

SOME PROBLEMS OF CHEMICAL AND PHYSICAL MICROMODIFICATION OF POLYMER SYSTEMS

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ABSTRACT

The experimental results from, and the approaches to, the study of the role of microadditives in polymer systems are reviewed. The influence of low-molecular weight plasticizer at levels of 0.1 to 0.5 per cent added to polymer which results in the abnormal decrease of the glass transition temperature, in the sharp decrease of specific viscosity of polypropylene melts, and other non-classical phenomena, is discussed. Some features of gel formation in the case of a system of comb-like polymer (polyhexadecyl acrylate) with aliphatic hydrocarbon or aliphatic alcohol are discussed. Such gels are structurally ordered systems, they are formed at very low concentrations of polymer (0.1 to 0.3 per cent), they behave as typical lyotropic liquid crystals and the role of the structure-forming agent of the polymer toward the low-molecular medium is clearly demonstrated.

The role of chemically attached microadditives is demonstrated on the example of copolymers of isopropyl acrylate and hexadecyl acrylate which retain the hexagonal crystalline lattice parameters typical of the homopolymer of the hexadecyl acrylate even at low content of the latter.

The other examples are self-stabilized polyvinyl chloride containing chemically attached organotin stabilizing groups in the chain, and macromolecular models of proteolytic enzymes with partially alkylated polyvinyl pyridine. In these systems a slight change in the content of chemical modifier in the chain provides inadequate change in the macroproperties of the total system.

The marked tendency of polymers toward structure formation not only within the crystalline state but in the amorphous one as well, and the ability of macromolecules to form associations even in dilute solutions oblige us to reconsider now the role of microadditives in polymer systems. Such additives being chemically bound to the macromolecular chain or being introduced as admixtures can change decisively all the physical and mechanical properties as well as the reactivity of the system. This direction of research in the field of modification of properties of polymer substances which has received much attention in the last few years has already resulted in a series of interesting and useful results. The aim of the present review is to discuss some recent results in this field, when the introduction of microquantities of 'foreign' groups or units into chains or microadmixtures in the amount of one molecule on average over dozens and hundreds of macromolecules brings about desired effects in the change of macroproperties of polymer systems.

As one of the examples of the influence of microadditives on physical properties of polymers, I would like to cite results on the structural plasticization of amorphous and crystalline polymers¹. In the early publications of P. V. Kozlov and V. A. Kargin² it was shown that besides the well-known mechanism of molecular plasticization of polymers there is another mechanism of structural plasticization when a low molecular substance scarcely compatible with the polymer is being introduced into the polymer and is situated on the boundaries between supermolecular structures where it plays a role of lubricant and favours the easy displacement of structural elements. This results in a sharp decrease of the glass transition temperature when the content of plasticizer is between 0.05 and 0.1 per cent. The typical situation is represented in *Figure 1*, where T_g of triacetylcellulose is plotted against the plasticizer content, the latter being a molecular or structural one depending on its chemical nature.

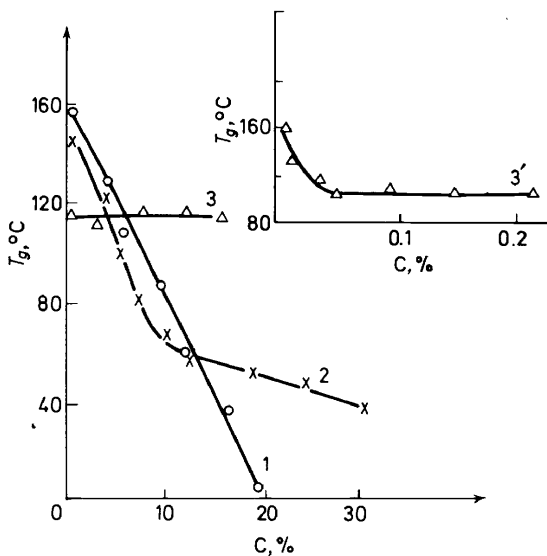


Figure 1. Glass transition temperature of cellulose triacetate as a function of plasticizer content: 1—1-nitro-2-methyl-2-propanol; 2—trimonochloroethylphosphate; 3—butyl stearate.

