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MOLECULAR STRUCTURE OF BRANCHED POLYMERS FORMED IN THE ANIONIC POLYMERIZATION OF ACRYLONITRILE IN THE PRESENCE OF CATALYTIC AMOUNTS OF 2-VINYLPYRIDINE

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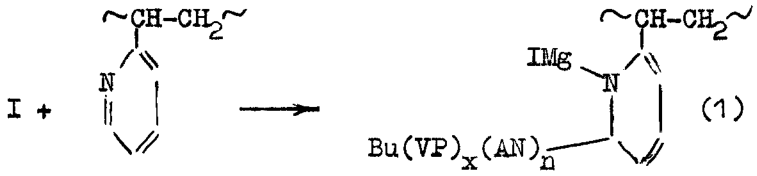
ABSTRACT

The polymerization in the system acrylonitrile (AN) - tributyl dimagnesium iodide (TDI) - toluene in the presence of small amounts of 2-vinylpyridine (VP) begins with the formation of short living oligo-blocks of VP which induce the polymerization of AN. The corresponding AN-growing chains undergo a peculiar deactivation consisting in the interaction with the pyridine rings of the VP-oligo-blocks. The repeated acts of this type lead to the formation of high molecular weight branched copolymers.

INTRODUCTION

According to Krasnoselskaya et.al.[1], the polymerization of AN in toluene with TDI in the presence of catalytic amounts of VP leads to the formation of growing AN-chains containing oligo-blocks of VP in their initial parts: $Bu(VP)_x(AN)_nMgI$ (I). This result was ascribed to the enhanced activity of VP as an electron donor leading to the preferable formation of the TDI•VP complexes (in comparison with the TDI•AN complexes) in the early stage of the process. This idea is in agreement with the existence of an induction period in the course of which the slow oligomerization of VP proceeds. The polymerization of AN begins after a decrease in the VP-concentration up to a certain critical level. The inability of the AN-anionic chains to react with VP (for details see[2]) excludes the participation of this monomer (a part of which could remain in the system) in the further process; the small number of VP-units is present entirely in the initial parts of the chains under consideration (see structure I).

The propagation reaction in this system is accompanied by the interaction of active sites with the VP-units of chains I; this is briefly shown below:



This conclusion follows from the presence of dihydropyridine rings in the polymers obtained (established by pyrolytic chromatography)[1]. The occurence of reaction (1) indicate its ability to compete with spontaneous deactivation which is characteristic of anionic AN-chains[2]. This peculiarity led to the suggestion about the probability of multiple participation of individual growing chains in the acts of type (1). This suggestion was confirmed by the molecular parameters of the above mentioned polymers estimated in the present investigation.

MATERIALS

Purification[3] of the solvents, AN, VP, and the synthesis of TDI[4] were carried out according to the published procedures. The GPC-analysis of the polymers was carried out using sorbents of the MPG/Ph-L-3 type (macroporous sodium-boron-silica glasses)[5]; they were obtained by treating chlorinated MPC (for details see[6]) with an ether solution of phenyl lithium.

METHODS

The methods of the polymerization, isolation of the polymers and their further treatement have been described previously[1]. High performance exclusion chromatography was carried out with the use of the 1304-M apparatus (USSR) with spectrometric and refractometric detectors. The chromatographic columns were 30 cm in length with internal diameter of 4 cm. MPG-particles were ~10 μ in size. Dimethyl formamide (DMFA) as eluent was used. The GPC-data were processed according to the principle of Benoit universal calibration dependence with the following constant values in the Mark-Kuhn-Houwink-equation K and a for polystyrene (PS) and polyacrylonitrile (PAN) - $K_{PS} = 1,23\cdot10^{-4}$, $a_{PS} = 0.60$, $K_{PAN} = 2.33\cdot10^{-4}$, $a_{PAN} = 0.75$. The system chosen does not permit an adequate interpretation of the MW-values of the order $2\cdot10^6$. We can only suppose (considering the GPC-data obtained) that the samples beginning from N°2 contain fractions with MW above $1\cdot10^6$ Da; their relative content increases from 10% for sample N°2 up to 29% for sample N°4.

