SURFACE TRANSFORMATIONS OF POLYMERS

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ABSTRACT

Polymeranalogous transformations due to the treatment of a compact polymer phase with liquid or gaseous agents lead—depending on the ratio of the diffusion penetration rate of the agent to the reaction rate—to more or less inhomogeneous products having a higher conversion on the surface than in the lower polymer layers.

In some cases the above finding can be used for the preparation of laminated structures having certain advantages compared to similar systems obtained by coating the polymeric substrate with a film of a different polymer.

The most important group has so far been represented by transformations of this type so chosen as to obtain thin layers exhibiting a specific chemical or biological activity on an inert substrate whose function is purely mechanical. Besides substitution transformations of hydrocarbon polymers by which e.g. ionizable groups are introduced, these reactions also involve chemical transformations of typical functional groups attached to a stable polymeric matrix. The foremost position in the latter category is held by acrylic and methacrylic polymers and copolymers in which it is possible to alter either the functions derived from the carboxylic group or functional groups attached by means of the ester or amide link.

The introduction of strongly hydrophilic groups into the surface of hydrophobic linear polymers may lead to their release from the substrate. This may be prevented by introducing crosslinks via polyfunctional reaction components simultaneously with the hydrophilization transformation. Such a precaution is not necessary for crosslinked polymers whose crosslinks resist chemical agents. Among these polymers a special role is played by macroporous gels, the large internal surface of which may be modified in many ways by chemical reactions of the functional groups.

When solid polymers react with agents which do not dissolve the original polymer or its reaction product the polymer surface remains macroscopically undamaged and the chemical transformation of the polymer proceeds continuously from the surface into the bulk. The thickness of the layer transformed, or more exactly the dependence of conversion on the distance from the surface, is determined by the rate of diffusion of the agent, the rate of its reaction with the polymer and the time of action of the agent. In any case, however, the transition from maximum conversion on the polymer surface to zero conversion in the unaffected bulk of the polymer is a continuous one. In this way the laminar structures obtained are funda-

mentally different from those arising by coating the polymeric substrate with foreign polymer layers. Obviously, such operations make sense only for polymers which have been subjected to definitive shaping, or for polymer fibres and films.

The scope of this Symposium envisages only such surface transformations which may be called 'chemical transformations of functional groups'. We therefore shall not be dealing here with by far the most extensive, and perhaps most important group of surface polymer treatments consisting in the grafting of a foreign polymer onto a polymeric substrate. It would not fit in with the conventional terminology to designate sites on which the graft starts growing as functional groups, and to classify the grafting itself as a chemical transformation of these groups. Moreover, the nature of grafting consists rather in the addition of a new polymer than in a functional transformation of the original polymer.

I shall here make a marginal remark about the transformations of polymers which do not contain any typical chemical functional groups and in which such groups only just start being formed due to treatment with extremely strong agents. Thus, for instance, even the very inert polytetrafluoroethylene may be modified on its surface by treating it with alkali metal solutions in liquid ammonia, whereby fluorine atoms are eliminated from the surface molecules and conjugated double bond sequences are formed owing to the zip character of the reaction[1]. The surface of a polymer thus prepared is then characterized by a greater adhesion to other materials and to surface-deposited metals. Polyethylene may be surface hydrophilized by treating it with chlorosulphonic acid[2] which introduces into the surface layer sulphonic, sulphoester, hydroxyl, carbonyl and carboxyl groups and double bonds[3]. Similarly, chromosulphuric acid introduces into the surface of polyethylene hydroxyl and carboxyl functions[4]. If the latter reaction is carried out at room temperature and by a short immersion, then—although the transformation of the extremely thin superficial layer may hardly be detected analytically— the adhesion of polyethylene treated in this manner to the hydrophilic films coated on it strikingly improves[5]. The surface layers of polymeric hydrocarbons may also be modified by the incorporation of highly reactive electron-deficient torsos, such as carbenes and nitrenes[6]. The substitution reaction of aromatic hydrocarbon polymers may also be restricted to their surface layers if the penetration of the agent into the polymer is slowed down. A comparative study concerning the localization of sulpho groups in the copolymer styrene–divinylbenzene according to the reaction conditions will also be presented at this meeting[7].

A continuous transition of the chemically modified surface layer into the unchanged substrate allows us to obtain mechanically stable structures by the transformation of typical functional groups even in the case of a very drastic change of properties of the surface layer. A typical example can be seen in the surface hydrolysis of poly(methyl methacrylate) combined with the crosslinking reesterification of a polyhydric alcohol[8]. The final product of this transformation is a loosely crosslinked polymer of methacrylic acid, which, particularly in the form of a neutral alkaline salt, is swollen by water to several times its dry value. In spite of this, such a strongly swollen surface layer remains safely connected with the completely unswollen poly(methyl

methacrylate) substrate even in the neutral aqueous medium; if the surface layer is not much thicker than about 100 μm, it resists even comparatively brutal abrasion. It is not possible to find a sharp boundary between the hydrolysed and undamaged substrate by removing the maximally swollen surface layer, although the transition between the fully hydrolysed and unchanged fraction is concentrated in a comparatively thin intermediate layer. Owing to the low reactivity of the polymethacrylic ester group the above reaction requires very drastic conditions: to attain a thickness of tens or hundreds of micrometres of the hydrolysed layer, it is necessary to treat the surface of poly(methyl methacrylate) during e.g. one minute by a mixture of concentrated sulphuric acid and glycerol in the ratio 1:4 at 100–115°C.