Much more effective are the results obtained by G. P. Andrianova and V. A. Kargin^{1,3} on the micromodification of polymeric melts. In *Figure 2* the effective viscosity of two polypropylene melts at fixed shear modulus is plotted against the content of oligomeric polydiethylsiloxane additive. The introduction of an amount of additive as small as 0.05 per cent results in a tenfold viscosity decrease without any change of mechanical properties of the crystalline polypropylene in the block. These data show the possibility of displacing structural elements on the supermolecular level in polymeric melts.

Depending on the nature of an additive the concentration dependence of the viscosity can be either an extreme or a permanent low viscosity value is reached which is not changed with further increase of the low molecular

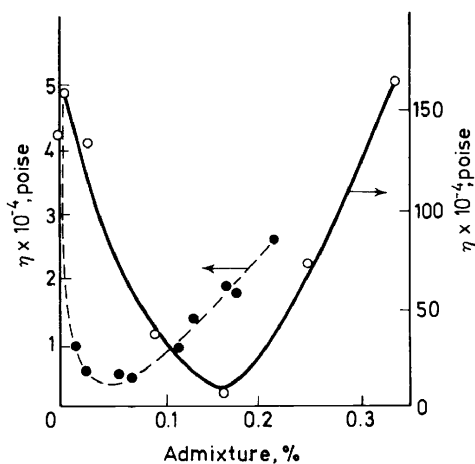


Figure 2. Effective viscosity of polypropylene melts at constant shear stress as a function of the ethylsiloxane oligomer content: 1—Moplen ($= 1 \times 10^5$ dyne/cm²); 2—ICI sample ($= 5 \times 10^4$ dyne/cm²).

component content. Both types of dependence are strictly different from the known mechanisms of plasticization of melts which lead to the exponential viscosity function in relation to plasticizer content.

Microadditives which act on the supermolecular level are capable¹ of increasing fatigue resistance sharply during the periodical loading of rubbers (12 to 15 times at the additive content of 0.1 per cent and without changing the stress/strain characteristics or other mechanical properties of the polymer). These additives can also produce a marked increase of adhesion of polymer material (the maximum of adhesional content of plasticized polyvinylchloride is at the additive content of 0.02 to 0.03 per cent).

The above results show that the efficiency of action of microadmixtures overlaps the usual additive scheme of interaction on the molecular level. The reason for this is that here one takes advantage of a chance to use and to develop the strong tendency of polymer substances to be organized and structured. Due to this fact the role of boundaries between structures in such microheterogeneous systems greatly increases and, consequently, very small amounts of additive are sufficient to ensure the desired effect. When one goes to higher concentrations of additives, the result is to change the mechanism of action and transfer all the phenomena into another more usual and in this sense less effective category.

A further problem concerns the role of microadditives if they are chemically bound to the polymer. The strong structurability of the macromolecules provided by the presence of a small number of interacting units and groups can be demonstrated by taking as an example a curious class of comb-like polymers of the acrylic series, which were studied in detail on account of their liquid-crystalline state⁴. We have recently found that polyacrylates, polymethacrylates and polyvinyl esters which have as ester group an aliphatic side group containing 10, 14, 16 or perhaps 18 carbon atoms, i.e. long side branches in each monomeric unit, are crystallized in a hexagonal

lattice with participation of side aliphatic chains. This type of packing is none other than one of the forms of smectic liquid crystals stable over a wide temperature interval⁴⁻⁶. As has been proved by x-ray analysis, such packing is achieved by close placement of the cylinders of side aliphatic branches with some mobility in azimuth around the C—O bond at the place of attachment to the backbone chain. Such structures give the appearance of long periods within the liquid crystalline state derived from the parallel packing of layers formed by the side branches. Small angle x-ray diagrams of polyhexadecyl acrylate and of polyhexadecyl methacrylate show a long period which is normally the sum of the lengths of two sidegroups plus the width of the main chain in the case of polyacrylates, and the length of sidegroups in the case of polymethacrylates (in the latter case the more rigid methacrylate chain does not enter the crystalline lattice)⁴⁻⁶. One of the peculiarities of the structure of such comb-like polymers is the abnormal stability of layer packing in these systems and a strong tendency to interbranch interaction of the aliphatic chains. The interplanar distances for some polymers and copolymers of this type derived from x-ray large angle and small angle analysis as well as data on temperature and heat of fusion are given in *Table 1*.

