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SYNTHESIS OF “LIVING” CHAINS OF POLYVINYLPYRIDINE AND THEIR APPLICATION TO THE CONSTRUCTION OF HOMO- AND HYBRID POLYMER WITH COMPLEX ARCHITECTURE

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Abstract. Experimental conditions ensuring the formation of living poly(2- and 4-vinyl pyridine) chains in the vinyl pyridine - allyl derivatives of chromium, molybdenum and tungsten systems are described. Variation of the reagents nature, polarity of the solvent permits to obtain polymers differing in their structural and molecular parameters. Synthesized polymers contain block and graft sequences, as well as macrocyclic fragments. Living chains under consideration were applied for polymerization of different monomers. Hybrid polymers obtained by this way were studied in detail by the same methods as the homopolymers.

INTRODUCTION

In the beginning of the present decade the authors started a series of investigation in the systems: of polyvinylpyridine-allyl derivatives of Cr, Mo, and W.

Even in the first works of this series universal phenomena have already been determined: the formation of a very high molecular weight polymer (~ 10^6) under unfavourable conditions in a molar ratio of the components 1:1. In this case the components were 2-vinylpyridine (2-VP) and tris-π-allylchromium (TAC). The detection of this effect triggered a detailed study of these processes.

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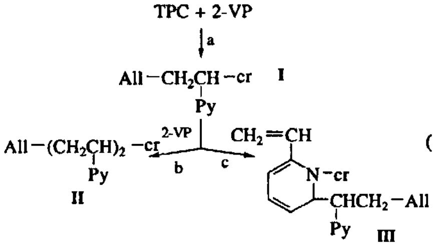
RESULTS AND DISCUSSION

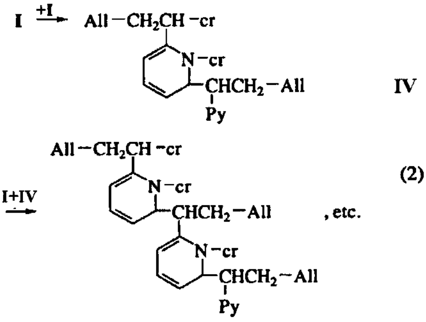
Homopolymers of 2- and 4-vinylpyridine

The interpretation of the above effect has been reported in previous papers [1-3]. According to this interpretation primary interaction between the reagents leads to the formation of two active centres (AC) which can be transformed into one another during polymerization. This is illustrated in scheme 1 where All is the allyl group and Py is the pyridine ring. For brevity only the scheme for 2-VP is given.



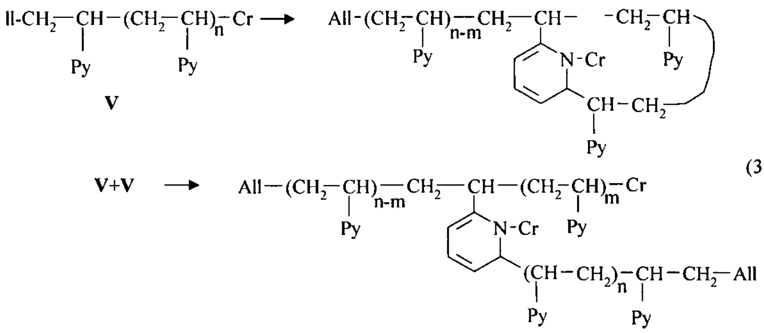
(1)

The most important transformations of adducts obtained in the initiation stage are shown in scheme 2.



(2)

When adduct 1 is consumed, reactions between "living" polymers take place. These intra- and intermolecular transformations are shown in scheme 3.



(3)

The reactions shown in schemes 2 and 3 lead to the formation of a considerable number of branched structures in the final product. Their quantity is established with the aid of the “branching factor” $g = [\eta]_{exp}/[\eta]_{lin}$, the ratio of the intrinsic viscosity of branched and linear polymers with the same MM (for strictly linear polymers the *g* factor is equal to unity, whereas for strongly branched polymers it can be even less than 0.1). Experiments have shown that the g value for soluble polyvinylpyridines ranges from 0.1 to 0.8 depending on polymerisation conditions (temperature and monomer-to-polymer concentration ratio).

Macromolecules of this type contain different structural fragments: block and graft copolymer structures as well as macrocyclics. This fact follows from structural data obtained with the aid of translational diffusion, light scattering and viscometry as well as with the aid of mass spectrometry thermal analysis (MTA).

