

Ellis Horwood Series in POLYMER SCIENCE AND TECHNOLOGY

CHEMICAL REACTIONS OF NATURAL AND SYNTHETIC POLYMERS

M. Lazár, T. Bleha, J. Rychlý



**CHEMICAL REACTIONS OF
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PREFACE

The systematic investigation of chemical reactions of macromolecules started by the successful empirical modification of natural materials such as leather, rubber and cellulose. Further development of macromolecular chemistry as a science followed the synthesis of various polymers which either replaced or complemented the existing spectrum of construction and protective materials.

Research interest nowadays is focused on the preparation of polymers with tailor-made properties; for such a purpose the chemical modification of properties of pre-existing macromolecular systems is sometimes the most effective way. Particular attention is thus paid to biopolymers in their biological functions and in modelling of artificial bioanalogous systems.

In textbooks of macromolecular chemistry, the chemical reactions of macromolecules are often eclipsed by the direct synthesis of polymers from low-molecular-mass monomers. Such a situation which has its rational and historical reasons prompted us to write a book devoted to chemical transformations of polymers. An attempt has been made to combine an introduction to the main principles of chemical reactions of macromolecules with an outlook to prospective developments of macromolecular chemistry as regards the enabling of more efficient technologies.

Our aim could not have been realized without the assistance of the staff of Publishing House Alfa, careful work of both reviewers prof. K. Veselý and dr. Z. Maňásek and without the support of colleagues from the Polymer Institute of Centre of Chemical Research, Slovak Academy of Sciences. We are especially grateful to Prof. T. J. Kemp, the editor of this English translation, for making innumerable constructive and helpful comments concerning both the language and the topic.

Authors

I. INTRODUCTION

Systematic investigation of the chemical reactions of polymers was initiated by the desire to improve the properties of natural materials, by such processes as the tanning of leathers the vulcanization of rubber and the etherification and esterification of cellulose. It seemed at first that the discovery of synthetic polymers would relegate the techniques of polymer modification to the periphery of research and applications. This did not happen however, since it was soon found that novel synthetic polymers may be produced by transformation reactions of macromolecules which feature properties hard to obtain by simple polymerization reactions of monomers.

Currently the topic of the chemical reactions of polymers as developed within macromolecular chemistry is relatively well-defined. It encompasses all reactions where macromolecular compounds act as starting materials. Specific transformations of functional groups in polymers taking place with minimal change in the degree of polymerization but with a distinct change of physico-chemical properties are termed "polymer-analogous reactions". In reactions leading to the destruction of polymers, the usually unwanted scission of the macromolecular backbone occurs by some physical perturbation or by attack of chemical reagents. The syntheses of graft and block copolymers and the reactions of polymer molecules leading to crosslinked polymers are also included in this overall category. The latter types of reaction require a relatively minor chemical intervention in the parent macromolecules and thus represent a modification of polymer structure at a quasi-supramolecular level. Minor and even reversible structural changes also take place in polymer catalysts. The reduced extent of chemical modification of the chains in these various processes does not imply however that such reactions are less important.

The types of chemical reaction of polymers outlined are universal for both synthetic and biological macromolecules. For example, the physiological fate of proteins *in vivo* is determined by a sequence of modification reactions. These are largely the enzymatically-controlled chemical modifications of the polypeptide

backbone and of the side groups, such as the formation of the disulphide linkage between the segments of a protein chain or its disruption, the linkage of carbohydrates to their side groups, the formation of crosslinking bridges between macromolecules or the scission of chemical bonds in the main chain. During the biosynthesis of collagen as many as ten stages of modification of the initial macromolecules have been identified.

Several polymer-analogous reactions such as preparations of cellulose derivatives, the chlorosulphonation of polyethylene, the saponification of poly(vinyl acetate) to poly(vinyl alcohol), the chlorination of poly(vinyl chloride), and the functionalization of polymer gels achieved industrial importance long ago. In these reactions, partial or even almost complete exchange of the original functional groups for a new ones takes place, and the final product has the character of a copolymer. Sometimes only a small number of the functional groups is incorporated into the macromolecule, displaying then specific physical, chemical or biochemical effects (to form polymer stabilizers, catalysts and drugs). The linkage of amino, sulphonato-, carboxylato- and phosphonato-groups to the polymer backbone is widely used practically in the production of ion-exchange resins. The alternative route involving the complete transformation of the functional groups, namely, the polymerization of the corresponding monomers, is sometimes complicated or even impossible.

The technology of processing polymer materials may also interfere with the direct synthesis of a polymer with desirable properties. For example, rubber products are initially formed to the required shape which is then fixed by subsequent vulcanization. Crosslinking is unavoidable in this case since natural rubber is a linear polymer. The crosslinking of synthetic elastomers also takes place as a subsequent process even though in this case the network structure could, in principle, be formed during their synthesis. However, the crosslinks fix the macromolecular structure to such a high degree that the final product cannot be fabricated by extrusion or moulding but only by cutting, latheing or other mechanical treatment. Economic grounds mean that such processing can be utilized only rarely.

The chemical transformations of polymers are aimed not only at broadening the spectrum of properties of conventional polymers but also to prepare the polymers for some specific purpose such as energy transducers, selectively permeable membranes, media of information storage, etc. This latter aspect, the preparation of speciality polymers and their applications, is very promising for the near future.

Knowledge of the mechanism and, in general, of the pattern of chemical reactions of functional groups in polymers enable us to control both desirable and unwanted processes in polymer materials. Finally, one has to proceed step-by-step in the clarification of the differences in the chemical transforma-

tions of biomacromolecules in the normal and pathological states of living bodies. Our understanding of these vital processes would have far-reaching and beneficial consequences for mankind.