The interaction between side chains and sufficient mobility of fragments of macromolecules within side branches permits introduction of the 'foreign' units into comb-like polymers without essential disturbance of their crystalline structure. The r_1 and r_2 values in the radical copolymerization of hexadecylacrylate and isopropylacrylate are $r_1 = 0.58 \pm 0.13$; $r_2 = 0.70 \pm 0.15$ and this allows us to consider the copolymers of these two components as statistical with the corresponding unit distribution along the chain. The data given in *Table 1* show that the introduction of up to 80 Mol. % of isopropylacrylate does not result in the disappearance of the hexagonal type structure or of layer packing. The long period is preserved, although its value changes for small contents of isopropylacrylate. This period tends to correspond not to two-layer but to one-layer packing, i.e. the introduction of isopropylacrylate units into the chain is equal, from this standpoint, to the appearance of an α -methyl group in the backbone chain because one-layer packing is typical for polymethacrylates.

The most interesting phenomenon is the existence of layer packing at the mole ratio one unit of hexadecylacrylate to four units of isopropylacrylate. There is some reason to suppose that the minimum critical concentration of long side monomer in the chain can be even less and still conserve layer packing, in other words, the long branches can still find each other in the polymer mass. On the other hand, the introduction of 4 to 6 mole per cent of hexadecylacrylate totally prevents the crystallization of polyisopropylacrylate—the polymer becomes amorphous due to the combined effect of two different tendencies toward crystallization—the one of polyisopropylacrylate which 'wants' to produce helical conformation of the main chains, and the other, of polyhexadecylacrylate, for which the hexagonal packing of side chains is typical. All this clearly demonstrates the influence of long side groups on crystallizability. This opens the way for regulation of such processes in polymers by means of the introduction of comb-like monomers into linear polymers by copolymerization.

Table 1. Interplanar distances, T_m and ΔH_m for comb-like polymers and copolymers.

Polymer	Interplanar distances, Å. Numbers of diffractonal maxima								T_m , °C (± 0.5)	ΔH_m cal/g
	Small angles				Large angles					
	1	2	3	4	5	6	7	8		
Polyhexadecyl acrylate, PA-16	42	14.7	8.34	6.06	—	4.19	2.43	2.10	38.0	19.9
Polyheptadecyl acrylate, PA-17	44.5	14.9	8.84	6.30	—	4.17	2.41	2.08	46.0	24.3
Polyoctadecyl acrylate, PA-18	47.0	15.8	9.50	6.60	—	4.15	2.40	2.10	49.0	24.6
Polyhexadecyl methacrylate, PMA-16	29.0	14.7	8.67	—	—	4.19	2.41	2.08	22.0	9.4
Polyoctadecyl methacrylate, PMA-18	30.0	14.9	9.90	—	—	4.17	2.42	—	40.0	—
Copolymer A-16-IPA (67:33)	26.5	13.6	8.69	6.34	—	4.19	2.43	—	32 (26.1)*	—
Copolymer A-16-IPA (56:44)	26.5	13.9	8.70	—	—	4.19	2.43	—	26.5 (21.3)*	9.2
Copolymer A-16-IPA (42:58)	27.0	13.6	8.81	—	—	4.19	—	—	18.0 (11.4)*	7.0
Copolymer A-16-IPA (22:78)	26.5	—	—	—	—	4.19	—	—	14 (-5.7)*	—
Copolymer A-16-IPA (2:98)	—	—	—	—	—	8.49	5.15	4.2	—	—

* Melting point predicted by Flory's equation for copolymers.

The tendency described above of comb-like polymers to structurize also results in the development of the role of these polymers themselves as effective modifiers of the system.

The intensive intramolecular interaction of the sidegroups leads to the fact that with increase of side chain length the optical anisotropy of the macromolecules strongly increases as will be seen from the data on dynamic birefringence (Table 2)⁴. In comb-like polymers the rigidity of the main

Table 2. Number of monomer units in thermodynamic Kuhn segment ν , the segment anisotropy ($\alpha_1 - \alpha_2$) and the anisotropy of monomer units ($a_{\parallel} - a_{\perp}$) for some esters of polymethacrylic acid.