When poorly soluble (strongly branched) or insoluble polymers (three-dimensional networks) are formed as a result of the polymerization of 2- and 4-VP under the effect of allyl derivatives of Cr, Mo or W, it is possible to study the polymerization mechanism by MTA. It was established that in the case of the polymerization of 2-VP under the effect of TPC in many cases (e.g. low or medium polymerization temperature and monomer:initiator ratio=10^3), the structure of the resulting polymers is close to that for P-2VP obtained by free-radical polymerization.

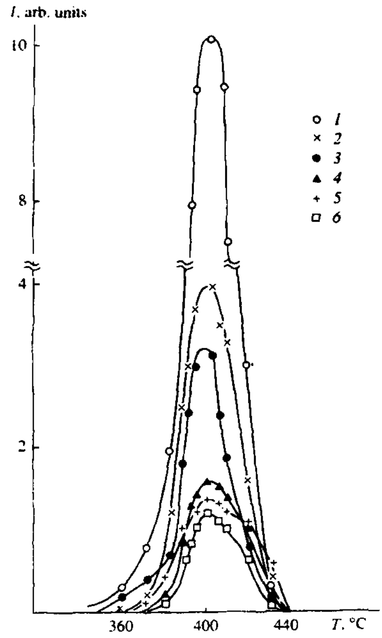


Fig.1. Yield of volatile products of thermal degradation of thermal degradation of P-2-VP-1 at the pressure in destructor 5×10^{-3} Pa and a heating rate of 4 K/min. Masses of characteristic ions: (*1*) 105 (monomer); (*2*) 79 (pyridine); (*3*) 104 (Table 1); (*4*) 210 (dimer); (*5*) 93 (picoline); (*6*) 118 (Table3)

Fig.1 shows the mass thermogram of these polymers, which is characterised by narrow and symmetric peaks of the yield of gas products in thermal degradation. The monomer peak is the most intensive, MM=105. In contrast, in the case of 2-VP polymerization in the monomer:initiator ratio close to unity, just as in the polymerization of 4-VP, in particular under the effect tetrakis-allyl W, the yield curves of thermal degradation products (Fig.2) are asymmetric and are drawn over a wide temperature range with a considerable shift towards lower temperatures.

In this case the characteristic feature is that it is not the monomer that predominates among degradation products, but compounds bound to fragments forming branching and crosslinking junctions and to fragments of macrocyclics. The presence of macrocyclics was also confirmed by MTA (Table 1, 2).

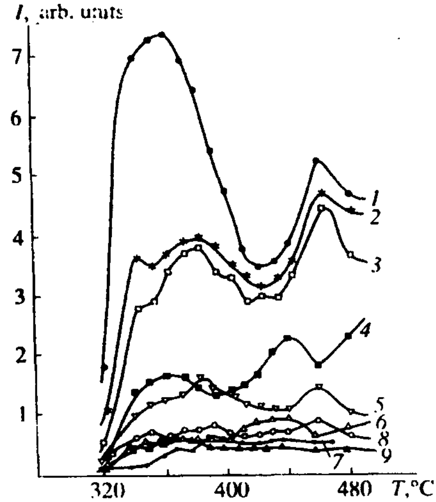


Fig.2. Yield of volatile products of thermal degradation of thermal degradation of P-4-VP-1 at the pressure in destructor 5×10^{-3} Pa. Masses of characteristic ions: (*1*) 93 (picoline); (*2*) 107; (*3*) 106; (*4*) 104 (monomer); (*5*) 121; (*6*) 104; (7) 198; (8) 79 (pyridine); (9) 78.

Table 1. Structure of ion fragments formed in thermal degradation of P-2-VP.

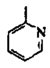
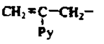
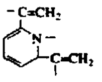
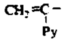
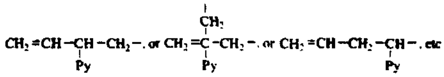
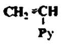
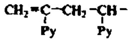
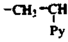
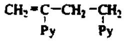
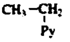
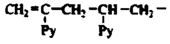
Ion mass	Structure	Ion mass	Structure
78		118	 $CH_2=\underset{Py}{C}-CH_2-$
79		129	
93	CH_3-Py		
104	 $CH_2=\underset{Py}{C}-$	132	 $CH_2=CH-\underset{Py}{CH}-CH_2-$, or $CH_2=\overset{|}{\underset{Py}{\overset{CH_2}{C}}}-CH_2-$, or $CH_2=CH-CH_2-\underset{Py}{CH}-$, etc
105	 $CH_2=\underset{Py}{CH}$	209	 $CH_2=\underset{Py}{C}-CH_2-\underset{Py}{CH}-$
106	 $-CH_2-\underset{Py}{CH_2}$	210	 $CH_2=\underset{Py}{C}-CH_2-\underset{Py}{CH_2}$
107	 $CH_3-\underset{Py}{CH_2}$	223	 $CH_2=\underset{Py}{C}-CH_2-\underset{Py}{CH}-CH_2-$

