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THE RADIOCHEMICAL PREPARATION OF ION-EXCHANGE MATERIALS

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The preparation of ion-exchange materials under the influence of ionising radiation is one of the few radiochemical processes which has found definite practical application. Thus homogeneous ion-exchange membranes have been obtained by grafting certain monomers on to various polymer-carriers under the influence of radiation[1-9]. These membranes have distinct advantages over those prepared by ordinary chemical methods. Moreover, ion-exchange resins prepared by the radiochemical method are in a number of instances not only better, but also cheaper, than ordinary standard ion exchangers[10].

The methods of radiation polymerisation, copolymerisation, and grafting have recently become fairly widespread, since they make it possible to prepare materials which differ from ordinary materials in their high purity, improved physicomechanical characteristics, and other valuable properties influencing their performance.

Grafting under the influence of radiation makes it possible in certain instances to obtain graft copolymers whose preparation is difficult or impossible by ordinary chemical methods. These copolymers can be used to prepare ion-exchange membranes with high mechanical strength, high selectivity, and low electrical resistance. All these features are responsible for the considerable interest in the radiochemical preparation of ion-exchange resins, the progress made in this field, and methods for its further development.

1. MEMBRANES

Most ion-exchange membranes are based on graft copolymers, so that it is convenient to examine briefly radiochemical methods for their preparation, and also the advantages and disadvantages of graft copolymers prepared under the influence of radiation, relative to ordinary copolymers.

The main radiochemical methods for the preparation of graft copolymers are as follows[11-26]: (*a*) direct grafting by irradiation of the polymer–monomer system; (*b*) grafting on to a polymer which is irradiated in a vacuum and then brought into contact with the monomer; (*c*) grafting on to a polymer irradiated in air with heating in a medium of the monomer; (*d*) intermolecular cross-linking of two polymers in the solid state, molten state, or solution; (*e*) grafting by the irradiation of emulsions or suspensions consisting of two polymers, or a polymer and a monomer; and (*f*) grafting under the influence of localised neutron irradiation.

It should be noted that in the preparation of graft copolymers by any of the above methods, block copolymers are also formed. As a rule, however, the relative quantity of block copolymers is extremely small; moreover, it is often impossible to decide whether a given copolymer should be described as a block copolymer or a graft copolymer[12,17]. The separation of block and graft copolymers also involves considerable methodological difficulties[27].

The efficiency of radiochemical grafting is determined by many factors, such as the nature of the polymers and monomers, the integral dose, the dose rate, temperature, the dimensions of the specimens being irradiated, the degree of crystallinity and phase state of the polymers, the rate of diffusion of the monomers in the polymers, the compatibility of the polymers making up the graft copolymers, the ability of the polymers to undergo swelling in the monomers, etc. The dependence of the rate of formation of graft copolymers on the above factors is so complex and varied that we can indicate only a few of the most general regular features, which may prove useful in an examination of problems related to the radiochemical preparation of ion-exchange membranes.

The preparation of graft copolymers by method (*a*) is at present the most widespread. The efficiency of the grafting is here determined chiefly by the quantity G_p/G_m where G_p/G_m are the yields of radicals on irradiation of the polymer and monomer respectively. The greater this quantity, the smaller the quantity of homopolymer formed. In this respect, the best system is the polyethylene–styrene system, for which $G_p/G_m \simeq 2-10$. The chief disadvantage of method (*a*) is that a large quantity of homopolymer is usually formed. The greater part of the ion-exchange membranes prepared by the radiochemical method are obtained, however, by this method.

One version of method (*a*) is vapour-phase radiochemical grafting, in which a large quantity of homopolymer is not formed[28-37]. Moreover, this method makes possible efficient grafting even when the quantity G_p/G_m is less than unity. The method of vapour-phase radiochemical graft polymerisation eliminates completely the possibility of capillary condensation in the pores and thus makes it possible to carry out grafting not only on organic polymers, but also on inorganic carrier-supports[28-34].

In grafting by method (*b*), almost no homopolymer is formed, but the rate of grafting is low, since the greater part of the macroradicals are destroyed on heating before they are able to initiate graft polymerisation. This method is seldom used to obtain ion-exchange membranes.

Method (*c*) is usually employed for surface grafting. By using sufficiently thin films and low irradiation dose rates, however, it is possible to introduce oxygen-containing groups throughout almost the entire volume of the polymer, and hence to achieve more or less uniform grafting. The disadvantages of the method include a slight deterioration in the physicomechanical properties of the carrier-polymer as a result of its radiochemical oxidation, and also the formation of an appreciable quantity of homopolymer under the influence of the $\cdot OH$ radicals produced by the thermal decomposition of polymeric hydroperoxides. It is possible, however, to avoid formation of the homopolymer by carrying out the decomposition of the hydroperoxides and the grafting in the presence of iron(II) salts[38]. This prevents the formation of the $\cdot OH$ radicals which inititate the homopolymerisation:

$$ROOH + Fe^{2+} \rightarrow RO\cdot + Fe^{3+} + OH^-.$$

Method (*c*) is fairly frequently used to obtain ion-exchange membranes.

