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The Polymerization of Isobutylene with VCl_4 and Ammonia

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Summary

The initiation effect of ammonia on the polymerization of isobutylene in the presence of VCl_4 has been revealed. The polymerizations were carried out in the dark without solvent and in heptane solution in the temperature range between 263 and 198 K, where the molecular weight of the polymer increased linearly with decreasing temperature (log $\overline{M}_\eta$ against 1/T). The polymer yield depended on the molar ratio of ammonia to VCl_4 and was highest at 1:1, but the polymerizations proceeded also at a molar ratio higher than 1. At NH_3/VCl_4 = 1 the polymerization rate increased with VCl_4 concentration and with decreasing temperature.

Introduction

Isobutylene ranks among typical monomers of the cationic polymerization initiated only with compounds of acid character. Of these, the Lewis acids such as $AlCl_3$ and BF_3 are the most active. In the sixties Japanese authors (YAMADA et al. 1966, YAMADA et al. 1967) proved that the polymerization of isobutylene with $VOCl_3$ or VCl_4 may be initiated by the addition of compounds of basic character, such as e.g. aromatic amines.

We were surprised to find out in our laboratory that we could demonstrate the initiation effect of the system VCl_4-ammonia on the polymerization of isobutylene. Until then, ammonia had been regarded as a catalytic poison of the cationic polymerization.

This paper is a study of the effect of ammonia on the polymerization of isobutylene in the presence of VCl_4.

EXPERIMENTAL

The drying and purification of heptane, argon, isobutylene and the storage and preparation of VCl_4 solutions in heptane have been described earlier TOMAN, MAREK 1976). Ammonia was redistilled from sodium into a pressure ampoule and taken in the gaseous state. It was dosed into the reaction medium with a syringe so

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that the metallic capillary used for feeding-in ammonia was immersed under the surface of the stirred reaction mixture. In all experiments the initiation components were dosed into the stirred monomer or its solution in the order VCl_4, ammonia. The polymerization proceeds, however, even if the order is reversed. The polymerizations were carried out in the dark in a stirred reactor described earlier (TOMAN, MAREK 1981). The polymerization rate was investigated in a stirred dilatometer (30 ml in volume), provided with a serum-type seal. The polymerizations were terminated by adding 2 ml of ethanol and the polymer was dried at reduced pressure (0.5 Pa at 313 K). The molecular masses of polyisobutylene thus prepared were determined viscometrically in heptane solution at 293 K (TOMAN, MAREK 1976). Elemental analysis of polyisobutylene samples was carried out with a Perkin-Elmer 240 apparatus.

RESULTS AND DISCUSSION

Isobutylene does not polymerize in heptane solution in the presence of VCl_4 in the dark within the temperature range under investigation (263-198 K) (MAREK, TOMAN 1972, TOMAN, MAREK 1976), but after the addition of ammonia the polymerization proceeds in the range 223-263 K immediately, without any induction period. At lower temperatures ($T \leq 213$ K) the polymerizations proceed after the addition of ammonia with a short induction period of approx. 0.5 - 1 min. The polymer yield depends on the molar ratio of the initiation components $VCl_4 : NH_3$ and is highest if the ratio is unity, as documented by Table 1. The molecular mass of polyisobutylene thus obtained (PIB) is not affected by the ratio of the components and varies within the limits of experiments with the maximal deviation ± 10%. On the other hand, the molecular mass of PIB increases with the monomer concentration. At 198 K in the absence of auxiliary solvent at the molar ratio $NH_3 : VCl_4 = 2$ ($[NH_3] = 2.56 \times 10^{-3}$ mol/l, $[VCl_4] = 1.28 \times 10^{-3}$ mol/l), yield = 22%, polymerization time 14 min, PIB was obtained with an approx. twofold molecular mass ($\bar{M}_\eta = 2.015 \times 10^6$) compared to PIB prepared in heptane solution with the monomer concentration $[M] = 4.65$ mol/l (Table 1). The molecular mass of PIB is also temperature-dependent and increases linearly with decreasing temperature according to the log $\bar{M}_\eta$ against 1/T dependence as shown in Fig.1. The approximate overall activation energy of the degree of polymerization E_{DP} is comparatively low $\sim$ - 11.2 kJ mol^{-1} and is approximately half that of E_{DP} measured by us earlier (TOMAN, MAREK 1981) for the photoinduced polymerization of isobutylene with VCl_4 in heptane solution ($E_{DP} = \sim -20.2$ kJ mol^{-1}). Both these log $\bar{M}_\eta$ vs. 1/T dependences are compared in Fig.1.