Table 2. Main products of thermal degradation of P-2-VP according to MTA.

Sample	Temperature of degradation, °C	Intensity of the fragment ion with various *m/z*											
		78	79	93	104	105	106	107	118	132	209	210	223
P-2VP-R	380 (T_b)*	33	330	100	310	1000	133	33	150	150	67	183	83
	395 (T_m)**	40	462	124	310	1000	124	14	124	149	65	150	70
	405 (T_c)***	33	550	158	320	1000	158	159	133	158	83	280	150
P-2-VP-1	380 (T_b)	37	571	178	357	1000	214	69	179	179	71	250	71
	400 (T_m)	39	455	159	318	1000	182	19	129	144	76	144	38
	420 (T_c)	34	450	380	333	1000	428	70	214	167	119	309	190
P-2-VP-2	380 (T_b)	45	490	422	356	1000	400	66	244	155	91	267	180
	395 (T_m)	46	486	570	430	1000	514	91	340	170	114	340	277
	410 (T_c)	55	550	777	444	1000	666	105	500	222	-	420	129
P-2-VP-3	375 (T_b)	52	539	470	402	1000	490	78	265	118	-	78	29
	385 (T_m)	62	435	648	417	1000	704	151	296	130	-	93	46
	405 (T_c)	90	550	1150	500	1000	950	380	350	350	-	350	200

Notes: P-2-VP-R was prepared by radical polymerization of 2-VP.

Table 3. Main products of thermal degradation of fractions P-4-VP.

Fraction	Thermodestruction temperature in °C	Intensity of signal from fragmentary ion of mass													
		78	79	93	104	105	106	107	118	119	121	132	198	210	223
F-1	T=300	333	541	1000	500	666	875	-	-	-	-	-	-	-	-
	T_m=390	344	965	1000	827	896	517	-	-	-	-	-	-	-	-
	T=480	700	900	1000	500	900	1000								
F-2	T_m'=360	67	81	1000	67	229	445	500	40	81	175	-	40	-	-
	T_m^2=460	94	169	1000	113	359	849	1094	75	113	216	-	132	-	-
	T=480	102	163	1000	142	489	775	1020	81	80	224	-	-	-	-
F-3	T_m'=390	235	179	1000	254	924	754	716	122	235	216	-	151	56	19
	T_m^2=420	158	150	1000	216	682	841	873	95	174	190	-	174	55	15
	T=480	88	176	1000	88	264	779	750	73	88	161	-	352	117	73
F-3	T=300	181	102	193	414	1000	181	73	102	96	-	68	57	414	267
	T_m=340	200	113	140	240	1000	140	43	51	64	-	29	45	140	100
	T=420	263	276	697	394	1000	434	315	289	263	-	236	223	868	618

T_m', T_m^2 - temperature of first and second minimum.

Table 2 gives MTA data for four fractions of P-4-VP obtained with the aid of tetrakis-allyl tungsten . It can be seen that the most intensive ion in the three fractions is an ion with the molecular mass=93 (methyl pyridine, the appearance of which is supposed to be related to branching and crosslinking junctions) rather than molecular ion with mass 105 characteristic of the case of linear P-2-VP and P-4-VP. Another ion characteristic of the branched and crosslinked structure is an ion with mass 78 which is related to the formation of the hexadiene ring from the pyridine ring as a result of interaction between the C-Me active centre and the pyridine ring of the monomer or polymer. It can be seen that this ion is more intensive than the ion with mass 79, whereas the reverse situation is characteristic of usual linear structures of P-2 and P-4-VP. The latter characterizes the mass spectra of the 2- and 4-VP monomer. As a result of mutual transformations of C-Me and N-Me active centres, polymer fragments are formed in the main chain. They contain C-N bonds which thermal stability is lower than that of the C-C bonds, which leads to a considerable decrease in the overall thermal stability of polymers.