Method (*d*) is usually characterised by low yields of block and graft copolymers, and involves considerable methodological difficulties. Attempts have been made to use this method to prepare ion-exchange membranes[26,39,40], but because of the high integral doses (500 Mrad) and highly brittle nature of the product, these materials are significantly inferior to membranes prepared by methods (*a*) or (*c*).

Methods (*e*) and (*f*) are usually characterised by a high selectivity of graft (or block) copolymer formation, accompanied in most instances by only slight homopolymer formation. Nevertheless, these methods have not found practical application, not only in the preparation of ion-exchange membranes but also in the chemistry of graft copolymers in general, because of the marked experimental difficulties.

The problem of chemical bond formation during grafting is of considerable importance for the quality of membranes prepared by the radiochemical method. The chief method for detecting the presence of graft copolymers involves extraction of the homopolymers with suitable solvents. When the molecular chains of two different polymers are closely intertwined, however, removal of one of them by means of solvents may be impossible[41]. This forms the basis of the preparation of inter-polymer membranes, which have found extensive application in laboratory studies[42-44].

A more reliable method for the identification of graft copolymers is by fractional precipitation of the individual components from solutions containing a mixture of the homopolymers and graft copolymers[45,46]. This method has been used to prove the formation of a poly(ethylene-graft-styrene) system, which subsequently formed a basis for the preparation of membranes containing $-SO_3H$ and $-CH_2N^+(CH_3)_3$ groups, with improved properties influencing performance[47]. Methods which can be used in addition to fractional precipitation and selective extraction include the following[48,49]: fractional dissolution, selective precipitation, turbidimetric titration, adsorption chromatography and elution, ultracentrifuging, etc. In most work on the radiochemical preparation of ion-exchange membranes, however, these methods are not used, and the presence of graft copolymers is usually established merely on the basis of data obtained by selective extraction.

The radiothermoluminescence method[50-52] can apparently be used in certain instances to detect the presence of chemical bonds in graft copolymers.

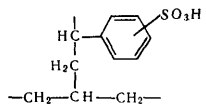
The quality of membranes based on graft copolymers should be higher than that of membranes prepared from a mixture of homopolymers. These membranes have a greater homogeneity and uniformity of composition, higher chemical resistance and mechanical strength, and superior ion-exchange and electrochemical characteristics. For a given quantity of graft polymer, the properties of the system, particularly its homogeneity, will generally be better, the shorter the graft chains. Non-uniformity is one of the main disadvantages of ion-exchange membranes based on graft copolymers.

The distribution of a graft polymer within the volume of a carrier-polymer can be estimated by a microinterferometric method[53]. The superior properties of membranes prepared by the radiochemical method, and their greater uniformity compared with ordinary membranes may be due to the greater probability of formation of true graft copolymers during irradiation, compared with chemical initiation.

As already noted, the chief disadvantage of both ordinary membranes and membranes prepared under the influence of radiation is non-uniformity of composition. This may be due to the presence of amorphous and crystalline regions or regions with different degrees of orientation, and also to the varied supermolecular structures of the polymers on to which the grafting is carried out. Such important factors, determining the efficiency of graft polymerisation, as the yield of radicals, the degree of swelling, the rate of diffusion of the monomers, the reaction rate constants for termination of the growing polymer chains, and various others, differ significantly in the crystalline and amorphous regions. In most instances, the rate of grafting on amorphous polymer specimens is high, and the copolymers obtained are fairly homogeneous, but the generally unsatisfactory physicomechanical properties of these products prevents their extensive application. The degree of crystallinity may change during grafting; for example, it sometimes decreases with increase in the quantity of graft polymer[54]. For each specific system, there apparently exists a definite degree of crystallinity at which membranes with optimal physicomechanical and electrochemical properties are obtained. Studies in this direction are still in the initial stages.

When ion-exchange groups are introduced into a graft copolymer, its non-uniformity may increase. The formation of hydrophilic and hydrophobic regions in the membranes is accompanied by partial separation into layers, a decrease in selectivity, and an increase in the water-permeability of the membranes. The probability of this undesirable process is much smaller, however, for membranes prepared by radiochemical methods, and this ensures satisfactory properties influencing performance.

Most studies of the radiochemical preparation of cation-exchange membranes have been carried out using the poly(ethylene-graft-styrene) system. Direct irradiation, with ^{60}Co γ-radiation, of polyethylene films immersed in liquid styrene, followed by sulphonation of the poly(ethylene-graft-styrene) system with sulphuric or chlorosulphonic acids and subsequent hydrolysis with alkali has been used to prepare strongly acidic homogeneous membranes[9,40,47,55-64], apparently having the following structure:



The efficiency of grafting is increased considerably by preliminary vacuum-treatment of the polyethylene–styrene system[40,57] or by irradiation of the system in an atmosphere of nitrogen[47,58].