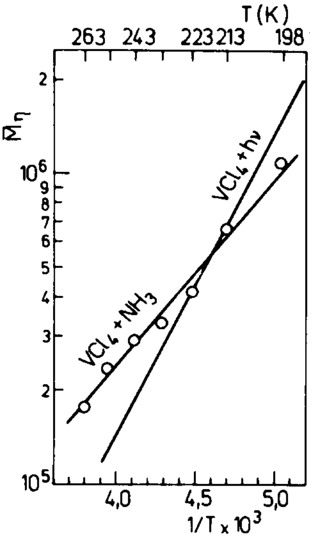

Fig. 1. Polymerization of isobutylene in heptane at constant $VCl_4:NH_3$ = 1:1; [M] = 4.65 mol/l, $[VCl_4]$ = $[NH_3]$ = 3.36 x 10^{-3} mol/l; dependence of log $\overline{M}_\eta$ on 1/T is compared with photoinitiated polymerization of isobutylene in heptane, ([M] = 4.94 mol/l, $[VCl_4]$ = 1.1 x 10^{-3} mol/l) determined earlier (Toman, Marek 1981)

With proceeding conversion, the molecular mass of PIB remains virtually unchanged up to 60% conversion ([M] = 1.26 mol/l); at 100% conversion it decreases to approx. half the value of the molecular mass of PIB prepared up to a conversion below 60% as shown in Fig.2.

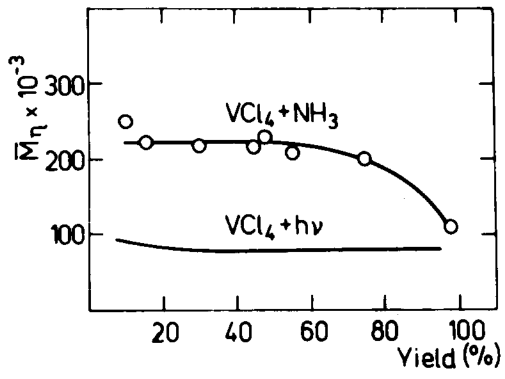

Fig.2. Polymerization of isobutylene in heptane at constant $VCl_4:NH_3$ = 1:1; effect of $\overline{M}_\eta$ PIB on conversion; [M] = 1.26 mol/l., $[VCl_4]$ = $[NH_3]$ = 3.09 x 10^{-3} mol/l, T = 253 K. The dependence is compared with the one determined earlier (TOMAN, MAREK 1976) for photoinitiated polymerization of isobutylene with VCl_4.
([M] = 1.23 mol/l, $[VCl_4]$ = 3.9 x 10^{-3} mol/l, λ = 436 nm)

The same Figure shows the dependence of $\overline{M}_\eta$ of polyisobutylene on conversion obtained earlier in the photoinitiated polymerization in presence of VCl_4 at 253 K

(TOMAN, MAREK 1976).

The polymerization rate increases with increasing VCl_4 concentration if $VCl_4 : NH_3 = 1$ is kept constant. The dependence of conversion curves on the initiator concentration is shown in Fig.3. The initial polymerization rates R_o calculated from the conversion curves are given in Table 2.

Table 1. Effect of ammonia - VCl_4 ratio on yield and molecular mass of PIB

$[NH_3] \times 10^{-3}$ (mol/l)	$\frac{[NH_3]}{[VCl_4]}$	Polymerization time (min)	Yield %	$\bar{M}_\eta \times 10^{-3}$
33.60	10	60	0.2	990.01
15.60	4.6	60	37.0	1035.04
10.80	3.2	25	31.0	943.74
3.36	1.0	10	32.0	1134.45
1.68	0.5	30	33.0	930.80

$[VCl_4] = 3.36 \times 10^{-3}$ mol/l, $[M] = 4.65$ mol/l, T = 198 K.

Table 2. R_o as a function of VCl_4 concentration at constant $NH_3 : VCl_4 = 1$

$[VCl_4] = [NH_3]$ (mol/l)	R_o (mol/l.s)
2.06×10^{-3}	2.6×10^{-4}
3.09×10^{-3}	6.3×10^{-4}
4.12×10^{-3}	35.7×10^{-4}

Polymerization of isobutylene in heptane: $[M] = 1.26$ mol/l
T = 253 K

The polymerization rate increases also with decreasing temperature. At 238 K, R_o was approximately twice as high ($R_o = 12.1 \times 10^{-4}$ mol/l.s ($[VCl_4] = [NH_3] = 3.09 \times 10^{-3}$ mol/l, $[M] = 1.26$ mol/l as R_o at 253 K (Table 2).

The calculated reaction order (n) related to the concentration of $[VCl_4]$ or $[NH_3]$ (R_o values from Table 2 were used in the calculation) is n =~4, while n =~3 if related to the monomer concentration (n was calculated by the differentiation method from the conversion curve B given Fig.3). The complicated character of the reaction orders does not make possible a simple interpretation of the mechanism of initiation. Obviously, consecutive reactions between VCl_4 and ammonia proceed in the reaction system in the course of polymerization and affect the polymerization rate. The low E_{DP} value may indicate that the monomer transfer is less temperature-depent than in other initiation systems, and therefore also at relatively high temperatures (from 263 to 243 K) PIB obtained by polymerization still exhibit very high molecular masses.

