Grafting of Gelatin during Polymerization of Methyl Methacrylate in Aqueous Medium

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Synopsis

When methyl methacrylate is polymerized in aqueous medium in the presence of gelatin, graft copolymer macromolecules with gelatine backbones and poly(methyl methacrylate) (PMMA) grafts are formed. Due to the presence of graft copolymer, polymolecular micelles consisting of about 100 macromolecules are created. These micelles prevent macroscopic precipitation of PMMA. Fractionation in demixing solvents has been used to separate the components of the polymerization mixture, and the light-scattering method has been employed to determine their molecular weights. Each grafted macromolecule carries about one graft. The hypothesis of random grafting from gelatin backbones seems to explain most of the experimental observations.

INTRODUCTION

Grafting of gelatin by various polymers has been studied with the objective of improving or modifying the properties of gelatin and in order to develop new materials combining the desirable properties of both natural and synthetic polymers.[1,2] Moreover, grafting may play an important role in the ability of gelatin to stabilize suspensions of polymers formed in the process of polymerization in aqueous medium.[3] Gelatin also appears to be a convenient polymer for basic studies of grafting, because it can be hydrolyzed easily, and the characterization of separated grafts may give a deeper insight into the grafting mechanism.

Gelatin is a polypeptide closely related to collageneous materials and glues by its chemical nature.[1] The amino acid composition of gelatin varies somewhat according to the source and manufacture. The most frequently occurring amino acids are glycine (26–28%), proline (14–18%), hydroxyproline (14–16%), and glutamic acid (10–12%).[2] Consequently, gelatin chains carry a number of functional groups, the most common being hydroxy groups followed by carboxylic and amino groups. It is the hydroxy group that is believed to be responsible for the radical grafting of gelatin, as briefly outlined below.

Grafting of Gelatin

When grafting the existing backbones in the presence of a suitable monomer via radical mechanism, two basic types of grafting are usually recognized. In grafting *from* backbone, radicals are generated on a polymer backbone and they start the polymerization of a monomer, which forms grafts. The grafting *onto* backbone consists in the termination or transfer reaction of the growing

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graft macroradical to the backbone. In both cases the formation of comb-like structures, obeying the definition of graft copolymers,[4] is anticipated.

This simple concept can hardly be expected to reflect reality fully, because mutual interaction of the radical species present in the polymerization mixture is more complex. In response to the initiation process (decomposition of initiators, irradiation, etc.) radicals are created of at least one of the following types:

(a) Growing graft-macroradical, when the initiation step starts the homopolymerization of monomer;

(b) backbone fragment, originated by degradation of the backbone in response to the attack by primary radicals;

(c) macroradical created on backbone by a transfer reaction or by reactions of functional groups; and

(d) macroradical formed by a similar mechanism on a graft polymer chain. In the latter two cases, a radical is localized on a polymer chain, but not necessarily at its end, as in the first two cases.

The use of persulfates for the grafting of gelatin has been reported in many cases.[5-22] For polymers carrying hydroxy groups, Ikada et al.[23] suggest the following mechanism of grafting

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\cdot-} \tag{1}$$

$$SO_4^{\cdot-} + \sim \underset{\displaystyle OH}{\underset{|}{CH}} \sim \longrightarrow \sim \underset{\displaystyle OH}{\underset{|}{\dot{C}}} \sim + HSO_4^-, \tag{2}$$

where radicals of both types are able to start the polymerization of monomers.

It is well known that persulfate initiators start homopolymerization of various monomers in aqueous medium. Obviously, macroradicals of type (a) are present in the system.

Degradation of gelatin backbone during grafting has been observed by Khismatullina et al.[12] The presence of macroradicals of type (b) cannot therefore be ruled out, although in this particular case the hydrolytic degradation is more likely.