It has been shown[7,9,40,56] that the optimal quantity of polystyrene in the graft copolymer should not exceed 20–40 wt. %. Membranes containing more than 50 wt. % polystyrene, despite their low specific volume electrical resistance, are too brittle, and unsuitable for prolonged use.

To obtain copolymers with a high polystyrene content, a small quantity of divinylbenzene is sometimes added to the styrene; this decreases considerably the degree of swelling of the resulting membranes and improves their physicochemical properties[56,57].

To obtain homogeneous membranes, the styrene is grafted on to polyethylene powder, film, or granules, and the graft copolymers are then subjected to hot rolling. It is claimed[62] that this method has certain advantages over those described above, since it gives fairly homogeneous membranes, and this is extremely important not only in the radiochemical but also in the ordinary methods of preparation.

In all the work cited above[9,40,47,55-64], the irradiation was carried out at dose rates in the range 4–100 rad s^{-1}. The integral doses required to obtain graft copolymers with optimal composition varied from tenths of an Mrad to several Mrad.

The membranes obtained had the following characteristics: capacity 1.5–2.5 mg-equiv. g^{-1}; resistivity 50–200 Ω cm; selectivity 97–98%; and tensile strength 100–200 kgf cm^{-2}. The membranes were characterised by improved properties influencing performance. For example, the energy consumption for the desalination of water by electrodialysis was less for membranes prepared by the radiochemical method than for membranes prepared by ordinary methods (Fig. 1).

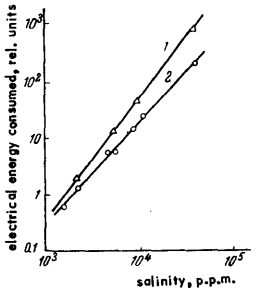


Fig. 1. Desalination of water. Dependence of the consumption of electrical energy on the salinity of the water[47]: 1) for ordinary membranes; 2) for membranes prepared by the radiochemical method.

The efficiency of grafting was greater for high-density polyethylene[45,55] and when thicker films were used[40,45,55,65]. This may be due to a decrease in the reaction rate constant for bimolecular termination of the growing polymer chains or to a change from bimolecular termination to linear termination under these conditions.

The presence of stabiliser (diphenylamine) in the polyethylene film decreases the yield of graft copolymer and the efficiency of grafting[40]. It is therefore better to use non-stabilised polyethylene film.

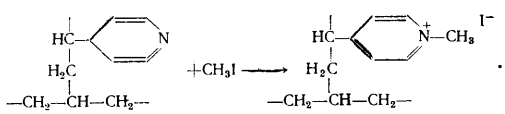
The addition of other monomers, for example acrylonitrile (10–20 wt. %), sometimes increases the elasticity of the membranes considerably. Thus a sulphonic acid membrane based on the poly[ethylene-graft-(styrene-co-acrylonitrile)] system is elastic even in the dry state, whereas the analogous membrane based on poly(ethylene-graft-styrene) can be kept only in the swollen state[59].

Certain solvents, in particular methanol, increase considerably the efficiency of graft polymerisation and make it possible to decrease significantly the doses required to achieve the optimal degree of grafting[59,66].

Some data[40,55] indicate an increase in the efficiency of the grafting of styrene on to polyethylene with decrease in temperature, but other results[14,41] indicate the opposite. In the preparation of ion-exchange membranes, there is evidently in each specific instance an optimal temperature, determined by many of the parameters characterising the system being irradiated.

A number of anion-exchange membranes containing quaternary ammonium groups[47,55,56,61,62] or secondary and teriary amino-groups[61] have been prepared from poly(ethylene-graft-styrene) systems obtained by direction irradiation. The first stage usually involves chloromethylation with mono-chloromethyl ether at the boiling point in the presence of tin(IV) chloride as catalyst and this is followed by amination by heating with a 25% solution of trimethylamine in methanol[47]. These membranes have the following characteristics: capacity 1.5–2 mg-equiv. g^{-1}, resistivity 100–200 Ω cm, selectivity 95–97%, and tensile strength 150–300 kgf cm^{-2}.

Weakly basic and weakly acidic membranes can be prepared by grafting monomers such as 4-vinylpyridine[7,56,64] or acrylic acid[57] on to polyethylene. Treatment of the poly(ethylene-graft-4-vinylpyridine) system with alkylating agents leads to the formation of strongly basic membranes[7,56,64]:



Macromolecular compounds other than polyethylene can also be used as carrier-polymers for the preparation of membranes. Methods have been described for the preparation of membranes based on poly(vinyl chloride-graft-styrene)[57], poly(tetrafluoroethylene-graft-styrene)[57,61], poly[(ethylene-co-propylene)-graft-styrene][59], poly(tetrafluoroethylene-graft-acrylic acid)[67,68], and poly(tetrafluoroethylene-graft-4-vinylpyridine)[67,68] systems obtained by direct irradiation. When the polymer does not undergo swelling in the monomer (polytetrafluoroethylene–styrene), satisfactory results are obtained by periodic irradiation[57]. In this way it is possible to achieve a high degree of grafting throughout the entire volume of the polymer. The direct action of ^{60}Co γ-radiation on polytetrafluoroethylene film in aqueous acrylic acid solutions containing $FeSO_4$ as homopolymerisation inhibitor made it possible to graft 10–20 wt. % polyacrylic acid[67,68]. These films had a high homogeneity, underwent uniform swelling in water, and were suitable for use as cation-exchange membranes.