Polymer	ν	$(\alpha_1 - \alpha_2) \times 10^{25} \text{ cm}^3$	$(a_{\parallel} - a_{\perp}) \times 10^2 \text{ cm}^3$
Polymethyl methacrylate PMA-1	7.0	+2	+0.2
Polybutyl methacrylate PMA-4	6.7	-14	-2.1
Polyhexyl methacrylate PMA-6	8.6	-40	-4.6
Polyoctyl methacrylate PMA-8	7.9	-47	-5.9
Polyhexadecyl methacrylate PMA-16	19.0	-170	-8.9
Cetyl ester of poly- <i>p</i> -methacrylyl oxybenzoic acid PMOB-16	25.0	-2500	-100.0

chain increases and the orientational order in the side chains goes up due to the interaction of alkyl radicals. The most perfect intramolecular structures arise in the solutions of esters of polymethacryloxybenzoic acid, which contains sidegroups capable of forming liquid crystals. The negative segment anisotropy of the PMOB-16 macromolecules is already comparable with the anisotropy of crystal-like molecules. Evidently, in these systems, specific physical polymer network formation can occur even in dilute solutions. This phenomenon was indeed observed^{4,7} in a series of our researches with polyhexadecylacrylate, which was found to be a very effective structure inducer and medium modifier, particularly a modifier of low-molecular solvent. The unexpected role of small amounts of polymer additives as structure organizers of the liquid medium becomes very evident.

Such an effect can be observed clearly when one uses as solvent the substances according to their chemical nature analogous to the side branchings of comb-like polymers. Thus, solutions of PA-16 in *n*-aliphatic hydrocarbons $C_{10}H_{22}$ to $C_{16}H_{34}$ and *n*-aliphatic alcohols ($C_7H_{15}OH$ to $C_{12}H_{25}OH$) are capable of forming gels. The latter are stable within a wide temperature interval at extremely low (from the viewpoint of gel formation) polymer concentrations (0.30 to 0.35 per cent by weight)^{4,7}. In practice, the melting temperature of gels in alcohols does not depend on the length of the solvent molecule, being 28° for heptyl and dodecyl alcohol. In hydrocarbons there is a strong relationship of the T_m of gels with the number of carbon atoms in the solvent (13° for decane, 18° for dodecane and 26° for cetane). Crystallization of the solvent over a wide concentration interval does not

destroy the gel structure and the gel exists in the range between the melting point of the solvent and that of the gel. DTA analysis shows two characteristic endothermic peaks of melting which correspond to melting of the solvent and independently to that of the gel.

The gels of PA-16 in aliphatic alcohols are characterized by the high degree of order in the form of layer structures which can be detected by x-ray analysis. They have a sharp diffraction maximum d_1 at small angles of diffraction and its value is a linear function of the length of the solvent molecule (Figure 3). Simultaneously, with the transition from heptyl to dodecyl alcohol the decrease of intensity and the increase of diffuseness of this reflex is observed showing a growth in defects in the gel structure of higher alcohols.

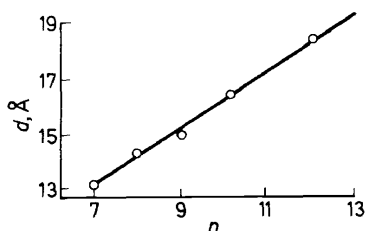


Figure 3. Interplanar distance d_1 (Å) in polyhexadecyl acrylate gels as a function of the aliphatic alcohol molecule length.

X-ray analysis of gels in these hydrocarbons has drawn attention to the absence of the d_1 period. In both cases the x-ray diagram has a diffractiional maximum corresponding to the interplanar distance of 4.5 to 4.6 Å. This maximum arises in gels independently from the number of carbon atoms in solvent molecules and it corresponds to the van der Waals interaction of methylene side chains. The melting of an alcohol gel is followed by disappearance of the d_1 reflex while preserving the d_2 reflex. The essential role in creating and stabilizing gel structure in aliphatic alcohols should be played by the hydrogen bonds between both solvent and polymer molecules because the addition of substances such as dimethylformamide results in the destruction of the gel.

