratovice, The Czech Republic) was freshly rectified before use and dried with a molecular sieve Potasit A3 (Lachema Brno, The Czech Republic). The initiator, *tert*-butyllithium, was prepared by a reaction between the lithium suspension and *tert*-butyl chloride[5]. Heptane used as the solvent of *t*-BuLi was rectified after removal of unsaturated hydrocarbons[6] and dried by refluxing in the presence of the Na–K alloy in an Ar atmosphere.

Methods

The moisture content in vinyl chloride (VC) was measured by means of a Dewpoint Meter apparatus (Shaw, Bradford, U.K.). The commercial apparatus was modified for our purposes by providing the inlet, outlet, and branch connections of the drying gas with closing valves. A rubber closure was attached to the apparatus for dosage of the measured gas.

Polymerization

The polymerizations took place in glass ampoules graduated up to 40 ml, provided with pressure closures, annealed and filled with Ar prior to use. The water concentration in the monomer was varied by dosing various quantities of dried and moist VC into ampoules with pressure glass burettes. Approximatively 15 ml of condensed VC was used in the moisture content measurements; the remaining 25 ml of the monomer was the amount used in the polymerization itself. The initiator was dissolved in such a small amount of heptane that its volume was negligible compared with the total volume of the reaction mixture. The solution of the catalyst was dosed with a stainless steel capillary using a pressure doser; its reservoir was filled with the solution in advance by means of Ar overpressure. The polymerization took place at 0 °C, at the initiator concentrations 0.0004 – 0.03 mol *t*-BuLi/mol VC, and at water concentrations in the monomer 6.5 – 80 ppm vol. ($2.5 \cdot 10^{-5} - 3.0 \cdot 10^{-4}$ mol H_2O/mol VC); the polymerization times varied between 1 and 24 h, depending on the initiator concentrations used. In order to evaluate the water concentrations in the monomer which stop polymerizations initiated with 0.017 mol *t*-BuLi/mol VC, polymerizations were carried out using vinyl chloride containing 500 – 1 000 ppm vol. of water (0.0019 – 0.008 mol H_2O/mol VC). In these polymerizations, the monomer containing the required amount of water was obtained by dosing water with a microburette into ampoules before the condensation of VC. The polymers thus obtained were washed with methanol and dried at 40 °C to constant weight.

The molecular weight parameters of the samples, M_w, M_n, and the polydispersity index M_w/M_n, were determined by gel permeation chromatography[7 - 10].

PVC Dehydrochlorination

Dehydrochlorination tests were carried out at 200 °C at the air flow 180 ml/min, and the amount of split-off hydrogen chloride was determined by continuous potentiometry[11]. PVC samples prepared from vinyl chloride with various moisture contents were compared on the basis of the average rates of dehydrochlorination calculated from the amount of split-off HCl in time intervals 0 – 20, 20 – 40 and 40 – 60 min. The heat stability was evaluated by the degree of discolouration of 0.5 g tablets, having 20 mm in diameter, which were heated in the air to 200 °C for 60 min.

RESULTS AND DISCUSSION

A series of polymerizations of vinyl chloride containing 6.5 – 80 ppm vol. of water ($2.5 \cdot 10^{-5} - 3.0 \cdot 10^{-4}$ mol H_2O/mol VC) showed that the conversion of vinyl chloride decreases with increasing water content in the monomer, while on the other hand, the molecular weights, M_w and M_n, of the corresponding isolated polymers increase. Since the dependences of the polymerization conversions and PVC molecular parameters on the moisture content are similar, they will be discussed for a typical series of polymerizations initiated with 0.0017 mol *t*-BuLi/mol VC (polymerization time 4 h).

The decrease in conversion and the increase in molecular weight, depending on the moisture content in the monomer, observed in these polymerizations are shown in Figs 1 and 2. The GPC measurements also showed that isolated PVC samples have a broad molecular weight distribution. With increasing moisture content of the monomer the distribution curves become broader, and their maxima are shifted to higher molecular weights. This finding suggests that the increasing water content in vinyl chloride results in an increased fraction of macromolecules having a higher molecular weight, which in turn makes M_w increase faster than M_n (Fig. 2*a*). The polydispersity index $I = M_w/M_n$ varies in the range 3.7 – 4.0 and its lower values correspond to polymers obtained by the polymerization of vinyl chloride with a lower water content (Fig. 2*b*).