The interaction of hydroxy groups on gelatin chains with persulfates resulting in the creation of macroradicals of type (c) proceeds according to schemes 1 and 2. The radicals located on the backbone can undergo mutual recombination, which manifests itself in gelation, as demonstrated by the example of poly(vinyl alcohol).[23] These radicals, however, can act as termination sites for growing graft polymer macroradicals initiated in solution, and in this case grafting *onto* backbone proceeds. If they start the polymerization of a monomer, grafting *from* backbone occurs. With radical copolymerization of this kind, both types of grafting are likely to operate simultaneously, and it is difficult to distinguish them from each other.

The transfer reactions resulting in the formation of radicals of type (d) on chains which form grafts is probably not the dominant reaction, provided the copolymerization is carried out in the presence of a diluent. It may become important with polymers carrying functional groups sensitive to radical attack.

The second initiation system used extensively in the grafting of gelatin is the redox reaction of ceric (IV) ion with hydroxy groups localized on backbones.[18,24-29] Macroradicals of types (a–d) also can be formed in this case, although their frequency may differ for both types of initiation. Attention should be paid to possible reactions of these macroradicals so that the structure of the final product of a grafting process could be estimated.

Micellization of Graft Copolymers

Grafting is expected to occur when polymeric substances carrying hydroxy groups are used as stabilizers in dispersion or suspension polymerization.[3,30] It is well known that copolymers consisting of blocks, that is, also graft copolymers, form micelles in selective solvents.[31] In such solvents, the copolymer blocks of one type are insoluble unlike those of the other type. The formation of supermolecular structures, viz., polymolecular micelles, has therefore to be anticipated in aqueous medium, when gelatin is grafted by water-insoluble polymers. So far, no attempts have been made to determine the molecular structure of grafted gelatin, and also the formation and characterization of polymolecular micelles has never been mentioned in this context. This is partly due to difficulties in the interpretation of experimental results obtained for branched copolymer structures by routine methods of molecular characterization, such as gel permeation chromatography (GPC) and viscometry.

In this article, we try to characterize on the molecular level gelatin grafted by PMMA by light-scattering, including the characterization of structures occurring in the polymerization mixture. We also attempt to elucidate the role of polymolecular micelles, arising as a consequence of the grafting process, in the heterogeneous polymerization of methyl methacrylate in the presence of gelatin.

EXPERIMENTAL

Materials

A sample of commercial photographic, alkali-treated bone gelatin, type 51 432, manufactured by Rousselot, France, has been used in grafting experiments. Corrections for moisture content, 14.4 wt%, were made wherever necessary. Weight-average molecular weight $\overline{M}_w$ = 400,000 was determined by light-scattering.[32]

Methyl methacrylate (MMA) (Lachema, Czechoslovakia), was distilled on a laboratory column prior to the polymerization experiment.

The other chemicals of analytical-grade purity and solvents for solution characterization of polymers were used as obtained. Distilled water was applied in experiments.

Grafting Experiment

Three grams of gelatin were dissolved in 260 mL of water at 60°C. The solution was stirred and bubbled with nitrogen. Next, 5.25 g of MMA and 6 mL of 0.25 *M* ammonium persulfate were added to the gelatin solution. Water was added to adjust the total volume to 300 mL. The concentrations of

components in the starting mixture were 1 wt% of gelatin, 1.75 wt% (0.175 *M*) of MMA, and 0.005 *M* ammonium persulfate; pH = 3.4. After 3 h, the reaction mixture was quickly cooled to 10°C and water was evaporated in vacuo. The copolymer product was decanted several times with methanol to remove the unreacted monomer, initiator, and its decomposition products. Direct precipitation of the reaction mixture into excess of methanol results in the formation of micellar solution containing a slowly sedimenting precipitate. This procedure cannot be recommended. Isolated material was dried in vacuo over silica gel to constant weight. Two separate polymerization experiments, denoted as I and II, were carried out under identical conditions to check the reproducibility of results.