Weakly acidic and strongly basic membranes[69-71], with excellent properties influencing performance, were prepared by grafting methyl methacrylate, ethyl acrylate, and acrylonitrile from the vapour phase on to polyethylene films, followed by alkaline hydrolysis of the ester and nitrile groups to carboxylate groups, or by grafting 4-vinylpyridine and 2-methyl-5-vinylpyridine, followed by alkylation of the products. The grafting was carried out at room temperature in the absence of atmospheric oxygen under the influence of ^{60}Co γ-radiation, at a dose rate of 2 rad s^{-1}. The doses required to achieve extensive degrees of grafting did not exceed 1 Mrad. Thus irradiation with a dose of 0.4 Mrad was sufficient to give poly(ethylene-graft-4-vinylpyridine) containing 70% graft poly(4-vinylpyridine). The capacity of this membrane after alkylation amounted to ~ 4 mg-equiv. g^{-1}.[69]

The method of vapour-phase radiochemical grafting was used to prepare copolymers based on polyethylene powder (100 mesh), which was irradiated with ^{60}Co γ-radiation at 0.5 rad s^{-1} or with a beam of accelerated electrons at 6×10^4 rad s^{-1} at 80°C in the presence of the vapours of methyl acrylate, ethyl acrylate, 4-vinylpyridine, 2-methyl-5-vinylpyridine, styrene, and vinyl acetate[72,73].

The efficiency of grafting for equal doses was greater when γ-rays were used than when a beam of accelerated electrons was used. The degree of grafting decreased in the following order: methyl acrylate > styrene > ethyl acrylate > 4-vinylpyridine > 2-methyl-5-vinylpyridine > vinyl acetate. These graft copolymers were then converted at 120°C and a pressure of 200 kgf cm^{-2} into films with thickness 0.1–0.2 mm. Treatment of poly(ethylene-graft-4-vinylpyridine) and poly(ethylene-graft-2-methyl-5-vinylpyridine) films with a $CH_3I + CH_3NO_2 + (CH_3)_2CO + C_2H_5OH + O(C_2H_4)_2O$ mixture gave membranes of the quaternary pyridinium type with a capacity of ~ 2 mg-equiv. g^{-1}. Sulphonic acid membranes were prepared by sulphonating poly(ethylene-graft-styrene) with conc. H_2SO_4 in the presence of Ag_2SO_4 at 30–100°C. Carboxylic acid membranes were prepared by hydrolysing poly(ethylene-graft-methyl acrylate) and poly(ethylene-graft-ethyl acrylate) with a 1 *N* solution of KOH in alcohol. In almost all instances the functional groups of the graft copolymers were converted almost completely into ion-exchange groups. Copolymers with a very low concentration of the graft polymer were an exception.

It has been noted[60,74-77] that membranes with a high uniformity of composition cannot be obtained by direct grafting. Uniformity is achieved by preliminary radiochemical oxidation of the polymer, followed by grafting with heating†.

The method of preliminary irradiation of the polymer in a vacuum or in an atmosphere of an inert gas, followed by treatment of the irradiated product with monomer, has also been used to prepare ion-exchange membranes[60,77-80]. Thus irradiation of polyethylene film by ^{60}Co γ-rays in an atmosphere of nitrogen (integral dose 0.3 Mrad, dose rate

† It has also been noted[40], however, that the peroxide method is unsuitable for the preparation of a graft copolymer with a sufficiently high degree of grafting.

60 rad s^{-1}) followed by heating at 40°C in styrene gives a graft copolymer containing up to 30% polystyrene. Subsequent treatment of this film with chlorosulphonic acid and alkali gives a fairly uniform membrane with a capacity of 1.6 mg-equiv. g^{-1} and resistivity 250–300 Ω cm.[60] By altering the conditions of irradiation and grafting, it is possible to prepare membranes with varied physicochemical and physicomechanical properties.

Irradiation with ultraviolet light has also been used to obtain block copolymers for the preparation of ion-exchange membranes[81-83]. Thus the copolymerisation of dibutyl vinylphosphonate and acrylic acid has been carried out under the influence of ultraviolet light. This copolymer was dissolved in alcohol, a cross-linking agent (triallyl cyanurate) was added, and the solution was used to prepare a film, irradiation of which gave a membrane which was insoluble in water but underwent swelling to the extent of 10–40%, and had a capacity with respect to Fe^{3+} equal to 9–12 mg-equiv. g^{-1}.[82] Membranes with satisfactory properties influencing performance were obtained by ultraviolet irradiation of systems containing butyl vinyl sulphonate, vinyl acetate, and ethyleneglycol dimethacrylate[83] or salts of styrenesulphonic acid and acrylic or methacrylic acids[81].

