

GRAFTING AND BRANCHING OF POLYMERS

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ABSTRACT

This review summarizes the present state of investigations concerning synthesis of various types of model macromolecules. Emphasis was given to those methods which enable preparation of well characterized macromolecules, suited well enough for morphological and thermodynamic investigations in dilute solution, and to get information on the influence of heterocontact interactions and/or of enhanced segment density on the properties of the polymers considered. It can be seen that for such an aim, the anionic polymerization techniques which are versatile and well adapted to such problems, have yielded decisive progress. The main disadvantage of these methods is that the number of adequate monomers is rather limited. Other polymerization techniques do not involve active sites which retain their activity long enough to be of great interest for such synthesis.

The properties of linear homopolymers have been investigated intensively for the past two years in many laboratories, in dilute solution as well as in bulk. The behaviour of such macromolecules is now more or less established. It is known, for example, that two parameters are sufficient to account for the dimensions of these molecules in dilute solution, one of these parameters characterizing the unperturbed gaussian distribution of segments around the centre of mass, the other the expansion which is due to the so-called polymer-solvent interactions.

But it has been shown that the theories which account satisfactorily for the behaviour of linear homopolymers fail to explain the experimental results on several other types of macromolecules, as block or graft copolymers and as branched homopolymers¹. This is one major reason for the recent development of methods of synthesis of model macromolecules of various types:

(1) Block-copolymers which are linear in structure and where incompatible homopolymeric sequences are connected by chemical bonds. Three different interaction parameters have to be considered here: between two A segments, between two B segments, and between an A and a B segment; the latter type is much less frequent in block-copolymers, owing to intramolecular phase separations which have been shown to occur².

(2) Graft-copolymers. Homopolymeric grafts A are linked, at random, on to a homopolymeric backbone B of a different chemical nature. In this case both the effect of heterocontact interactions and the effect of the branched structure of the molecule have to be considered³.

(3) Branched-homopolymers. The high density of segments which characterizes branched structures influences the solution properties of these macromolecules⁴. The well-known 'simple contact approximation' is therefore not valid here. Amongst branched homopolymers two types of macromolecules have been synthesized, characterized and studied: (a) Comb-polymers: these are graft-copolymers in which grafts and backbone are of the same chemical nature. The grafts are distributed at random along the backbone; (b) Star-shaped polymers; in these p individual homopolymeric chains are connected by one of their chain ends on to a small central nucleus.

The purpose of this paper is to review briefly the chief methods of preparation of these various types of macromolecules; emphasis will be given to those methods which lead to real 'model macromolecules' i.e. to macromolecular samples which are little polydisperse in mass, of satisfactory homogeneity in composition, and in which the molecular structure is defined unambiguously by the conditions of preparation.

Many attempts were made in the past fifteen years to synthesize block-copolymers, graft-copolymers, and branched-homopolymers; several methods, however, yielded products which could not be characterized adequately. Let us first consider the preparation of block-copolymers and of graft-copolymers and, in a second part, the methods of synthesis of branched homopolymer molecules.

I. BLOCK- AND GRAFT-COPOLYMERS

(A) Methods involving radical polymerization of the monomers

Obviously, polymerization of a mixture of two monomers cannot yield block- or graft-copolymers, whatever the reactivity ratios of the system may be.

It should be recalled that the lifetime of a radical site in a liquid is very short, and attempts to initiate polymerization of monomer A in a tube while flowing into a vessel filled with another monomer B yielded only very small amounts of block-copolymer⁵.

Many attempts to synthesize block- or graft-copolymers proceed in two steps. The first step involves preparation of homopolymer sequences fitted with active sites. The second step involves polymerization of the second monomer, using the active sites as initiators. If the sites are located at chain ends a block-copolymer will be obtained. If they are distributed at random along the chain, the process will yield graft-copolymers. In both cases, homopolymers will be present in the reaction medium, and have to be separated by careful fractionation.