Fractionation in Demixing Solvents

Water and methylethylketone (MEK) were allowed to form two coexisting phases at 25°C and used as a stock solvent. The same volume of each phase was added to a part of the copolymer product (2 wt% of copolymer in the system) and temperature was increased until a macroscopically homogeneous, although turbid, solution was formed. The solution placed in glass cells was centrifuged for 1 h at 10,000 rpm at 25°C in a swinging bucket rotor SW 28 on a Beckman L55 preparative centrifuge. Three phases could clearly be identified in each of the cells. The upper, MEK-rich phase contained the attendant PMMA homopolymer, the middle phase the swollen graft copolymer and the lower, water-rich phase the ungrafted gelatin. The phases were separated and the graft copolymer fraction was again treated with both phases of the stock solvent. The whole procedure, including centrifugation, was repeated three times at 40°C, 25°C, and 40°C to ensure the complete removal of homopolymers. The collected phases were evaporated in vacuo, decanted in methanol, and dried. Three fractions, viz., attendant PMMA, true graft copolymer, and ungrafted residual gelatin, were obtained.

Hydrolysis

The polymeric material to be hydrolyzed was boiled in 2 N HCl for 1 h under reflux condenser (concentration of polymer ca. 1 wt%). These conditions are sufficient for complete hydrolysis of gelatin.[1,33] The properties of PMMA are unaffected by hydrolysis,[34] as also confirmed by an independent experiment. The PMMA precipitate was separated, washed with methanol, and dried. No nitrogen could be detected in hydrolyzed samples by elemental analysis.

Chemical Composition

The gelatin content in different samples and fractions was calculated from nitrogen content determined by elemental analysis. It was also checked by the decrease of weight after hydrolysis. The results of both methods differed by less than 2 wt% of gelatin.

Molecular Weights

The weight-average molecular weights $\overline{M}_w$ were determined by the light-scattering method using the Sofica 42.000 apparatus with vertically polarized

primary beam of wavelength 546 nm. The solutions were optically clarified by pressure filtration through a sintered-glass filter G5 (VEB Jenaer Glasswerk, GDR). The refractive index increments, dn/dc, were determined with a Brice-Phoenix BP-2000-V differential refractometer at 546 nm. For copolymers, their values were calculated assuming a linear dependence of dn/dc on chemical composition. All measurements were performed at 25°C.

Formic acid is the only common solvent for gelatin and PMMA. To suppress the polyelectrolyte effect, 0.1 *M* LiCl in formic acid was used. The potential preferential sorption of the added electrolyte had to be neglected, because it is extremely difficult to determine its extent experimentally. The refractive index increments dn/dc were 0.154 cm^3/g for gelatin (0.180 cm^3/g after correction for water content in gelatin[32]) and 0.107 cm^3/g for PMMA. The dissolution of all samples in formic acid is easy and has to be performed at room temperature shortly before the light-scattering experiment. Even a short exposure of the solution to 100°C to speed up the dissolution causes a degradation of gelatin. No degradation could be detected at room temperature within 8 h after dissolution; after 24 h, about 10% decrease of gelatin molecular weight was observed by light-scattering.

Molecular weights of PMMA homopolymers were checked by an independent measurement in MEK, those of gelatin similarly in 0.5 *M* aqueous KSCN solutions.[32] An agreement within ±10% in values of molecular weights was achieved for both polymers in different solvents.

In principle, graft copolymer samples are expected to be chemically heterogeneous. In this case, the light-scattering method yields an apparent molecular weight,[35] which may differ from the true molecular weight. Because the refractive index increments of both gelatin and PMMA in 0.1 *M* LiCl–formic acid are relatively high, the apparent molecular weights were identified with the true ones as a first approximation.[35]

The total concentration of polymers in the reaction mixture was determined by precipitating the known volume of solution into methanol. Direct determinations of weight-average particle weights of polymolecular micelles in the reaction mixture were performed after dilution with water and addition of KSCN up to 0.5 *M* concentration to suppress both the gelation and polyelectrolyte effect. For this case, the refractive index increment 0.140 cm^3/g was determined for both samples after the establishment of osmotic equilibrium[36] between the micellar solution and 0.5 *M* KSCN.