Irradiation with accelerated electrons (dose 5 Mrad) of glass fibre in a solution containing ethyl acetate, polyethyl acrylate, and divinylbenzene[9,84] was used to prepare a reinforced homogeneous membrane. The ester groups were hydrolysed with concentrated alkali solutions.

Membranes obtained by the copolymerisation of styrene and tetrafluoroethylene have particularly high mechanical strength, chemical resistance, and heat resistance[9,61]. Ion-exchange groups are introduced into these membranes by the usual methods.

In the preparation of ion-exchange membranes, the use of radiation is not restricted to the initiation of block and graft copolymerisation. There are data indicating the promising possibilities of using radiation for the formation of three-dimensional insoluble structures containing ion-exchange groups[85]. Thus the irradiation, with ^{60}Co γ-rays (dose 10 Mrad), of films of a copolymer of styrene and butadiene, followed by treatment with conc. H_2SO_4, gave homogeneous membranes of fairly high quality[9,86]. The irradiation, by ^{60}Co γ-rays (dose 30–150 Mrad) and accelerated electrons (dose 150–500 Mrad), of block copolymers of salts of styrene sulphonic acid and acrylic acid was accompanied by the formation of membranes with a capacity of 3–10 mg-equiv. g^{-1}, which were insoluble but underwent swelling[81]. As already noted, the preparation of membranes by the irradiation of a mixture of polyethylene and polystyrene is not promising, because of the high values of the integral doses and the poor physicochemical characteristics of the membranes[40,87]. The same disadvantages are shown by membranes obtained by sulphonating polystyrene films, cross-linked by irradiation[88].

Irradiation of heterogeneous ion-exchange membranes may improve their properties. Thus the durability of membranes based on KU-2 resin‡ and polyethylene is increased by irradiation[40]. Radiochemical vulcanisation is a fairly promising process for heterogeneous membranes consisting of ion-exchange resins and rubbers, since it does not require the elevated temperatures necessary in ordinary vulcanisation, during which there is a considerable deterioration in the properties of the ion-exchange resins present in the membranes.

The radiochemical method can be used to prepare membranes which do not contain ion-exchange groups but which nevertheless exhibit extremely important properties. Thus the radiochemical cross-linking of poly(vinyl alcohol) or a mixture of poly(vinyl alcohol) with bifunctional monomers makes it possible to prepare chemically pure membranes, which may find application in biochemical processes[89].

The above data show that ion-exchange membranes prepared under the influence of radiation differ from ordinary membranes in their more uniform composition, increased thermal and chemical resistance, high mechanical strength, low electrical resistivity, increased selectivity, etc. Similar conclusions have been reached by others[90-94].

2. RESINS

Ionising radiation is used much less frequently in the preparation of ion-exchange resins than in the preparation of ion-exchange membranes, but the use of radiation in this field is fairly promising and makes it possible to obtain ion-exchange resins with improved physicochemical and physicomechanical properties.

One of the main stages in the preparation of polymerisation ion-exchange resins—the copolymerisation—can be effectively initiated by ionising radiation. This is true primarily of suspension (drop) copolymerisation, in which ion-exchange resins with regular spherical shape and almost any particle size from 1 μm to 2 mm can be obtained. Suspension copolymerisation under the influence of ionising radiation has the following advantages over the methods usually employed.

1. The copolymerisation can be carried out at room temperature and below, and this improves the conditions of heat transfer, improves the physicomechanical and physicochemical properties of the copolymer, decreases the probability of adhesion of the granules, and improves the stability of the suspensions. Radiation copolymers of styrene and divinylbenzene have greater mechanical strength and thermal stability than the ordinary copolymers[95]. Thus for a divinylbenzene content of up to 10 wt. %, the breaking stress for a copolymer prepared by irradiation amounts to 700 kgf cm^{-2}, whereas that for the ordinary copolymer is not more than 490 kgf cm^{-2}. The degradation temperature of the copolymer obtained by irradiation is 23 deg higher than that of the ordinary copolymer. Both types of copolymer show a decrease in breaking strength with increase in the divinylbenzene content above 10%, but the decrease is much less marked for the copolymer prepared by irradiation.