The study of the temperature dependence of dielectric loss and dielectric permeability (Figure 4) for PA-16 in cetane has shown that in the interval from 20° to 30° there is a phase transition from gel to solution. The change of $\tan \delta$ and ϵ' in the region of their maximum values at various frequencies is typical for the relaxation process of dielectric polarization and testifies to the high mobility of structural elements in the gel.

The ordered state of gels, small value of heat elimination during the gel-solution transition, sufficient mobility of structural units in the gel—all this is characteristic of the liquid-crystalline (mesomorphous) state of the system of comb-like polymer with solvent. This state is close to that of the lyotropic liquid crystals which are formed on dissolution of several biopolymers (e.g. poly- γ -benzyl-L-glutamate) and low molecular substances in suitable solvents. Gels in alcohols being characterized by the layer structure can be

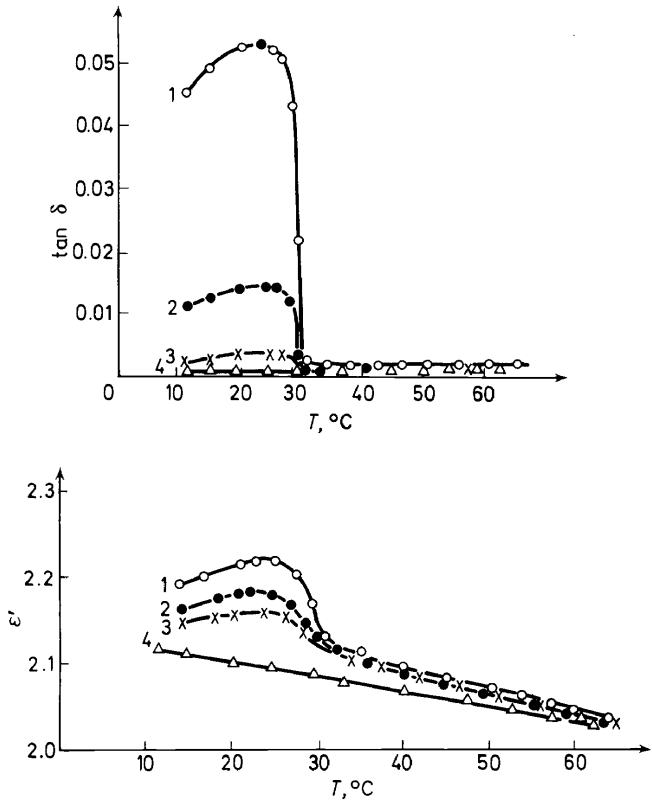
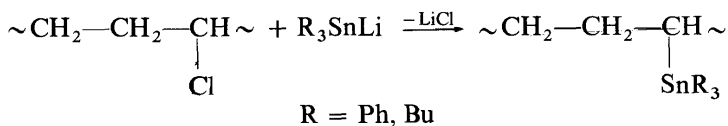


Figure 4. Temperature dependence of dielectric losses for PA-16 gels in cetane (1-3) and pure cetane (4) at the frequencies 800 (1); 5000 (2) and 10^4 (3) Hz.

considered as smectic liquid crystalline systems and gels in hydrocarbons without layer structure are close to the mesomorphic nematic type. The above-described ability of comb-like polymers to make association on intra- and inter-molecular levels shows that these polymers can be used as active structure-inducing agents. The specific structure of these branched polymers which combine the mobility of sidegroups with order in their arrangement facilitates consideration of this class of polymers as self-organizing systems towards their proper macromolecules as well as towards molecules of low-molecular solvents.

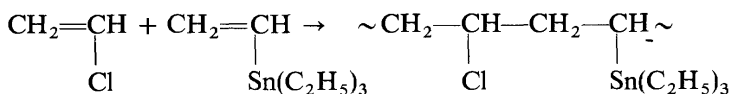
Another problem in the aspect under consideration is the relationship between physical and chemical methods of modifying polymer materials. One of the interesting questions is the introduction into the macromolecule of a particular chemical group which, being analogous to a known stabilizer, can behave as a stabilizer inside the macromolecule. In fact, it is the problem of macromolecular stabilizers or that of self-stabilized polymers. At the previous Bratislava Conference I reported on some possibilities of modification of halide-containing polymers with organotin compounds⁸. As a result

of such modifications one can successfully introduce the SnR_3 sidegroups into the polymer:



Such tin-containing polyvinylchloride possesses increased stability toward dehydrochlorination, having stabilizing groups in its macromolecules. This was one of the first examples of self-stabilized polymers obtained by reactions in the chain without further mechanical admixture of stabilizers.