Number-average molecular weights of PMMA were determined with a membrane osmometer Wescan, model 230, in toluene solutions.

RESULTS AND DISCUSSION

Supermolecular Structures

Grafting is supposed to take place during the polymerization of monomers in the presence of gelatin. Let us accept this as a working hypothesis and discuss whether the experimental results substantiate its validity.

Several minutes after the polymerization of MMA in the presence of gelatin was started, bluish opalescence of solution develops, and becomes more pronounced as polymerization proceeds. No macroscopic precipitate is formed,

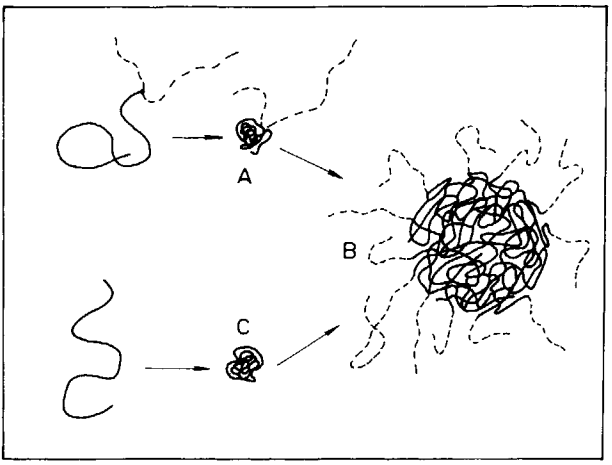


Fig. 1. Model of formation of polymolecular micelles in the polymerization mixture during grafting of gelatin by MMA in aqueous medium: A PMMA block (solid line) attached to gelatine backbone (broken line) collapses and forms a monomolecular micelle (A), which can start the formation, or become part, of a polymolecular micelle (B); the micelle is able to solubilize a certain amount of PMMA homopolymer (C) formed simultaneously with PMMA grafts.

even though PMMA is insoluble in water. If, alternatively, the polymerization of MMA is carried out under similar conditions in the absence of gelatin, PMMA separates as a sticky solid precipitate.

The stabilizing role of gelatin has been known for a long time and used practically in suspension (pearl) polymerization. This ability has been attributed to the formation of graft copolymer macromolecules, since gelatin alone lacks the emulsifying effect on the monomer and is not able to disperse PMMA in water. If we assume that grafting of PMMA to gelatin does take place, the whole process can be vizualized as follows (Fig. 1):

In the first step, some of the growing PMMA macroradicals are attached to gelatin macromolecules by a transfer or termination reaction. Alternatively, the growth of a PMMA graft may be started by a radical localized on the backbone. The PMMA chain collapses, as it is insoluble in aqueous medium, and a unimolecular micelle is formed (A in Fig. 1). There is nothing to prevent the aggregation of both unimolecular micelles and ungrafted collapsed PMMA particles (C in Fig. 1). Both species may associate to form a polymolecular micelle (B in Fig. 1).

The water-soluble gelatin chains surrounding the polymolecular micelles form a highly solvated shell which prevents mutual contact of the PMMA cores, and thus also aggregation of micelles resulting in the macroscopic precipitation of the polymer. They do not, however, hinder the incorporation of small collapsed PMMA particles (A and C in Fig. 1) into a polymolecular micelle. The surface concentration of gelatin chains has to be sufficiently high to prevent aggregation of polymolecular micelles.