2. The absence of copolymerisation initiator from the system makes it possible to obtain copolymers with a high degree of purity. The use of ionising radiation makes it possible to reduce the number of components in the complex reaction mixture, which, in addition to monomers, usually contains initiators, stabilisers, and other substances which make it difficult to isolate the resulting copolymers in pure form[96,97]. This is particularly important in the preparation of nuclear grade resins[98-101] and

‡ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

resins for analytical purposes[101], which should differ from ordinary standard ion-exchange resins by having a high degree of purity. For example, in nuclear grade resins the percentage concentration of impurities should not exceed the following values: iron 5×10^{-3}, copper 10^{-3}, and lead 10^{-4}.[101] Resins for analytical purposes must satisfy even stricter requirements; the percentage concentration of impurities should not exceed the following values: iron 10^{-4}, copper 8×10^{-5}, nickel 5×10^{-6}, lead 2×10^{-5}, and aluminium 1.5×10^{-3}; the total ash content should not exceed 4×10^{-2}%.[101]

3. Other conditions being equal, the maximal degree of conversion is greater when ionsing radiation is used than when chemical initiators are used, apparently due to an increase in the mobility of the macromolecular segments under the influence of radiation[102]. This feature is particularly important when the reaction mixture contains an appreciable (> 10–15%) quantity of cross-linking agent, for example, in the preparation of non-swelling macroporous resins, where in chemical methods of preparation ~ 20–30% divinylbenzene takes part in the copolymerisation for only one double bond[103].

Resins with a highly developed specific surface can be prepared under the influence of ionising radiation. For example, macroporous copolymers can be obtained by carrying out the radiation copolymerisation of styrene and divinylbenzene in granules of silica gel, which is then removed by dissolving it in concentrated alkali solution. This method of preparation makes it unnecessary to introduce into the reaction mixture the foaming agents or inert solvents which are usually employed in the preparation of macroporous ion-exchange resins[101–107]. In addition to silica gel, it is also possible to use other porous matrices whose chemical decomposition can be carried out fairly simply.

Since in many polymers irradiation leads to intensive cross-linking, it is sometimes possible to use irradiation instead of cross-linking agents. For example, linear buadiene–styrene copolymer is converted into a three-dimensional insoluble product by treatment with ^{60}Co γ-radiation (dose about 10 Mrad). Subsequent sulphonation of the resulting three-dimensional polymer with concentrated sulphuric acid leads to the formation of a strongly acidic cation-exchange resin[86]. It should of course be borne in mind that this cross-linking is effective for systems with a fairly high value of $G_{\text{cross-linking}}$. For systems with a low value of $G_{\text{cross-linking}}$, however, the doses required to obtain the necessary number of cross-linkages are too large. Thus the formation of the same number of cross-linkages as are present in a copolymer of styrene with 4% divinylbenzene requires irradiation of polystyrene with a dose of ~ 10 000 Mrad, and this is quite unacceptable.

The use of ionising radiation in the production of ion-exchange resins is not limited to the copolymerisation stage. In a number of instances irradiation produces various desirable properties in previously prepared resins. This is true primarily of sulphonic acid cation-exchange resins, whose functional groups are fairly stable towards radiation[108]. For example, specimens of the resins Dowex-50 (2–24% divinylbenzene) and Amberlite IR-120 (8% divinylbenzene), irradiated with ^{60}Co γ-radiation (dose 10–450 Mrad; dose rate 550 rad s^{-1}), were found to be much more stable towards hydrolysis at high temperatures than the original specimens. Non-irradiated ion-exchange resins at 180°C lost 25–30% sulphur and became almost completely soluble, whereas the stability of the resins towards hydrolysis under these conditions increased considerably after irradiation and the loss of sulphur was reduced to 10–15%.[109]

Irradiation has a definite influence on the selectivity of the sorption of various ions[108]. This feature can also be of some practical importance. For example, irradiated KU-2 resin shows an increase in selectivity for the caesium ion in the exchange of H^+ by Cs^+.[110] An analogous phenomenon was observed for the sorption of organic compounds, for example, phenol[111,112].

3. FIBRES, FABRICS, PAPER

Ion-exchange fibres and fabrics have recently become fairly widespread[113,114]. These materials can operate simultaneously as mechanical and ion-exchange filters. They are particularly promising for the technological development of continuous countercurrent processes[115]. Ion-exchange textiles show a combination of properties which sometimes makes them superior to ordinary resins[116]. They have a more highly developed surface than granulated resins, as a result of which ion-exchange processes take place at high rates on these materials. The use of ion-exchange fabrics makes it possible to carry out ion exchange on small-scale equipment of the filter-press type. This makes it possible to remove ions from a pulp and to carry out mechanical filtration, and this is almost impossible on ion-exchange columns. Ion-exchange fabrics can be used for the preparation of the framework of heterogeneous membranes.

