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Formation of Graft Copolymers of Complex Structure: In Tee Interaction of Acrylonitrile with Polyvinylacetate Activated with n-Butyl Lithium

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FORMATION OF GRAFT COPOLYMERS OF COMPLEX STRUCTURE IN
THE INTERACTION OF ACRYLONITRILE WITH POLYVINYLACETA-
TE ACTIVATED WITH n-BUTYL LITHIUM

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ABSTRACT

The polymerization of acrylonitrile (AN) by polyvinyl-
acetate (PVA) activated with n-BuLi results in forma-
tion of complex graft copolymers. Their molecular pa-
rameters suggest the participation of the grafted AN
growing chains formed in the first stage of the over-
all process in the secondary reactions.

INTRODUCTION

The products of grafting of AN onto PVA have a very
modest place in the vast literature concerning graft
copolymers. The corresponding data are restricted to
our recent results obtained by the use of PVA activa-
ted with n-BuLi as an initiator of AN polymerization.¹
The conditions used in ref.¹ have led to the forma-
tion of considerable part of insoluble fraction (up
to 20%) and to a broad MWD of the fractions soluble
in DMF (M_w/M_n 10-15). These effects could be ascri-
bed to the high M_w -values of the initial backbone
polymers ($5 \cdot 10^5$ and $8 \cdot 10^5$). They could favor the
parallel secondary intra- and intermolecular reacti-

ons of the growing chains. The existence of the second type of these reactions is confirmed by the molecular parameters of the synthesized copolymers¹. It seemed possible to obtain the products of higher uniformity and to avoid the formation of insoluble fractions by using activated polymers (PVA*) and oligomers (OVA*) of lower molecular weights. Accordingly, we carried out similar syntheses using PVA and OVA with M_w -values of $4 \cdot 10^4$ and $2 \cdot 10^3$, respectively. In the former case the content of the soluble fractions increased to ca 95%. In the latter case completely soluble copolymers were obtained with the M_w/M_n -value near to 3. These copolymers were characterized by a sharp discrepancy between their composition and the M_w -values. In particular, for a copolymer containing 25% AN, this value was near to $5 \cdot 10^5$, which was ca 100 times higher than could be foreseen for the above mentioned composition.

In the present work we try to interpret the mechanism of reactions responsible for this non-trivial result.

MATERIALS

Oligovinylacetate (OVA) was obtained using benzoyl peroxide as initiator and methyl ethyl ketone as solvent at 70°C. AN and DMF were dried over CaH_2 and distilled directly before use. THF was dried with Na-K alloy.

METHODS

The activation of PVA and OVA was carried out in THF by n-BuLi under argon at -30°C; other conditions see in Table 1. After activation DMF was added to the reaction mixture, THF was evaporated and AN was introduced into this system at the same temperature. The resulting solution was deactivated by DMF, acidifi-

Table 1

Activation of poly- and oligovinylacetates
Solvent THF, temperature -30°C , reaction time 1 h

Exp. N°	PVA (OVA)			$[\text{n-BuLi}] \cdot 10^2$, mol/l
	$[\eta]$, dl/g	$M_w \cdot 10^{-3}$	$[\text{VA-unit}]$, mol/l	
1*)	1.10	300	0.10	0.50
2	1.13	40	0.15	0.75
3	1.13	40	0.17	0.75
4	-	2	0.30	1.50
5	-	2	0.30	1.50

*) Data from ref.¹

Table 2

Grafting conditions and characteristics of the copolymers. Solvent DMF, temperature -30°C

Exp. N°	AN, mol/l	Time, min	AN		$[\eta]$ dl/g	$M_w \cdot 10^{-6}$	$A_2 \cdot 10^{-4}$ ***)
			con- ver- sion, %	con- tent, %			
1*)	0.27	60**)	100	62	0.64	1.80	4.0
2	0.15	5	40	19	0.19	4.60	6.0
3	0.30	5	100	59	0.55	0.63	3.7
4	0.30	5	57	25	0.09	0.54	3.5
5	0.60	5	70	46	0.19	0.76	3.5

*) The numeration corresponds to Table 1

***) Temperature was -10°C

****) A_2 is the second virial coefficient

ed with HCl and filtered. After the evaporation of the solvent, the residue was dried under vac. The AN content was estimated by elemental analysis and refractometrically.

