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NOVEL BRANCHED BLOCKCOPOLYMERS FROM POLY(VINYLPYRIDINE) BY CHROMIUM ALLYL COMPOUNDS

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Abstract: Novel branched blockcopolymers from polyvinylpyridine are formed by chromium allyl compounds. Our present work shows results for the homopolymerization of vinylpiridine (VP), dimethylacrylamide (DMAA), *tert* - butylacrylate (t - BA) as well as the graftcopolymerization of poly(vinylpyridine) (PVP), using *tris* (π – allyl) chromium (TPC) as initiator. PVP activated by TPC was used for grafting with DMAA - "grafting from". On the other hand living PDMAA polymerized by TPC, was able to react with PVP chain - " grafting onto".

INTRODUCTION

Allyl derivatives of group VI^B metals were first mentioned in the literature by Wilke and Oberkirche (1). It was later established, that these compounds are good initiators for the homopolymerization of acrylonitrile (2,3) and methylmethacrylate (4,5). Especially interesting results were obtained for the TPC activated polymerization of 2-VP and 4-VP (6). The polymerization of 2-VP by TPC at 60°C ensured a 100% yield of the polymer with a high M_w value during less than 1 min. This reaction led to the formation of branched PVP. With activated P(2-VP) and P(4-VP) is it possible to form branched blockcopolymers with

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acrylonitrile(7). This present work shows first results of graftblockcopolymers onto linear polyvinylpyridine, made by typical radical or anionic polymerization, with dimethylacrylamide. Also the homopolymerization of DMAA was investigated comparing with the homopolymerization of 2VP and 4VP.

EXPERIMENTAL

Materials

The synthesis of TPC was carried out according to ref. (3). Monomers and solvents were dried over CaH_2 and distilled directly before use. The reactions were terminated by addition of ethanol. The polymers were precipitated with water, dissolved in ethanol and reprecipitated in hexane.

Methods

The intrinsic viscosities $[\eta]$ of the polymers were determined in ethanol/water - solution at 25°C ($[\eta]$ of PDMAA was measured in water at 25°C). We have used the following equations: 1) $[\eta] = 1{,}22 \cdot 10^{-4} \cdot M^{0{,}73}$; 2) $[\eta] = 2{,}32 \cdot 10^{-4} \cdot M^{0{,}81}$ (ref. (8,9)). The thermal degradation of the polymers was studied by the method of mass - spectroscopic thermal analysis (MTA) using MX - 1320 mass - spectrometer.

RESULTS AND DISCUSION

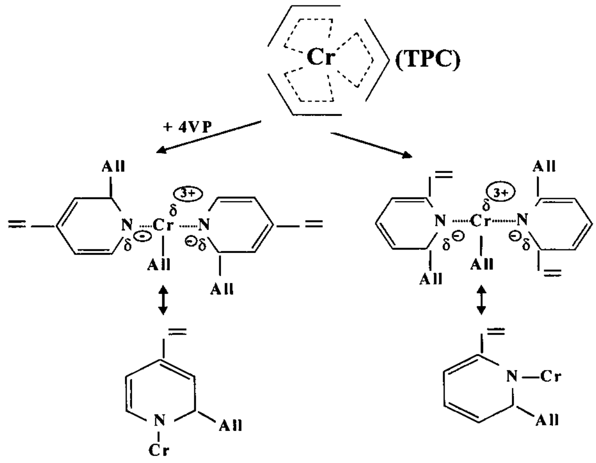
The PVP was prepared by the polymerization of VP initiated by AIBN, n - BuLi and TPC. The main characteristics of the polymers and the reaction conditions are listed in table 1