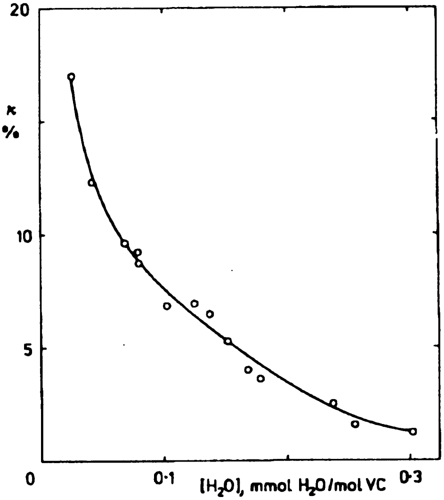

FIG. 1

Effect of moisture in vinyl chloride on its conversion in the polymerization initiated with 0.0017 mol *t*-BuLi/mol VC (polymerization time 4 h)

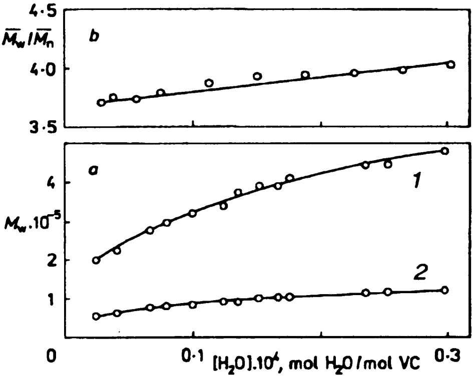

FIG. 2

Effect of moisture in vinyl chloride on the molecular weight (*a*) and polydispersity index (*b*) of PVC in the polymerization initiated with 0.0017 mol *t*-BuLi/mol VC (polymerization time 4 h). *1* M_w, *2* M_n

The experimental results obtained in the whole polymerization series always show the same effects of moisture present in vinyl chloride, i.e. the decrease in conversion and the increase in molecular weight of PVC obtained. This phenomenon might be explained in a simple way by assuming that in the polymerization of moist vinyl chloride the initiator is decomposed with water present in the reaction medium and only the remaining *t*-BuLi initiates the polymerization. The higher the water content in the monomer, the lower the real effective concentration of the initiator. These experimental findings are very useful from the technological point of view because they allow to make an approximate estimation of the water concentration in the monomer at which the polymerization of vinyl chloride virtually does not occur at all. The values of such limiting moisture concentrations depend, of course, on the amount of the initiator used and, e.g., at the initiator concentrations 0.001 mol *t*-BuLi/mol VC, the polymerizations stop at a water content in vinyl chloride below 100 ppm vol., i.e. 0.00038 mol H_2O/mol VC. As we tested, a tenfold rise in the concentration of the initiator changes the limiting water concentration in vinyl chloride approximately also ten times.

On the other hand, this simple concept of moisture effect fails when trying to explain the increase in molecular weight observed. The experimental data of polymerization initiated with 0.0017 mol *t*-BuLi/mol VC (Fig. 2) demonstrate that the effect of moisture is much higher than corresponds to mere decomposition of initiator. Thus, assuming a simple anionic polymerization mechanism of vinyl monomers with organometals one could expect that the M_n of PVC, prepared in the presence of 0.0003 mol H_2O/mol VC, should reach the value about 45 000. However, the observed M_n is about 110 000 (Fig. 2*a*). It is therefore obvious that the polymerization does not proceed according to the assumed anionic mechanism. On the basis of the results obtained earlier[1] one can suggest that the polymerizations proceed by a more complex mechanism, probably involving the co-ordination of reaction intermediates and resembling Ziegler polyinsertion, where the activity of polymer growing centres is affected by products of decomposition of the initiator with water. A detailed mechanistic description is currently investigated.