Shaped objects made from polyacrylic polymers may be modified similarly, but under considerably milder conditions. A special importance is assigned to the surface hydrophilization of the block copolymers of acrylonitrile and acrylamide obtained by the zip hydrolysis of polyacrylonitrile[9]. These polymers, which if swollen with water are elastomers of excellent mechanical properties, may be further hydrolysed by immersing them in a mixture of sulphuric acid and polyhydric alcohol for a short time with simultaneous loose crosslinking, thus obtaining extremely hydrophilic surface layers of the polyanionic gel[10].

If cellulose esters, e.g. triacetylcellulose films, are treated with sulphuric acid, a narrow range of experimental conditions may be found under which there is no visible corrosion of the surface, but the surface is nevertheless strongly hydrophilized, probably as a consequence of the reesterification substitution of the acetoxyl groups with acidic sulphoester groups. This is reflected in a marked antifogging effect and affinity to dyes[11].

Three-dimensional polymeric systems are particularly suited for such surface substitutions if their crosslinks remain unperturbed during the reaction. If, for example, shaped objects made from the hydrophilic loosely crosslinked 2-hydroxyethyl methacrylate gel are exposed on drying to the vapours of sulphur trioxide, the hydroxyl groups in the thin surface layer are transformed into sulphoester groups[12]. On equilibrium swelling in water the resulting enhanced hydrophilic nature and negative ionic charge of the surface layer produce, for example, reduced friction in contact with living tissues.

A special group of the surface reactions of polymers is represented by their reversible transformations which allow the regeneration of the original polymer and whose value consists in an interruption of the ordering of macromolecules in the surface layer, thus enabling a new order to be established during regeneration. An example can be seen in the treatment of a polyamide fibre with iodine followed by the regeneration of macromolecules with thiosulphate in a different crystalline arrangement, which is supposed to give the fibres an increased adhesion to deposited metals[13]. The surface crystalline structure of polyamide fibres may also be disturbed by a short-term exposure to the vapours of strong acids, e.g. hydrogen chloride, or to solutions of strong acids in nonpolar solvents[14]. The crystalline structure can then be regenerated in a modified form by neutralization; the fibres which were in contact in the acidic cycle remain strongly connected and as

if welded after neutralization. This fact could be used for the preparation of some textile structures.

Typical functional changes concerning exclusively the polymer surface are represented by chemical bonds of biologically active compounds on polymeric carriers. Despite the great variety and importance of such surface reactions we shall not be dealing with them now, since they were dealt with at a recent conference in Prague. Let us only recall that it may also be useful to direct to the polymer surface those transformations which lead to carrier synthesis. It should be borne in mind that the homogeneous distribution of ligand groups or their precursors need not always be in accordance with the final requirements of the carriers of biological polymers. What we require from these carriers are two more or less opposite properties: (i) high modulus of elasticity, i.e. a rigid structure which is in the first place determined by a limited degree of swelling in the medium used, and (ii) the highest possible mobility of the specifically reactive groups attached to the surface which is above all aided by the high degree of swelling of their surroundings. Better than by applying a compromise, i.e. a uniform carrier structure, this conflict may be resolved by the maximal possible fulfilment of these requirements in two domains of the carrier, i.e. in its rigid skeleton and in its surface, the chemical functions of which may be varied without jeopardizing the good mechanical properties of the whole system to any essential degree. In this respect, there seems to be a wide scope of applications of macroporous gels which, besides possessing a widely adjustable porosity and good mechanical properties, also contain chemical functions able to undergo a number of surface chemical transformations. Macroporous glycol methacrylate gels may be cited as an example of such widely modifiable prefabs for the preparation of specific carriers. If they are treated in the dry or slightly swollen state with agents in which gels do not swell, various substitution transformations of the hydroxyl groups may be carried out, preferentially on the internal surface of the macroporous gel. Thus, by treating the gel with gaseous phosgene or solutions of the latter in nonpolar solvents, chloroformate groups may be formed on the surface of this gel which can become the site of further chemical transformations[15]. By treating the gels with phosphoryl-chloride and pyridine in vapours or inert solvents, it is possible to achieve phosphorylation of the surface groups; by treating these groups with vapours of sulphur trioxide, they may be transformed into acid sulphuric acid esters. These and similar reactions do not lead to any changes in the internal rigid structure of the gel, although new functional groups arise on its surfaces, which if uniformly distributed throughout the bulk of the polymer could cause some undesirable swelling effects.

In conclusion, I should like to summarize the practical goals of the surface transformations of polymers. They are as follows:

(i) Modification of the surface of a plastic for a better adhesion of foreign polymeric films coated on it.

(ii) Creation of functional layers on polymer carriers; these functions may be mechanical (lowering of surface friction or drag reduction), sorptional (chromatography, antifogging treatment), increased affinity to dyes, fixation of biological materials or synthetic catalysts, improved tolerance of plastics to the biological medium.

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It seems that the latter possibilities of application are the strongest stimuli for taking an interest in improving our mastery of this technique. We are particularly attracted by the hope that the surface treatment of some mechanically satisfactory materials would allow us to attain antithrombogenic properties which so far have been lacking in all the known synthetic materials. We have in mind the surface fixation of heparinoid structures which would prevent blood clotting in a similar way to surface-bonded heparin, but which in contrast with the bonded natural heparin would resist heparinase or other enzymes of the blood medium. The progress already achieved by the introduction of anionic structures with a high degree of swelling of the surface layer is encouraging, although we are fully aware how far we still are from the accomplishment which would allow the chemists to lay safe foundations for alloplasty of the blood system and organs bound to blood circulation.

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