The volume of a polymolecular micelle is roughly proportional to the number N of macromolecules it contains. The surface concentration of gelatin chains also increases with this number and is proportional to $N^{2/3}$ in a first

TABLE I
Characterization of Reaction Mixture in the Polymerization of MMA in Aqueous Medium in the Presence of Gelatin[a]

	Run I	Run II
Conversion of MMA to PMMA, wt%	51	56
Weight-average molecular weight of micelles,[b] $10^{-3}\ \overline{M}_w$	90 500	102 000
z-Average radius of gyration of micelles,[b] nm	54	68
Weight-average molecular weight of graft copolymer,[c] $10^{-3}\ \overline{M}_w$	1 050	1 030
Chemical composition of graft copolymer,[d] wt% gelatin	49	48

[a] Composition of starting mixture: 1.75 wt% MMA, 1 wt% gelatin and 0.005 M ammonium persulfate in water. 60°C, 3h.
[b] By light-scattering in 0.5 M aqueous KSCN.
[c] By light-scattering in 0.1 M LiCl-formic acid.
[d] By elemental analysis; raw copolymer includes both homopolymers.

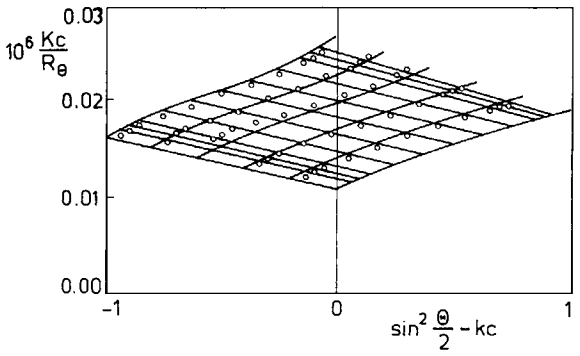
approximation. The association of a sufficient number of graft copolymer macromolecules gives rise to a stable, nonaggregating polymolecular micelle. The oligomolecular micelles with low surface concentration of gelatin, of course, aggregate to form larger stable micelles.

In the case under investigation, the particle weights of micelles in the polymerization mixture were determined by light-scattering (Table I) after dilution of the mixture and addition of potassium rhodanide to prevent gelation and to screen off the polyelectrolyte effect [Fig. 2(a)]. For both polymerization runs the weight-average particle weights are close to 10^8 and the dimensions, given by the z-average radius of gyration, are about 60 nm. From the linearity of the concentration dependences in the Zimm plots [Fig. 2(a)], it can be deduced that no substantial change in the structure of polymolecular micelles takes place upon dilution and additon of KSCN.

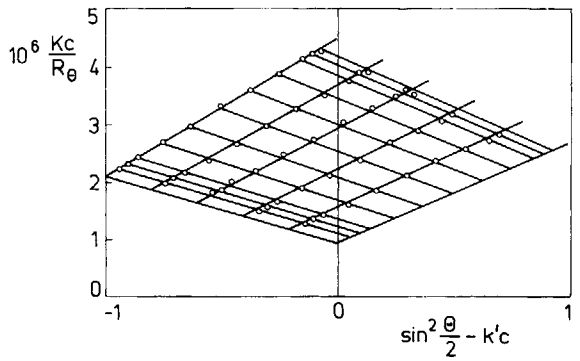
The weight-average molecular weight of the unfractionated polymerization product was estimated after its isolation also by light-scattering (Fig. 2(b), Table I). On the average, a polymolecular micelle contains approximately 100 individual macromolecules. The reproducibility of the polymerization experiment can be regarded as good (Table I).