Light scattering was measured in DMFA at 20°C using "Sofica" photogoniodiffusometer according to the standard method[7]. The $[\eta]$-values were estimated in DMFA, the respective M_v-values were calculated using the Cleland-Stockmayer equation[8].

RESULTS

The conditions of polymerization are given in Tab.1, the molecular parameters of the polymers are shown in Fig.1 and Tab.2.

Table 1

Polymerization of acrylonitrile in toluene by trimetil dimagnesium iodide in the presence of 2-vinyl pyridine at -75°C. Concentrations: AN 3 mol/l, TDI 0.01 eq/l, VP 0.05 mol/l

Exp. N°	Time, min	Conversion, %
1	0.5	5.0
2	1.0	19.5
3	10.0	31.5
4	60.0	33.0

Table 2

Molecular parameters of the polymers (numeration corresponds to that in Tab.1)

Sample, N°	$M_v \times 10^{-5}$	GPC-data (see Fig.1) $M_{p1} \times 10^{-5}$	$M_{p2} \times 10^{-5}$	$M_{add.}$ *) $\times 10^{-5}$	$M_w \times 10^{-5}$	A_2 **) $\times 10^{-4}$
1	0.57	-	-	0.45	-	-
2	2.45	0.7	6.0	2.15	3.6	0
3	4.00	0.6	7.0	3.80	5.5	0
4	9.00	3.0	10.0	8.00	31.0	7

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*) M_{add} is the mean value of molecular weight.

**) A_2 is the second virial coefficient.

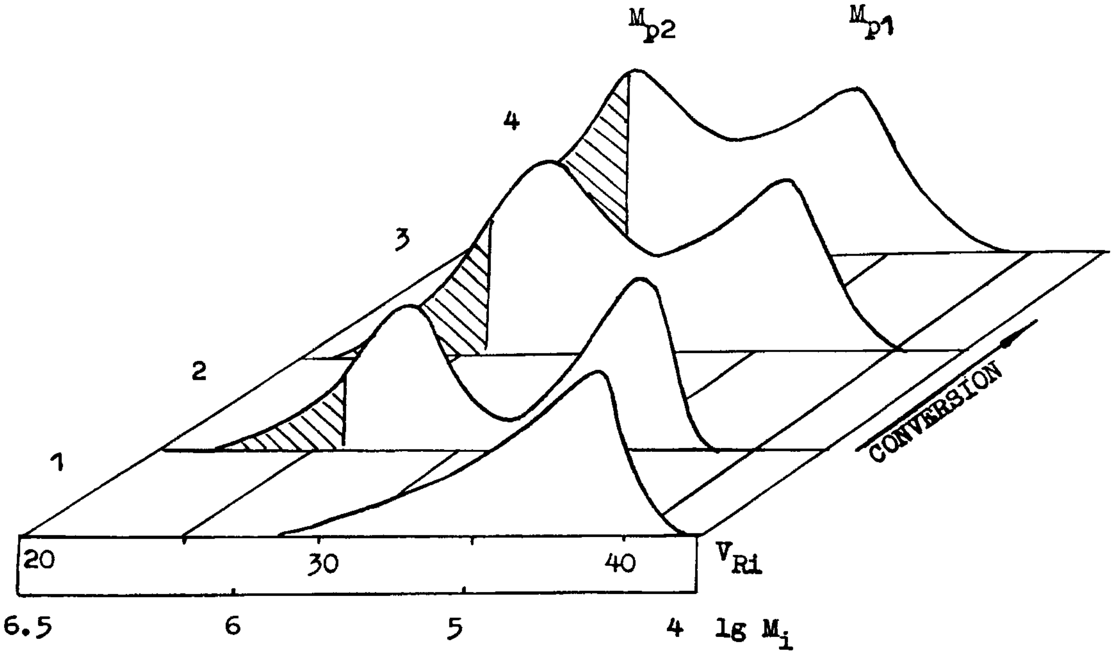


Fig.1. GPC-data for polymer samples N° 1–4. Conversion,%: % (1), 19.5 (2), 31.5 (3), 33.0 (4). All conditions are given in Tables 1,2 and in the Section Methods.