The homopolymerization of 4-VP is of particular interest because this monomer is characterized to a greater extent by unusual details of the mechanism of anionic polymerization occurring under the effect of allyl derivatives of chromium, molybdenum and tungsten. Experiments were carried out in which the concentrations of 4-VP and initiator, the polymerization temperature and monomer conversion were varied. Samples were analyzed by MTA and thermogravimetric analysis (TGA) (Fig.3).

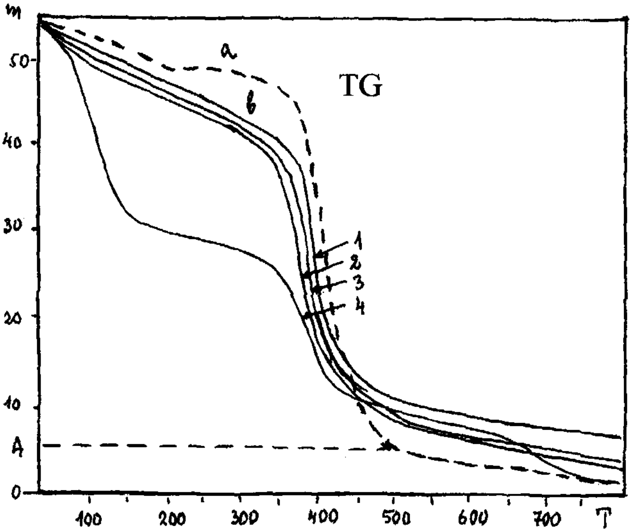


Fig.3. The curves TG of the samples of P-4-VP: m - mass (mg), T - temperature (°C).

a) The sample was prepared by the radical polymerization.

b) The numbers of the curves, corresponding to the numbers of the sample (Table 3). A - mass of the three-dimensional residue.

The high intensity of ions with mass 78, 93 and 198 in the mass spectra of degradation products indicates that a crosslinked three-dimensional structure is formed. Its basis is formed during polymerization and then becomes more complex with increasing thermal degradation of the polymer. In order to understand better the formation of a resulting complex structure of 4-VP polymers which are obtained under the effect of allyl Cr, Mo and W derivatives, the crosslinked residue formed during thermal degradation was determined quantitatively by TGA. TGA curves for four P-4-VP samples which were obtained with the aid of TPC under the conditions when the difference between them is only a few per cent of monomers conversion were analyzed. This analysis shows that with increasing conversion the fraction of the polymer which is transformed during degradation into a three-dimensional structure or into crosslinked residue decreases. This fact implies that the above process of active centres transformation, the formation of branched or crosslinked structures and macrocyclics proceed most intensively in the early polymerization stages forming microcrosslinked structures. During further polymerization these structures become increasingly surrounded by linear polymer fragments.

It should be pointed out, however, that if the deactivation of the "living" polymer after polymerization completion is not carried out, after a certain period of time intermolecular interactions between the active centres and the pyridine rings are possible. This can lead to the formation of post polymerization branching and crosslinking.

Hybrid polymers

"Living" polyvinylpyridines based on allyl derivatives of Cr, Mo and W are effective initiators of the polymerization of the acrylonitrile (AN), methylmethacrylate (MMA), tert-butylacrylate (TBA), dimethylacrylamide (DMAA) and other monomers, thus making it possible to obtain hybrid polymers. In these cases when vinylpyridine polymerization yields linear polymer molecules, when a second monomer is added it is possible to obtain block copolymers. Under the conditions of the formation of the branched and crosslinked structures, graft copolymers can be obtained. It should be noted that in some cases it is possible to synthesize hybrid polymers with a variety of structures by using direct and reverse sequence of monomers introduction into the polymerization process. This can be particularly clear if hybrid polymers based on TBA and DMAA are taken as an example [5]. They differ in the order of their introduction into the polymerization process. This change in monomer incorporation leads to a considerable change in the structure of the resulting polymer. Hence, if other polymerization conditions (temperature and monomer:initiator ratio) are also varied, it is possible to obtain polymers with the required characteristics, in particular with a given degree of branching and crosslinking.

Consequently, the use of the system: vinylpyridine:allyl derivatives of Cr, Mo, and W, leads to the formation of living homopolymers with a great variety of structural forms, with broadens the possibility of obtaining hybrid polymers. By varying the polymerization conditions and the order of monomer introduction into the reaction it is possible to construct block and graft copolymers with a complex architecture.

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