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Effect of the Alkyl Chlorsilanes on the N-Vinyl Pyrrolidone Polymerization

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SUMMARY

It is shown that the alkyl chlorsilanes both induce and inhibit the N-vinyl pyrrolidone polymerization simultaneously. The conversion increases with the concentration rise of the alkyl chlorsilanes, but the molecular weights of the polymerization products are constant. These polymerization characteristics do not depend from the concentration ratio: [alkyl chlorsilane] /[azobisisobutyronitrile].

EXPERIMENTAL

The polymerization is carried out in glass ampoules in vacuo at 60°C. The purification of the oligomers was ran by their reprecipitation in diethyl ether from dioxan. The solvent was remouved in vacuo at 65°C. The quantity of the nonseparated monomer was determined photometrically (GALPERN et al. 1966). The conversion was determined gravimetrically and molecular weights of the oligomers - by the ebulliometry in chloroform.

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The elementary analysis of the oligomers (Calcd: %H=8,11; %C=64,12; %N=12,56; Found: %H=8,25; %C=64,15; %N =11,85) and their UR-spectra concide well with the analysis and spectra of the poly(N-vinyl pyrrolidone).

Recently (SEMCHIKOV et al. 1977) it was shown that the different dialkylchlorsilanes are efficient chain transfer agents for the radical polymerization of styrol, methyl methacrylate, vinyl acetate, 2-vinyl pyridine etc. But our results (TABLE 1) indicate that

TABLE 1

Relationship of the conversion (q) and the degree ($\bar{P}_n$) of the N-vinyl pyrrolidone polymerization against the concentration of azobisisobutyronitrile (AIBN) and dichlormethylsilane (DCMS). Temp.:60°C. Time: 3,5 h.

№	[DCMS] (mol.l^{-1})	[AIBN] (mol.l^{-1})	$\frac{[DCMS]}{[AIBN]}$	$\bar{P}_n$	q (%)
1.	5.10^{-3}	0		2,6	2,3
2.	10^{-1}	0		3,0	6,5
3.	10^{-3}	5.10^{-3}	0,2	3,1	-
4.	5.10^{-3}	10^{-2}	0,5	-	2,2
5.	10^{-2}	5.10^{-3}	2,0	2,4	3,8
6.	5.10^{-2}	10^{-2}	5,0	2,8	-
7.	10^{-1}	10^{-2}	10,0	-	6,7
8.	10^{-1}	5.10^{-3}	20,0	2,7	-
9.	5.10^{-3}	5.10^{-1}	10^{-2}	2,5	2,9
10.	0	10^{-2}	0	-	93,4

dichlormethylsilane (DCMS) is not chain transfer agent in the induced from azobisisobutyronitrile (AIBN) polymerization of the N-vinyl pyrrolidone (N-VP). Actually, the polymerization products are the oligomers and the degree of the polymerization is 2,8±0,3 does not depend on the DCMS concentration and the ratio [DCMS] / [AIBN] . It was observed the conversion rise with the increasing of the DCMS concentration also. Similar results were obtained for dimethyldichlorsilane and trimethylchlorsilane. Therefore the alkyl chlorsilanes have a double function in the N-VP polymerization: both as initiators (experiments 1 and 2 in Table 1) and as effective inhibitors. It was assumed previously (SIDELCOVSKAIA 1970 and BISWAS 1973) that the alkyl chlorsilanes induce the cationic N-VP polymerization. Molecular weights of the polymerization products were not determined in these works, and owing to this, the question for the rapid termination of the polymerization was not treated.

The results presented on the figure 1 (curves 1 and 2) indicate the **DCMS** ability for inhibition of the N-VP radical polymerization. From tha data in the Table 1 (experiment 9) it is obvious that **DCMS** causes a inhibition the polymerization even so its concentration is much less (200 fold) then the AIBN concentration. This result exludes the inhibition effect of DCMS on the N-VP polymerization through its direct interaction with the propagation radical. It follows from outher results in the figure 1 (curves 3 and 4) that the inhibition effect of DCMS is maintained after its participation in a polymerization initiation for a long time. Actually, the conversion does not increase

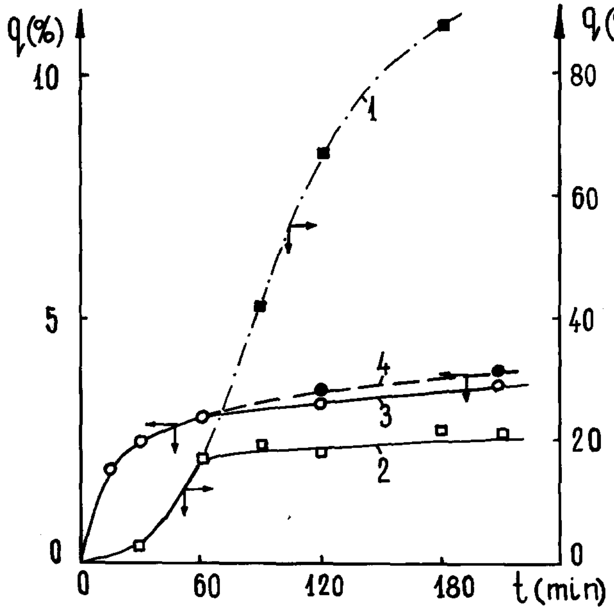

Fig.1. Kinetic of the N-VP polymerization at 60°C.

1. Initiator: AIBN. [AIBN] = 10^{-2} mol. l^{-1}.
2. DCMS is introduced in the reaction medium in an hour after the mixing of N-VP and AIBN. [AIBN] = 10^{-2}mol.l^{-1}. [DCMS] = 10^{-2}mol.l^{-1}.
3. Initiator: DCMS. [DCMS] = 10^{-2} mol.l^{-1}.
4. AIBN is introduced in the reaction medium in an hour after the mixing of N-VP and DCMS. [AIBN] = 10^{-2} mol. l^{-1} [DCMS] = 10^{-2}mol.l^{-1}

practically (curve 4) after introducing AIBN in the polymerization medium in an hour after mixing of N-VP and DCMS. Probably some products of the specific interaction between alkyl chlorsilanes and N-VP inhibit the N-VP polymerization. The nature of these products is unknown and its determination will be a subject of the further investigation.

The results so obtained allow to control the conversion and molecular weight of the products in a radical N-VP polymerization.

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