Table1: Homopolymerization of VP by TPC, BuLi and AIBN

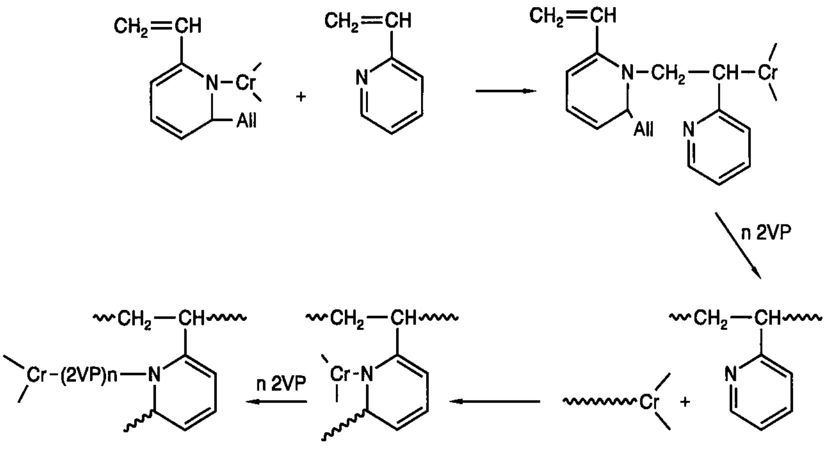
Initiator	$[C]_{initiator}$	Monomer	$[C]_{mon.}$	Solvent	Time	$T_{reaction}$	Yield	M_w	M_η
--	mol/l x 10^{-2}	--	mol/l	---	min	°C	%	g/mol x 10^6	
AIBN	2	2VP	2,3	MeOH	240	65	70	--	0,14
	2	4VP	2,4	MeOH	240	65	52	--	0,09
BuLi	5	2VP	1	Toluene	150	-50	85	--	0,02
	0,7	4VP	0,6	Toluene	150	-50	90	--	0,02
TPC	0,07	2VP	1	THF	1	60	100	1,2	--
	0,07	4VP	1	THF	1	60	100	0,7	--

The big difference in molecular weights between PVP, synthesized by BuLi and by TPC should be noted. The concentration of TPC was considerably lower than $[C]_{BuLi}$.

Nevertheless, in the case of TPC - initiation, the molecular weight of the PVP was twice higher that of the M_η of PVP, obtained by n - BuLi initiated anionic polymerization. Furthermore, the reaction temperature in the first case (TPC polymerization) was 60°C, while the typical anionic reaction by means of BuLi was carried out at -50°C. No polymerization reaction of 2 -VP occured at 0°C using TPC as initiator. We propose the following mechanism(10) The first step led to fast complex formation:



In the following scheme the complexes are written in a more simple way. The polymerization step can be shown as follow:



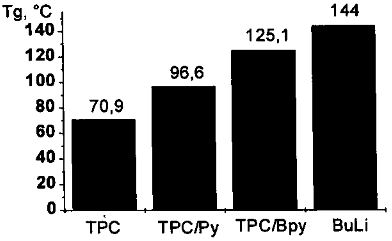
In the present paper the basic interest was in the possibility to synthesize graftcopolymers based on PVP and DMAA using TPC as initiator. The chronology of building from simple to more complicated structures was determined in our initial task - homopolymerization of DMAA. These types of polymerizations with TPC have not been investigated. The bulk polymerization of DMAA initiated by TPC led to instantaneous formation of polymer accompanied with the heat of separation. Table 2 shows data for the DMAA homopolymerization in THF.

Table 2: Polymerization of DMAA by TPC

DMAA	TPC	Time	$M_\eta x10^4$
mol/l		min	g/mol
1	0,01	10	4,6

The main products of thermal decomposition (MTA) of this polymer give peaks at m/e = 98 and m/e = 99. The peak at m/e = 99 corresponds to the DMAA monomer and the peak at m/e = 98 the structure obtained from the degradation of the branched PDMAA link. PDMAA was polymerized also using n - BuLi and modificated TPC with Bipyridine and Pyridine (TPC/Bpy; TPC/Py). The polymerization of DMAA by n - BuLi led to linear PDMAA. In contrast, using TPC -, TPC/Py - and TPC/Bpy - initiators, polymers with different degrees of branching were obtained.

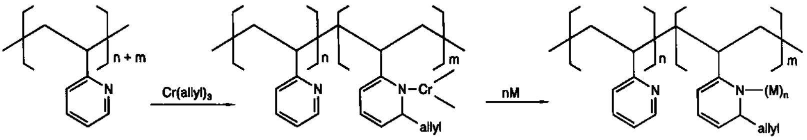
This conclusion is based on the DSC analyses, presented in the following diagram:



The lower T_g temprature indicates more branching. Linear PDMAA obtained by typical anionic polymerization, using n - BuLi as initiator, has the highest glass tempreture (T_g = 144°C). On the other hand, the lowest T_g, that means highest degree of branching, was obtained by the polymer synthesized using TPC as initiator (T_g = 70,9°C).