But the special features and complications of chemical transformations with macromolecules (configurational, conformational and supermolecular effects)⁹ make the synthesis of derivatives of given structure difficult. An easier way to introduce analogous organotin groups into PVC is the radical copolymerization of vinyl derivatives of trialkyltin with vinyl chloride¹⁰:



The copolymer composition curve looks like that shown in *Figure 5* and $r_1 = 1.2 \pm 0.3$ (vinyl chloride); $r_2 \rightarrow 0$ (triethylvinyltin). The introduction of organotin monomer into the chain results in the decrease of dehydrochlorination to a constant value as well as causing modification of polyvinylchloride with trialkyltinlithium⁸ (*Figure 6*).

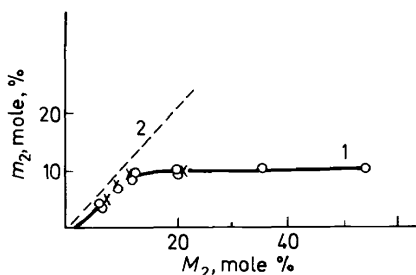


Figure 5. Copolymer composition curve of vinyl chloride and triethylvinyltin (m_2 —organotin monomer content in feed mixture; M_2 —organotin monomer unit content in the copolymer), measured as Sn (1) and Cl (2) contents in the reaction product.

The study of the mechanism of hydrogen chloride uptake by PVC organotin groups brought out certain features by comparison with the earlier known mechanism of dehydrochlorination of triphenyl- and tributyl-tin derivatives¹¹. The application of Mössbauer spectroscopy was very successful in elucidating the chemical scheme of the process. If for triphenyltin derivatives the two-step mechanism of phenyl group substitution by chlorine was established with subsequent rupture of the polymer-tin bond to form SnCl_4 , for tributyl derivatives the immediate formation of tributyltinchloride was observed, then with triethyl derivatives the first step

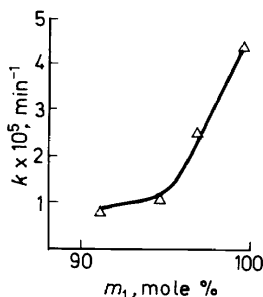
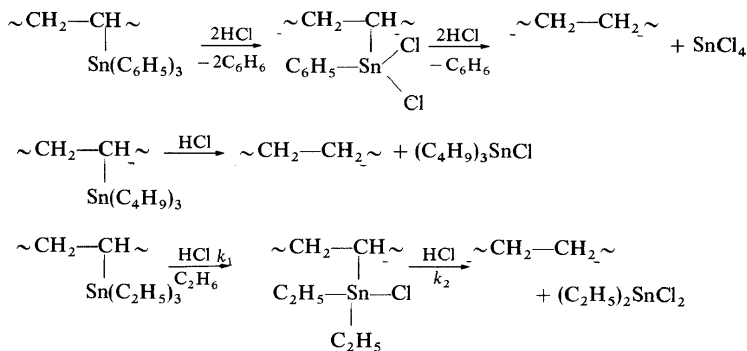


Figure 6. Dehydrochlorination rate constant k of the vinyl chloride-triethylvinyltin copolymers (m_1 —vinyl chloride content in the copolymer).

is substitution of one ethyl group on to chlorine followed by rupture of the polymer-tin bond with formation of diethyltinchloride. The ethyl group has an intermediate stability toward hydrogen chloride between those of the phenyl and butyl groups. All the reactions can be represented by *Scheme 1*¹¹:

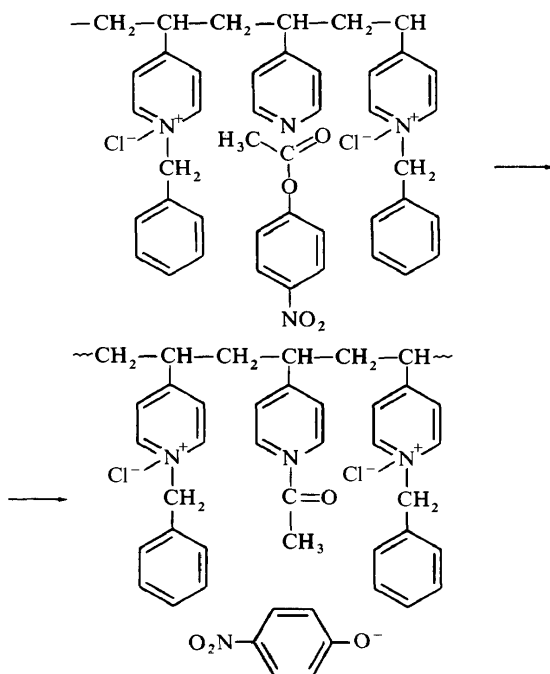


Scheme 1.

The main role in thermostabilization of an organotin derivative of PVC at low contents of the $\text{Sn}(\text{Et})_3$ group is played by the reaction of the ethyl group substitution with formation of organic tin monochloride as a side group in the polymer.

The role of chemically attached microadditives becomes especially important if one is dealing with biologically active polymers. We know very well how dramatic the consequences of chemical distortion in the case of enzymatic action can be. V. A. Kabanov and Yu. E. Kirsch have recently shown that synthetic models of proteolytic enzymes reveal exclusive sensitivity to chemical micromodification of the chain.

It has been found that poly-4-vinyl pyridine partially alkylated with benzyl chloride provides high catalytic activity in the hydrolysis of ester bonds (in *p*-nitrophenyl acetate, for instance) which is three to five orders higher than the activity of its monomeric analogue 4-ethyl pyridine. It is known that the catalytically active part is a non-alkylated pyridine nucleus playing the role of an active nucleophilic agent:



Such highly catalytically active polymers are only those polyvinyl pyridines which have a very specific and particular degree of substitution or a particular content of non-alkylated pyridine rings (α per cent). It has been discovered that the catalytic efficiency values v (the fraction of active pyridine rings over the whole amount of non-alkylated pyridine nuclei) have a sharp extreme character. For each molecular weight there is a maximum of catalytic activity at a definite value of α_{crit} (Figure 7). The interval of the sharp change

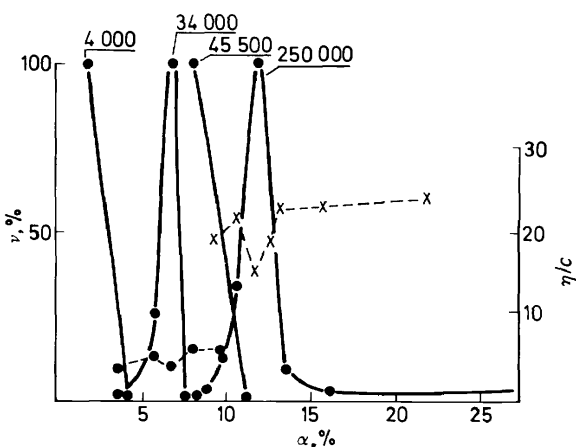


Figure 7. Catalytic efficiency v and solution viscosity of polyvinylpyridine catalyst as a function of the fraction of free pyridine nuclei (α).

of activity around $\alpha_{crit.}$ is very small and corresponds to between two and three per cent of alkylation. It seems that at the critical value of α a sharp conformational change takes place which results in the formation of 'active holes' consisting of free pyridine nuclei and side alkylated groups. The substrate nitrophenyl acetate is extracted into these active holes by the forces of hydrophobic interaction and reacting with pyridine as with a nucleophile to form nitrophenol and *N*-acetyl pyridinium. It has been shown that kinetic behaviour of these polymers is totally analogous to the behaviour of natural hydrolytic enzymes, e.g. α -chymotrypsin.

This example demonstrates that a small quantitative change in a macromolecule (one to two per cent in degree of alkylation) leads to a sharp qualitative shift in the properties following the principle 'Yes-No'.

The effects and reactions described above do not definitely fit all the possible pictures of the important role of micromodification of polymers. I am sure that such an approach will lead us to many other interesting results in both theory and practical application.

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