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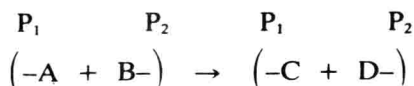
II. CHARACTERISTIC FEATURES OF CHEMICAL REACTIONS OF MACROMOLECULES

It is a common assumption in macromolecular chemistry that the reactivity of a functional group does not depend on the size of the molecule to which is attached. This assumption is essential for the kinetic analysis of polymerization reactions since a constant rate is postulated for the reaction of monomer with a growing chain regardless of its gradually increasing mass. As to the resulting macromolecules, it has indeed been verified experimentally that a functional group attached to a chain reacts with approximately the same rate as the same group present in small molecules. The functional group can be a part of each repeat unit of the polymer chain or may form only an occasional reaction site in the macromolecule.

At first glance it may thus appear that both the reactivity of a functional group in a polymer chain and the composition of the reaction products will be the same as in small molecules and do not require special study. It is known however that in reality numerous exceptions from the above rule exist, denoted by the general term the "polymer effect". The level of reactivity of the functional groups in macromolecules is connected with a more condensed and differently organized systems of reactants. The reactions of a macromolecular compound and of its low-molecular-mass analogue will probably follow a similar course when the reaction system is homogeneous, with a sufficiently large diffusional mobility of all reactants, intermediates, and products and when only one type of functional group reacts. However, the low molecular compound selected for comparison should mimic as far as possible the steric conditions on the polymer chain. The reduced diffusional mobility of macromolecules and steric hindrance to the approach of reagents to functional groups are frequent causes of a lower reaction rate in a macromolecular system. The polymer effect sometimes manifested in an enhanced reaction rate of a polymer reagent is a consequence of the specific primary, and especially secondary and tertiary structure of the polymer chain.

The largest reduction in reactivity of a functional group is observed in the

bimolecular reactions of mutually noncomplementary macromolecules. The reduced rate follows from steric and/or electrostatic hindrance to the reaction centre by the macromolecular backbones P_1 and P_2 . We can express this formally by the scheme



which should indicate both obstruction to the approach and to suitable juxtaposition of the reacting groups A and B. It is evident that arrangements with more accessible functional groups created, for example, by conformational transitions, should be more reactive.

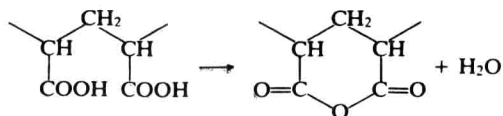
In the reaction between a macromolecular reagent and a low molecular compound, again, the shielding of a functional group by the chain may retard reaction. However, an opposing influence is also possible, namely the preferential inclusion of compound B into functional group A. This formal scheme can be applied to enzymatic reactions. In this case, however, the catalytic effect of the rest of the macromolecule involves not only the preferential inclusion of the reactant but also its proper orientation and cooperative activation by neighbouring groups.

The problem of the influence of the macromolecular chain is completely different in a monomolecular reaction

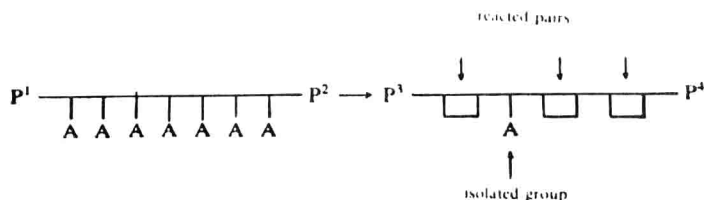


when the reaction can be faster or slower than a reference low-molecular reaction, depending on the compensation of the activation factors from the environment and the reduced mobility in the transition state.

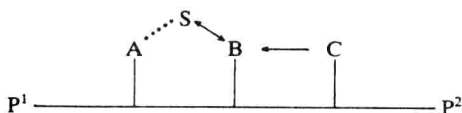
Macromolecular reactions can be classified as monofunctional and multifunctional depending on the number of functional groups on the chain entering in one reaction step. Monofunctional reactions includes many polymer-analogous reactions such as methylation, acetylation, halogenation or hydrolysis of a side group in the chain. In multifunctional reactions, generally two neighbouring groups are mutually transformed as in the formation of polymer anhydrides by cyclization, for example from poly(acrylic) acid



A lower degree of conversion is achieved in multifunctional reactions as compared to the corresponding reactions of low-molecular-mass compounds. The difference results from the random siting of functional groups during reaction;

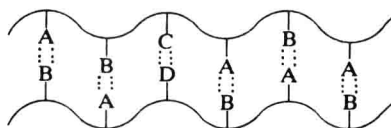


isolated groups lacking an active neighbour cannot react. Multifunctionality is also typical of enzyme catalysis. By means of the multifunctional cooperation of the functional groups and the reacting substrate S



the substrate is bound by intermolecular forces to group A so that the time of contact increases and a suitable orientation of the neighbouring reacting group B, activated by group C is ensured. The rigidity of the carrier of the functional groups promotes the selectivity of reaction.

The specificity of a multifunctional reaction can be enhanced by the mutual complementarity of segments of two rigid macromolecules due to the physical interaction of groups A and B



Due to this attractive interaction, a close approach of the reacting groups C and D is achieved and spontaneous reaction takes place.

A comparison of the reactivity of a given functional group in polymers prepared by various methods is affected by the distribution of the defect centres along the macromolecular chain that is hard to detect by conventional analytical techniques but which could be significant for the reactivity of the chain. The various low-molecular additives, impurities, and residues of initiation systems could all have similar effects on reactivity as defects in the constitution of