Fractionation

The product of graft copolymerization consists of the true graft copolymer, ungrafted gelatin backbones, and attendant PMMA homopolymer, not linked to gelatin. These components are generally difficult to separate by classical fractionation procedures because of the tendency of the graft copolymer to form micellar solutions. Therefore, the separation in a demixing solvent pair, recommended by Kuhn[37] for this purpose, was attempted. Water and methylethylketone are partly immiscible at 25°C and form two coexisting phases. PMMA dissolves in the upper, MEK-rich phase, while gelatin is soluble in the lower, water-rich phase. A mixture of PMMA and gelatin separates to its



(a)



(b)

Fig. 2. Zimm plots for (a) the polymerization mixture (run I) in 0.5 *M* KSCN, i.e., solution of polymolecular micelles; (b) the solution of individual macromolecules of unfractionated copolymer product in 0.1 *M* LiCl-formic acid. K is the optical constant, c is the concentration of the polymer, R_Θ is the Rayleigh ratio for scattering angle Θ; k = 1660, k′ = 350.

components quantitatively in this system. When applied to a product of graft copolymerization, three phases are formed at 25°C after dissolution in a one-phase MEK-water mixture at a higher temperature. Centrifugation had to be applied to ensure complete separation of phases. Moreover, it was found that, at 25°C, ungrafted gelatin remains trapped in the graft-copolymer middle phase, probably due to cogelatination. Temperature had to be increased above the gelation point to ca. 40°C to achieve its perfect separation. The PMMA homopolymer was separated from the MEK-rich phase at 25°C, because at 40°C this phase contains too much water for PMMA to be completely soluble. This made the whole procedure rather tedious (cf. Experimental).

The results of fractionation indicate (Table II) that a graft copolymer is formed during polymerization. Approximately one third of the material can be regarded as the true graft copolymer. The formation of the true graft copolymer is also confirmed by the value of molecular weight of that fraction, which is substantially higher than that of a gelatin-PMMA mixture with the same composition.

TABLE II
Results of Fractionation of the Copolymer Product in Demixing Solvent Pair, Water-MEK[a]

Fraction	Run	w	$\bar{x}$	$10^{-3}\bar{M}_w$
True graft copolymer	I	0.31	0.32	1570
	II	0.40	0.38	1450
Ungrafted gelatin	I	0.32	1.00	36
	II	0.27	0.99	41
Attendant PMMA	I	0.37	0.05	760
	II	0.33	0.06	700

[a] w is the weight fraction of the particular fraction, $\bar{x}$ is its chemical composition expressed at wt fraction of gelatin, and $\bar{M}_w$ is its weight-average molecular weight.

Properties of the Gelatin Backbone

It has been observed that the molecular weight of gelatin used in the present experiments, $\bar{M}_w$ = 400,000, decreases in a blank experiment in the absence of MMA to $\bar{M}_w$ = 280,000. It remains unchanged also if ammonium persulfate is not added. The observed degradation may be explained by a partial hydrolysis of gelatin backbones, due to the acidic reaction of the polymerization mixture (pH < 4) in the presence of ammonium persulfate. Alternatively, the moderate degradation of gelatin could occur on an interaction with the radicals created by decomposition of the initiator. If this were the case, gelatin fragments would carry a radical at the end which, in a grafting experiment, could either terminate PMMA macroradicals by recombination or start the polymerization of MMA. In both cases, block copolymer molecules would result.

A rather puzzling observation is that the molecular weights of residual ungrafted backbones (Table II) are very low. Their values were checked by an independent determination in 0.5 *M* aqueous KSCN to rule out the potential hydrolysis when formic acid was used as solvent in the light-scattering experiments. A decrease of molecular weight of ungrafted backbones is expected in the random grafting process,[38,39] because a backbone with a higher molecular weight has a higher probability to be grafted. Also, since the longer gelatin macromolecules are more likely to undergo degradation and subsequent incorporation of fragments into copolymer molecules, a decrease of molecular weights should be observed as well, if block copolymer molecules were formed. Nevertheless, the difference between the molecular weight of the original gelatin and of residual ungrafted backbones seems to be too great to be explained by a simple model of grafting.[39]

Hydrolysis and Characterization of PMMA Grafts

The use of gelatin in grafting experiments offers an attractive possibility of subsequent hydrolysis of gelatin chains. In this way, the backbone can be destroyed and the molecular weight of the individual grafts can be determined.