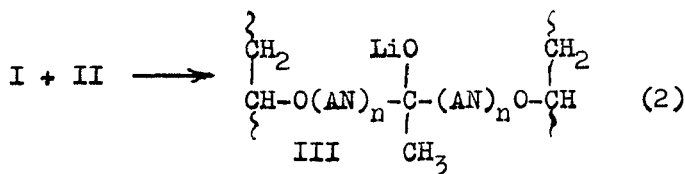
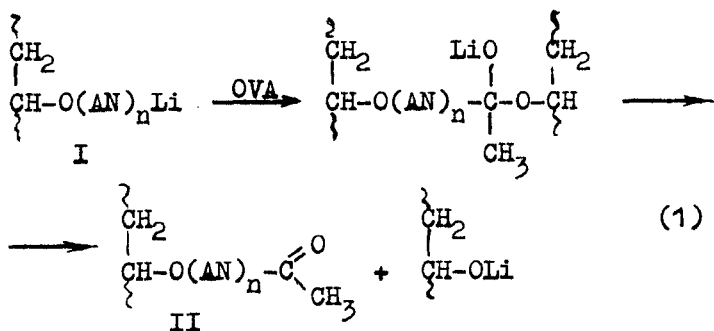
The physical measurements were carried out in DMF at 21°C. Light scattering was measured by a Sofica photogoniometer according to standart method², taking into account the specificity of the polymers investigated. The sedimentation analysis was carried out using the MOM-3180 ultracentrifuge (Budapest) at a rotation speed of 45000 rpm; the corresponding calculations were performed by the known method³.

RESULTS

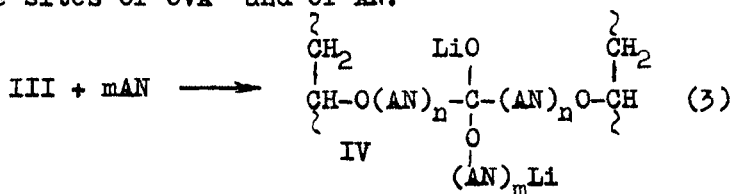
The reaction conditions and their results are given in Tables 1 and 2 together with those from one of the experiments related to ref.¹ (to compare the data obtained for PVA with various M_w -values). The complete interaction between the reagents in the activation stage was assured by the long storage of the systems before the introduction of AN. For the estimation of the molecular parameters of the graft copolymers, the solutions free of microgels were used. Microgels were found only in the products obtained by the use of PVA*. They could be formed because of the content of the $-\text{CH}_2\text{CHOH}-$ units appearing as a consequence of the hydrolysis of the LiO-groups of PVA* which did not participate in the grafting reaction. As shown in¹, the hydrolysed PVA*, ever obtained at a high PVA/ $n\text{-BuLi}$ ratio is (in contrast to PVA) insoluble in DMF. This fact suggests that the reaction between OVA* and AN (not accompanied by microgel formation) proceeds with complete consumption of the active sites of OVA* in the grafting reaction.

DISCUSSION

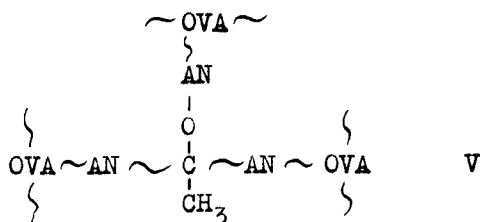
The marked discrepancy between the composition and M_w -values of the graft copolymers under consideration (see Table 2) must be ascribed to some secondary reactions leading to the formation of „multi-graft“ copolymers. The reactions of the following types seem possible:



Similar repeated acts may lead to high M_w -values of the copolymers with the above mentioned composition. Besides reaction (1) and (2), the participation of the „twice-grafted“ initiator III in the formation of the AN-growing chains cannot be excluded. It seems clear that interactions (3) become especially real in the stage of a considerable consumption both of the active sites of OVA* and of AN:



This situation favors the further complication of the structure of the copolymers because in this stage the VA-units are present in a great excess in comparison with „free” AN. Under this condition the reaction between IV-living chains and the backbone chains is the most probable. Its result reflects the simplified structure V:



It must be emphasized that the interaction under consideration is not restricted to the formation of the structures of this type alone. Taking into account e.g. the data of Exp. 4 and 5 (Table 2) we can see that they do not correspond to structure V; this structure could be characterized by the M_w -value of ca $15 \cdot 10^3$. Much higher experimental M_w -values of the synthesized copolymers must be a consequence of many repeated attacks of multigraft copolymers V by grafted living chains I.

Summarising the results obtained we come back to the M_w/M_n -ratios belonging to graft copolymers formed on high molecular weight backbones (M_w 500-800 $\cdot 10^3$) and on the oligomer chains (M_w 2 $\cdot 10^3$). The higher uniformity of the products obtained by the use of OVA* can be caused by a greater accessibility of the active sites for AN in comparison with the situation in the case of PVA* which is a complex thermodynamic system. It can also be assumed that the lower molecular weight of the backbone leads to a decrease in the number of the grafted chains in respect to the individual backbone

chain; this condition may favor the formation of macromolecules of higher regularity.

The graft copolymers formed on OVA can be considered as compact coils, which follows from their $[\eta]$ -values (see Table 2). It is a simple consequence of the dependence of the molecular structure of the products under consideration on their branched nature. The A_2 -values given in Table 2 suggest that DMF is a thermodynamically „good” solvent for the copolymers investigated.

The characteristics of the new systems which have not yet been studied make it possible to ascribe to them the structure of three-dimensional quasi-uniform network.

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