The radiochemical method for preparing these materials is apparently more effective than other methods of preparation. The grafting of acrylic and methacrylic acids, methyl methacrylate and acrylonitrile (with subsequent hydrolysis), 4-vinylpyridine and 2-methyl-5-vinylpyridine (with subsequent alkylation), styrene (with subsequent sulphonation or amination) and various other monomers from the liquid or gaseous phase on to polyethylene, polypropylene, poly(tetrafluoroethylene), poly(vinyl chloride), poly(ethylene terephthalate), cellulose, and other fibres not only gives the fibres and fabrics ion-exchange properties but also in a number of instances leads to a marked improvement in their mechanical strength and thermal stability[33]. Grafting on to fibres usually takes place with high radiochemical yields; even at doses of 1–2 Mrad, the quantity of polymer grafted amounts to several dozen percent, and this gives fabrics with a total exchange capacity of 1–5 mg-equiv. g^{-1}.[117,118]

Fibres exhibiting weakly acidic or weakly basic properties are obtained by irradiating polyethylene and polypropylene fibres in air at room temperature and then heating with acrylic acid or 2-methyl-5-vinylpyridine. The total exchange capacity of fibres containing 40–50 wt.% graft polymers amounts to 2–3 mg-equiv. g^{-1}. The presence, in the fibres, of antioxidants of the substituted phenol and aromatic amine type decreases the efficiency of grafting[118].

The grafting of acrylic acid or acrylonitrile (followed by treatment with alkali) on to polypropylene fibres gives fibres with an exchange capacity in neutral solution up to 4 mg-equiv. g^{-1}.[74]

Ion-exchange fibres and fabrics can be prepared by surface grafting, whereas with ion-exchange membranes the grafting should take place throughout the entire volume of the irradiated polymer.

Cellulosic ion-exchange materials containing functional groups, in particular various papers, can be used successfully in analysis, particularly for the chromatography of biochemical materials: proteins, enzymes, nucleic acids, etc.[119]

Ion-exchange papers and fibres can be obtained by the radiation grafting of various monomers, containing ion-exchange groups, on to cellulose, or by the subsequent introduction of these groups into the graft copolymer. The radiochemical preparation of ion-exchange materials based on cellulose, however, is of much less practical importance than that based on synthetic fibres. This is due to the fact that the introduction of a comparatively small quantity of ion-exchange groups (1–2 mg-equiv. g^{-1}) into cellulose leads to a sharp increase in its ability to undergo swelling and to a deterioration in the physicomechanical properties. Moreover, the grafting of various vinyl monomers on to cellulose can hardly give sorbents with advantages over ordinary ion-exchange celluloses.

The radiation grafting of styrene on to cellulose under the influence of γ-radiation, followed by the introduction of ion-exchange groups into the graft polymer, makes it possible to obtain ion-exchange paper with a greater stability towards radiation than the original cellulose[120]. Thus on irradiation with a dose of ~ 50 Mrad, the tensile strength of pure cellulose decreases by 83%, whereas the corresponding figure for a copolymer containing ~ 35 wt.% graft polystyrene is only 47%.[121] When hydrophobic polymers such as polystyrene or poly(methyl methacrylate) (in quantities greater than 13–20 wt.%) are grafted on to cellulose, there is a marked change in the Rf values, the times required for separation, and the form of the spots in the molecular chromatography of aliphatic acids and dyes[120]. Ion-exchange papers can be prepared from materials other than cellulosic materials. For example, the grafting of acrylonitrile and acrylic acid on to polypropylene fibres under the influence of ^{60}Co γ-radiation makes it possible to obtain cation-exchange papers with a thickness of 0.2 mm, a capacity of 4 mg-equiv. g^{-1}, and a resistivity of 12 Ω cm (in 1 N NaCl)[74].

4. MINERAL-ORGANIC SORBENTS§

A number of ion-exchange materials consisting of an inorganic carrier-support and an organic fraction containing various functional groups capable of ion exchange have recently been prepared. These materials have certain advantages over ordinary ion-exchange resins. They show an increased thermal and radiochemical stability, a high rate of attainment of ion-exchange equilibrium, a low degree of swelling in the working solutions, and the ability to act as mechanical filters. The disadvantages of most of these materials generally include poor chemical stability and a lower exchange capacity on a weight basis than ordinary ion-exchange resins.

The mineral-organic products on which the subsequent preparation of the ion exchangers is based may be obtained by chemical[122,123] or chemical and mechanical[124] methods¶. For example, cation exchangers with capacities up to 0.5 mg-equiv. g^{-1} have been prepared by condensing dibenzyldichlorosilane with the hydroxyl groups of silica gel or aerosil and then sulphonating the products[125]. Cation exchangers with a capacity of 1 mg-equiv. g^{-1}, which are stable at 300°C and have found application as catalysts, have been prepared from silica gel and sulphonated benzyltrichlorosilane[126]. The reaction of silica gel with various aminosilanes gives anion exchangers with capacities up to 0.8 mg-equiv. g^{-1}, stable at temperatures above 200°C.[127]

The most universal method for the preparation of mineral-organic products, however, is the radiochemical method. It can be used for grafting on to surfaces which do not contain groups capable of undergoing condensation. It does not require mechanical subdivision and makes it possible to carry out grafting on highly dispersed materials. Finally, the radiochemical method can be used to obtain products with a high concentration of organic fraction, whereas this is generally difficult or impossible by chemical or chemical-mechanical methods.