By hydrolysis of the raw copolymer product, a mixture of attendant ungrafted PMMA and PMMA grafts is obtained. The attendant PMMA homopolymer is isolated as one of the fractions in the fractionation. Finally,

TABLE III
Weight- and Number-Average Molecular Weights, $\overline{M}_w$ and $\overline{M}_n$, of PMMA, Grafting Efficiency, E, and the Average Number of Grafts in True Graft Copolymer, m_n^+

Species		Run I	Run II
Total PMMA	$10^{-3}\overline{M}_w$	830	720
	$10^{-3}\overline{M}_w$ (calc.)	766	661
Attendant PMMA	$10^{-3}\overline{M}_w$	760	700
	$10^{-3}\overline{M}_n$	420	360
	$\overline{M}_w/\overline{M}_n$	1.8	1.9
Grafted PMMA	$10^{-3}\overline{M}_w$	775	620
	$10^{-3}\overline{M}_n$	450	440
	$\overline{M}_w/\overline{M}_n$	1.7	1.4
	E	0.41	0.48
	m_n^+	1.2	~ 1.0

hydrolysis of the true graft copolymer yields PMMA which had been grafted to gelatin (Table III). From the weight amounts of PMMA, it is possible to calculate the grafting efficiency E defined as the weight ratio of the grafted PMMA to the total amount of PMMA formed. This efficiency is relatively high and roughly one half of total PMMA was incorporated in the graft copolymer (Table III).

The weighted average of molecular weights of the attendant PMMA and grafted PMMA should be equal to the molecular weight of total PMMA in the raw copolymer product. For both runs, the latter is somewhat higher but still within the limits of experimental error (Table III).

No significant difference is observed between the molecular weights of the ungrafted and grafted PMMA (Table III). Within experimental error, Khismatullina et al.[12] and Ikada et al.[23] also found no difference between both types of PMMA. Kuwajima et al.[19] observed that the attendant PMMA had molecular weights somewhat lower than the grafted PMMA. These facts support the hypothesis that the grafting *from* backbones occurs rather than the grafting *onto*. The latter would manifest itself by an increase of molecular weight of the attendant PMMA, where the termination proceeds at least partly, by recombination of two PMMA macroradicals, compared to the grafted PMMA, where growth of the chain is prematurely terminated by transfer to the backbone or by coupling with a radical located on the backbone.

Average Number of Grafts

The average number of grafts in a copolymer macromolecule m_n is defined[38,39] as the ratio of the number-average molecular weight of the whole graft part M_{nB} to the same average of single grafts M_{nB}^*

$$m_n = \frac{M_{nB}}{M_{nB}^*} = \frac{(1 - \bar{x})\overline{M}_n}{M_{nB}^*} \tag{3}$$

where $\bar{x}$ is the average chemical composition given by the weight fraction of

the backbone and $\overline{M}_n$ in the number-average molecular weight of the copolymer. Formally, the same relation holds for the average number of grafts in a true graft copolymer m_n^+ provided the proper molecular weights and composition are introduced into Eq. (3).

There is a difference between the average number of grafts in a graft copolymer which contains ungrafted backbones, m_n, and in a true graft copolymer, m_n^+, which is obtained after the removal of residual ungrafted backbones. Always, the inequalities $m_n > 0$ and $m_n^+ > 1$ hold. A value of $m_n < 1$ is relevant in a case when the fraction of ungrafted backbones, carrying "zero" grafts, is large and, at the same time, the extent of grafting is small. If backbones have the most probable distribution of molecular weights and grafting of backbones is random, then it can be shown that[38,39]

$$m_n^+ = m_n + 1, \tag{4}$$

otherwise the mutual relation is more complex.[38]