Turning back to the TPC polymerization mechanism given above, we have assumed that it is possible to activate PVP with TPC.

Thus, this active form of PVP can be copolymerized with DMAA and t - BA (grafting form).



where M = DMAA, t - BA

Some examples are shown at table 3.

Table 3: Interaction of activated PVP with DMAA

P(2-VP)	DMAA	TPC	T_g	[η]
(g/mol - mon.)/lx10^{-1}	mol/lx10^{-1}	mol/lx10^{-3}	°C	dl/g
2,6	5,5	5,5	78,9	0,31

Toluene; $[\eta]_{P2VP}$ = 0,7 dl/g; M_{P2VP} = 142 000 g/mol

It must be mentioned that the intrinsic viscosity of the obtained graftpolymer is lower than that of the initial P(2-VP). This fact can be explained by the transition from linear to grafted structure. More interesting is the case, when DMAA was polymerized using TPC and the living PDMAA was reacted with linear P(4-VP) - "grafting onto" (table 4).

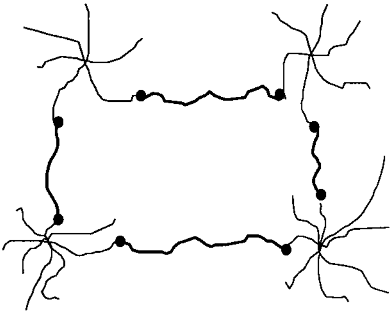
Table 4: Graftpolymerization between DMAA initiated by TPC and PVP

DMAA	P(4-VP)	TPC	[η]
mol/lx10^{-1}	(g/mol - mon.)/lx10^{-1}	mol/lx10^{-2}	dl/g
5,5	2,6	5,5	0,31

Toluene; [η]$_{P4VP}$ = 0,5 dl/g; M$_{P4VP}$ = 89 000 g/mol

We suggest the following structure in that case:

Where: The knots are branched PDMAA macromolecules connected each other with linear PVP chains.



CONCLUSION

A wide spectrum of polymers have been synthesized, based on VP, DMAA and PVP using TPC as the initiator. It was established that the TPC - initiated homopolymerization of DMAA and VP led to the formation of branched polymers. Using "grafting from" and "grafting onto" methods graftcopolymers (PVP/PDMAA) were obtained with complicated architecture. The mastering of the polymerization process initiated by TPC can be used in order to receive polymers with exact determinate structures.

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REFERENCES

(1) G. Wilke, W. Oberkirch, K. Tanaka, *Angew. Chemie*, **78** (1966) **157**

(2) Ballard, E. G. H., T. Medinger, *J.Chem. Soc.,* **B** (1968) **1168**

(3) L. A. Fedorova, V. V. Mazurek, N. A. Shirokov, L. D. Turkova, *Vysokomol. Soed,* **A 23** (1981) **1749**

(4) N. A. Shirokov, V. V. Mazurek *Vysokomol. Soed,* **A 18** (1981) **2687**

(5) L. A. Fedorova, So Zen Juk, C. F. Bortashevich, S. I. Klenin, B. L. Erussalimsky, *Vysokomol. Soed.*, **A 32** (1991) **804**

(6) L. A. Fedorova, A. V. Yakimanski, B. L. Erussalimsky, *Macromolecular Reports,* **A 32** (1995) **175**

(7) S. I. Klenin, L. A. Fedorova, B.L. Erussalimski *Polymer Science* **34** (1992) **380**

(8) S.Arichi, *Bull. Chem. Soc. Japan* **39** (1966) **439**

(9) L. Trossarelli, M. Meirone *J.Polym. Sci* **57** (1962) **445**

(10) L. A. Shibaev, T. A. Antonova, L. A. Fedorova, S. I. Klenin , B. L. Erussalimsky *Vysokomol. Soed,* **A 37** (1995) **1874**