Mineral-organic ion exchangers have been prepared by radiochemical vapour-phase graft polymerisation[10,128-131]. The mineral-organic products were made in the apparatus illustrated in Fig. 2. The inorganic carrier-support was placed in a thin-walled glass ampoule (*1*), and the liquid monomer was placed in the flask (*2*). The ampoule was separated from the flask by the glass filter (*3*). The apparatus was evacuated to a residual pressure of 10^{-5}–10^{-6} mmHg and sealed off. The ampoule was placed in the air thermostat (*4*) fitted with a window of thin aluminium foil (*5*) to permit irradiation. The flask containing the monomer was immersed in the water or oil thermostat (*6*), in which a temperature determined by the vapour pressure of the monomer in the system was maintained. The apparatus was rotated by means of a small motor (*7*). After irradiation by X-rays or a beam of accelerated electrons, the apparatus was opened and the homopolymer was separated from the mineral-organic product by extraction with a suitable solvent. The quantity of graft polymer usually amounted to 10–20 wt.%. When the graft polymer contained functional groups capable of ion exchange—for example, poly(acrylic acid)—the mineral-organic ion exchanger was obtained in a single stage. Otherwise, the functional groups were introduced into the graft polymer by further chemical reactions. Graft polystyrene was sulphonated or aminated, graft poly(4-vinylpyridine) was alkylated, and poly(vinylphosphonic dichloride) was hydrolysed with water. The following mineral-organic ion exchangers were prepared in this way: macroporous silica gel–sulphonated polystyrene; macroporous silica gel–aminated polystyrene; macroporous silica gel–alkylated poly(4-vinylpyridine); macroporous glass fibre–alkylated poly(4-vinylpyridine); "white soot" [powdered silica gel (Ed. of Translation)] (or aerosil)–sulphonated polystyrene;

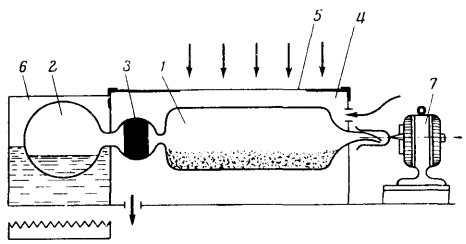


Fig. 2. Apparatus for vapour-phase radiochemical graft polymerisation[29].

§ Since these sorbents are based on synthetic inorganic materials, it would be more correct to call them inorganic-organic sorbents.

¶ Methods for the preparation of mineral-organic products have been reviewed in detail by Morozov[34].

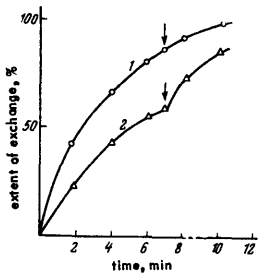
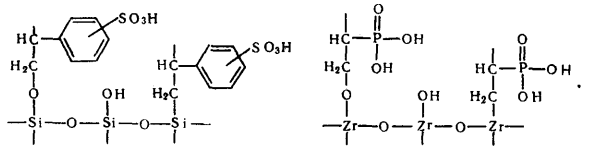


Fig. 3. Rate of exchange of H^+ by Cs^+:[130] 1) for a mineral-organic ion exchanger (macroporous silica gel–sulphonated polystyrene); 2) for KU-2-6 resin. The arrows mark the points at which the sorbents were removed from the solutions for 12 h.

"white soot" (or aerosil)–poly(acrylic acid); and zirconium oxide–poly(vinylphosphonic acid). The suggested structures of mineral-organic sorbents of the macroporous silica gel–sulphonated polystyrene and zirconium oxide–poly(vinylphosphonic acid) types are given below:



The ion exchangers obtained have a capacity of 1–2 mg-equiv. g^{-1} in neutral solutions, undergo slight swelling in water (5–10%), and have a highly developed specific surface, varying from several dozen to several hundred square metres per gramme. Most of them can also be used as mechanical filters. The rate of attainment of ion-exchange equilibrium in these ion exchangers is usually not limited by internal (gel) diffusion, as in ordinary resins (Fig. 3). The rate is very high even in dilute solutions. Thus the half-saturation time (the time required for 50% of the capacity of the resin to be realised) in the exchange of H^+ by Na^+ in 2×10^{-4} N NaCl amounts to only a few minutes for mineral-organic ion exchangers, compared with 30–40 min for KU-2-6 resin. Mineral-organic ion exchangers also have a high radiochemical stability. Thus an ion exchanger based on the system formed by macroporous silica gel with polystyrene containing $-CH_2N^+(CH_3)_3$ groups loses only 40% of its capacity on irradiation in water with a dose of 500 Mrad, whereas AV-17 anion-exchange resin†, which contains analogous groups, loses its ion-exchange properties completely under the same dose[132].

Finally, various mineral-organic ion exchangers show a high heat resistance, retaining their ion-exchange properties up to 300°C.

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THE USE OF GAS CHROMATOGRAPHY IN THE STUDY OF POLYMERS

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Chromatography is a physical method for the separation of compounds, in which the substances being separated are distributed between two phases, one of which is stationary,