Unfortunately, in our case $\overline{M}_n$ of the graft copolymer could not be determined, because the only available solvent, 0.1 *M* LiCl-formic acid, is detrimental in membrane osmometry. For the sake of demonstration, let us assume that for the true graft copolymer $\overline{M}_w/\overline{M}_n = 2$. Then, using the data in Tables II and III, we obtain according to Eq. (3) the values of m_n^+ practically equal to unity (Table III). Thus, each graft copolymer macromolecule seems to carry about one graft. If the nonuniformity of the copolymer were still higher, $\overline{M}_w/\overline{M}_n > 2$, then $m_n^+ < 1$, and physically meaningless results would be obtained; if $\overline{M}_w/\overline{M}_n < 2$, then only a slight deviation of m_n^+ from unity would be found. Of course, according to Eq. (4) the average number of grafts m_n in the whole copolymer will be always much lower than unity.

Kuwajima et al.[19] grafted gelatin by MMA and found the average number of grafts $m_n = 0.3$–1.2 depending on reaction conditions. Sudesh Kumar et al.[40] estimated the number of grafts using the relation

$$m_n = \frac{(W_B/M_{nB}^*)}{(W_A/M_{nA})}, \tag{5}$$

where W_B is the weight of the polymer grafted, M_{nB}^* is the molecular weight of single grafts, W_A is the initial weight of gelatin backbone, and M_{nA} is its molecular weight. This relation is correct provided no degradation of backbone takes place during grafting. These authors found $m_n = 0.09$–0.68 for the grafting of poly(ethyl acrylate) under various conditions,[40] and $m_n = 0.15$–0.30 for the grafting of poly(methyl acrylate) on gelatin.[6,7] Kuwajima et al.,[19] and similarly Sudesh Kumar et al.[40] suggest that the low degree of grafting should be attributed to the structure of gelatin, where the number of hydroxy groups prone to the generation of free radicals is small in number. However, Ikada et al.,[23] when grafting poly(vinyl alcohol) by PMMA, found that the average number of grafts in a copolymer macromolecule was $m_n = 0.9$, that is, also low, even though in this case the number of hydroxy groups on the backbone was much higher. The authors of the above study offer an

explanation that the recombination of radicals on the backbone is preferred to the initiation of graft growth. Conflicting information comes from the report by Khismatullina et al.,[12] who estimated the number of grafts to be m_n = 13–17. However, the molecular weight of grafts isolated after hydrolysis was determined by viscometry and is reported to be exceptionally low, of the order of magnitude 10^3, contrary to other authors' findings.

In our opinion, a low number of grafts seems to be a typical feature of the graft copolymerization carried out under heterogeneous conditions. Ikada et al.[23] compared the extent of grafting under homogeneous and heterogeneous conditions and found that, in a homogeneous dimethyl sulfoxide solution, the degree of grafting of PMMA to poly(vinyl alcohol) was much higher, m_n = 2.6–3.9. One of the reasons for the low degree of grafting under heterogeneous conditions may be connected with the preferential solubilization of monomer in both monomolecular and especially polymolecular micelles. The monomer present in micelles is thus inaccessible to further formation of grafts which proceeds in the surrounding aqueous medium. Also, the incorporation of grafted molecules into polymolecular micelles may affect the ability of backbones to undergo additional grafting.

A simple model of random grafting of backbones which have the most probable distribution of molecular weights predicts[39,41] the relation between the average number of grafts in true copolymer m_n^+ and the weight fraction of ungrafted backbones w_A^0 as

$$w_A^0 = (1/m_n^+)^2 \tag{6}$$

In our case, $m_n^+ \leqq 1.2$ (Table III), which corresponds to $w_A^0 \geqq 0.69$. From the results of fractionation (Table II), the weight fractions of ungrafted backbones (with respect to the total amount of gelatin) are found to be 0.76 and 0.64 for runs I and II, respectively. This observation is compatible with the random grafting hypothesis. It thus seems that the grafting of gelatin, although affected by the heterogeneous conditions of copolymerization, remains random by its character, and corresponding models of random grafting[38,39] can be applied in the discussion of experimental results.

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