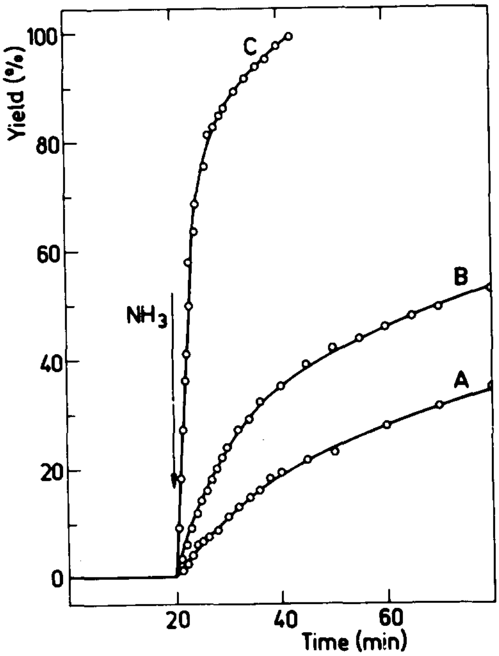

Fig. 3. Polymerization of isobutylene in heptane depending on concentration of components at constant $VCl_4 \cdot NH_3$ = 1:1.
[M] = 1.26 mol/l, T = 253 K, conversion curve A : $[VCl_4] = [NH_3] = 2.06 \times 10^{-3}$ mol/l; conversion curve B: $[VCl_4] = [NH_3] = 3.09 \times 10^{-3}$ mol/l; conversion curve C: $[VCl_4] = [NH_3] = 4.12 \times 10^{-3}$ mol/l

The authors (Fowles, Nicholis, 1958) have reported that in pentane solution at 237-228 K the reaction between VCl_4 and NH_3 gives rise to an insoluble compound of amidochloride V^{IV}, $(VCl(NH_2)_3)$ and a soluble one of ionic character $[NH_4][VCl_2(NH_2)_3]$ which according to the authors is more stable for vanadium with the coordination number 5 in the form of a dimer $[NH_4]_2[V_2Cl_4(NH_2)_6]$. Using tensimetric measurements, the authors try to describe the reaction between ammonia and VCl_4 by a summary equation which gives two NH_4Cl molecules per one VCl_4 molecule, in agreement with their study:

$$VCl_4 + 6\,NH_3 = VCl(NH_2)_3 + 3\,NH_4Cl = [NH_4][VCl_2(NH_2)_3] + 2\,NH_4Cl$$

In our reaction system, however, isobutylene in the presence of VCl_4 forms a CT complex isobutylene-VCl_4, the existence of which has been demonstrated earlier (TOMAN, MAREK, JOKL, 1974). This finding must not be omitted in suggesting the initiation system also in the presence of NH_3. Since the polymerization of isobutylene by VCl_4 initiated with ammonia is inhibited with oxygen, we are inclined to adopt the view that the initiation probably proceeds by the radical-cationic mechanism suggested for polymerizations carried out in the presence of aromatic amines (YAMADA et al. 1966).

With respect to the similarity between $VOCl_3$ and

VCl_4 in their ability to initiate isobutylene in the presence of aromatic amines and condensed polycyclic hydrocarbony, such as naphthalene, anthracene and fluorene (YAMADA 1967), we also examined the effect of ammonia on the polymerization of isobutylene in the presence of $VOCl_3$, without, however, any evidence as to the initiation effect. The reaction was studied without solvent at 203 K at various concentrations of $VOCl_3$ and NH_3. At the concentration $[VOCl_3] = 4.7 \times 10^{-2}$ mol/l and $[NH_3] = 6.4 \times 10^{-2}$ mol/l the polymerization did not occur for two hours, but after a small amount of VCl_4 (3.1×10^{-3} mol/l) had been added to this completely nonreactive mixture, explosive polymerization took place immediately.

Also with $TiCl_4$, the initiation effect of ammonia on the polymerization of isobutylene was not demonstrated. Only a yellow insoluble compound of amidochloride Ti^{IV}, ($TiCl(NH_2)_3$), was formed as reported in the literature (FOWLES, POLLARD, 1953). No polymerization was observed with WCl_6. In the presence of $SnCl_4$, PIB was detected in the reaction mixture after two hours, but the conversion was only 3.5 % ($[M] = 4.65$ mol/l, $[SnCl_4] = [NH_3] = 1.6 \times 10^{-2}$ mol/l, T = 233 K, polymerization investigated in heptane). Bannister and Fowles (1958) report that in the reaction between $SnCl_4$ and NH_3, $SnCl(NH_2)_3$ is formed at 210 K (a white and insoluble compound). At higher temperatures, in the range 228-237, i.e. in the range of our polymerization experiment, a soluble compound of ionic character is also formed, $[NH_4]_2[SnCl_3(NH_2)_3]$.

In PIB prepared with the initiation system VCl_4-ammonia, no nitrogen has been detected by elemental analysis. The investigation of the polymerization of isobutylene using the system VCl_4- ammonia showed that the polymerizations proceed at high rate also at a VCl_4 concentration twenty times lower than with aromatic amines, giving rise to PIB of high molecular masses.

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