The heat stability of the PVC samples was assessed in dehydrochlorination tests and by evaluating the degree of discolouration in the thermal treatment. The results of dehydrochlorination measurements shown in Fig. 3 indicate that the average rates of dehydrochlorination obtained within 0 – 20 min are virtually unaffected by a change in the moisture of vinyl chloride. With increasing time of degradation, however, the polymers prepared from the monomer with a higher moisture content are dehydrochlorinated more slowly (cf. the average rates of dehydrochlorination during 20 – 40 min and, in particular, during 40 – 60 min, Fig. 3). The evaluation of colour stability gave opposite results. The tablets made from polymers obtained by the polymerizations of vinyl chloride with the water content up to 40 ppm vol. (0.00015 mol H_2O/mol VC) show much lighter discolouration after heating to 200 °C than the tablets of PVC prepared from vinyl chloride with a higher concentration of water. The slightly higher dehydrochlorination resistance of PVC samples prepared from the monomer with a higher water content can be explained by the increasing content of LiOH arising by the decomposition of *t*-BuLi with water, from polymer propagation centres, or, sometimes, from metallated intermediates[1]. LiOH reacts with split-off HCl, which is reflected in the apparently lower rate of dehydrochlorination. The real heat stability is given by colour stability, which again is negatively affected by the increasing content of LiOH or LiCl (ref.[1]). A similar behaviour was observed in the investigation of the effect of concentration of LiCl, added to PVC in amounts comparable with those formed from initiator, on the heat stability of PVC.

The results reported above demonstrate a strong negative effect of moisture in the monomer on the conversion of vinyl chloride polymerization initiated with *t*-BuLi. Unlike conversion, the heat stability of PVC prepared from vinyl chloride with a water content up to 40 ppm vol. (0.00015 mol H_2O/mol VC) is only little poorer. With respect to the fact that the industrially used monomer usually contains about 30 ppm vol. of water (0.00011 mol H_2O/mol VC), higher catalyst concentrations must be used in order to reach high conversions. From the technological point of view, using the monomer of a given quality the polymerization process should each time be given economic consideration; only then can it be decided whether the high conversions of polymerization should be reached by additional drying the monomer and/or by dosing a major amount of the initiator.

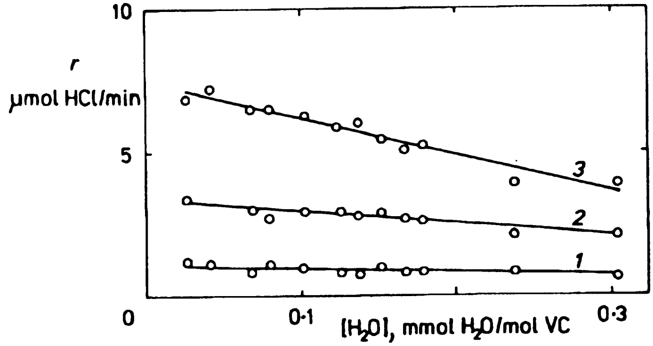

FIG. 3

Effect of moisture in vinyl chloride on the average rates of dehydrochlorination of PVC prepared in the polymerization initiated with 0.0017 mol *t*-BuLi/mol VC (polymerization time 4 h). In time interval: *1* 0 – 20 min, *2* 20 – 40 min, *3* 40 – 60 min

REFERENCES

1. Jíšová V., Kolínský M., Lím D.: J. Polym. Sci., A-1 *8*, 1525 (1970); Czech. 156 723 (1970); U.S. 3 875 131 (1975); Ger. 2 127 412 (1971).
2. Jíšová V., Kolínský M., Lím D.: J. Polym. Sci., Polym. Symp. *42*, 467 (1973).
3. Kolínský M., Jíšová V., Lím D.: J. Polym. Sci., Polym. Symp. *42*, 657 (1973).
4. Wesslén B., Wirsen A.: J. Polym. Sci., Polym. Chem. Ed. *13*, 2571 (1975).
5. Lochmann L., Pospíšil J., Vodňanský J., Trekoval J., Lím D.: Collect. Czech. Chem. Commun. *30*, 2187 (1965).
6. Kincannon C. B., Manning E.: Ind. Eng. Chem. *47*, 149 (1955).
7. Kolínský M., Ryska M., Bohdanecký M., Kratochvíl P., Šolc K., Lím D.: J. Polym. Sci., C *16*, 495 (1967).
8. Grubisic Z., Rempp P., Benoit H.: J. Polym. Sci., B *5*, 753 (1967).
9. Kolínský M., Janča J.: J. Polym. Sci., Polym. Chem. Ed. *12*, 1181 (1974).
10. Jíšová V., Janča J., Kolínský M.: J. Polym. Sci., Polym. Chem. Ed. *15*, 533 (1977).
11. Světlý J., Lukáš R., Michalcová J., Kolínský M.: Makromol. Chem. *185*, 2183 (1984).

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