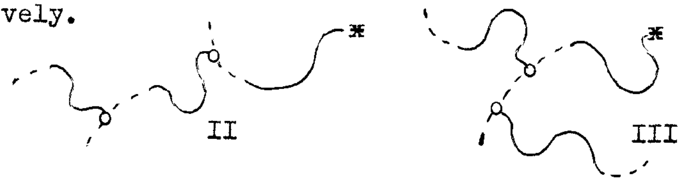
DISCUSSION

Among the results obtained those of Exp.N° 3 and 4 are especially attractive. They show a remarkable increase in the $\bar{M}$-values at a very small difference in conversion. This phenomenon suggests a high competing ability of reaction (1) with respect to the spontaneous deactivation of the growing chains. This evidently refers to both short and long chains characterized by the M_{p1}- and M_{p2}-values, respectively.

Let us consider the possible causes of the bimodality of the MWD of the polymers formed after the initial period of the process. In usual anionic systems, this character of MWD can often be ascribed to the coexistence of active sites differing in their reactivity. In the case under consideration another explanation must be attracted. The low VP-content used makes it possible to suggest that the x-values (see structure I) lie mainly in the region from 3 to 5. Nevertheless, the difference in the absolute x-values of individual chains can influence their relative tendency to reaction (1). The possible consequence of this difference can be the formation of polymers differing in the "degree of grafting" and, hence, in the polymodality of the MWD of the final products. It cannot be ruled out that the bimodality of samples N° 2-4, shown in Fig.1 is a simplified picture of the real situation as the data estimated by GPC are restricted to the M_p-values not exceeding $2\cdot10^6$ (see METHODS). On the other hand, the M_w-value for sample N° 4 was found to be $3.1\cdot10^6$.

The comparison of the $\bar{M}$-values obtained by the GPC and light scattering methods shows a discrepancy between their results. This discrepancy enhances with conversion, i.e. with the increase of the relative part of the high molecular weight fraction of the polymers. The cause of this effect is the above mentioned restricted estimation ability of the GPC-system used with respect to the polymers of high $\bar{M}$-values. For instance, the high molecular weight part of sample N°4 (not taken into account by this method) was found to be approximately 1/3 of the overall yield of the polymer. However, the high molecular weight parts of all the samples studied are of considerable importance for the M_w-values resulting from the light scattering method.

The formation of high molecular weight fractions of the polymers can be caused by repeated acts (1). Their overall result is expressed by simplified structural variants II and III; the solid lines, dotted lines, the signs o and ⁎ correspond to the AN-chains, oligo-VP-blocks, the branching points and active sites, respectively.



The probability of the formation of each of these variants depends both on the x-values of chains I and on their conformation which is (among other factors) influenced by the number of the branching points.

The data given in Tab.2 suggest the preference of the formation of "quasi-linear" chains II in the early period of polymerization and that of branched chains II in the later stage of the process. This follows from a relatively small difference in the M_v- and M_w-values of sample N°2 and a remerkable increase in this difference for sample N°4.

The authors take into account the inapplicability of the viscometric data for the calculation of the $\bar{M}$-values of branched polymers. The application of the estimated M_v-values to the case under consideration seemed to be of use for the interpretation of the observed effects. These values reflect the deviation of the polymer structure from the linear type.

To exclude a possible misunderstanding, we have to emphasize, that the product of reaction (1) does not initiate the polymerization of AN. As shown before, the metal amides of the dihydropyridine series are (in contrast to the compounds of the types R_2NLi and R_2NMgX) passive with respect to AN[2]. Hence, only those pyridine rings which did not participate in reaction (1) are responsible for the formation of branching junctions.

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