Numerous methods of this type have been developed and they have to be mentioned, even if none of them has ever yielded what we call model macromolecules, as defined above.

Many different ways have been used to create active radical sites on a polymer backbone, either randomly distributed or selectively located at chain ends. Let us briefly recall some of them:

(1) Some authors⁶ have used bifunctional initiators, such as di-isopropyl-

benzene dihydroperoxide, to initiate the polymerization of a monomer (styrene). The polymer is thus fitted with hydroperoxide end groups which may then participate in redox initiation for the polymerization of a second monomer (methylmethacrylate).

(2) Peroxidation of polystyrene results in chain scissions and in formation of terminal hydroperoxide groups, able to initiate the polymerization of methylmethacrylate and of acrylonitrile⁷.

(3) Various chemical methods have been described⁸. One can for instance start with a random copolymer of methylacrylate and acrylylchloride, and react the latter units of the copolymer with *t*-butylhydroperoxide. The perester functions obtained may initiate various polymerizations, such as that of styrene.

(4) Much work has been performed on grafting processes involving irradiation of a polymer, to create active sites, and using the latter to initiate the polymerization of a second monomer.

Different types of experimental procedures have been used⁹⁻¹³:

(a) One can irradiate a polymeric film swollen in a monomer. Grafting takes place, but much homopolymer is formed, too; furthermore gel effect is involved in the process, owing to an extended lifetime of the radical sites. Therefore this grafting process, though very efficient, does not yield very homogeneous samples.

(b) The pre-irradiation method is also used, especially with crystalline polymers. Irradiation of such polymers yields trapped radicals, and these sites act as initiators on contact with another monomer. The grafting process lasts only for a short time, until all radicals have disappeared. The same technique can also be carried out in the presence of oxygen, yielding thus peroxy radicals which are more stable but can also act as initiators for the polymerization of a second monomer.

(5) To be exhaustive, it should be mentioned that in some cases grafting may result from a transfer reaction. Several monomers, when polymerized using a radical initiator, in the presence of a polymer, yield transfer reactions between the growing chains and labile C—H bonds of the polymer. This process yields radical sites on the polymer, which can either contribute in turn to the initiation of the second monomer, or react with the growing radicals by recombination¹⁴⁻¹⁷.

All these methods involving radical processes have been used to produce graft copolymers, but in none of these cases has it been possible to characterize precisely the obtained species: from analysis and spectrographic methods the content of each of the constituents can be established, but neither the number of branch points, nor the length of the backbone, nor the size of the individual grafts can be determined; besides, the samples are quite polydisperse in mass and in composition.

(B) Methods involving ionic polymerization of the monomer

Decisive progress was made when the anionic polymerization techniques in aprotic media, involving no termination reactions, had been developed, especially by Szwarc and his co-workers¹⁸. It is well known now that metal-organic derivatives such as butyl-lithium, cumyl-potassium, fluorenyl-sodium do initiate the polymerization of various monomers having an electro-

attractive substituent. The polymerization goes to completion and the polymers thus obtained are called 'living' because they retain reactive carbon-metal bonds at chain ends. Further addition of monomer results in an increase of the length of the chains. It has been established that the obtained polymers exhibit a narrow molecular weight distribution, if they have been synthesized under adequate conditions.

We shall distinguish here between methods meant to prepare block copolymers and ways of preparation of graft copolymers. Obviously these methods are restricted to anionically polymerizable monomers.

(1) Block-copolymers—To synthesize block-copolymers a monomer B is added to a solution of living polymer A. The carbanionic sites initiate the polymerization of monomer B and, since initiation is an addition process, a two-block-copolymer is formed, provided the electroaffinity of monomer B is at least that of monomer A^{19,20}. Many systems were tested in recent years, and a whole series of different block-copolymers were obtained by this method, as can be seen from a recent review²⁰. Vinyl, diene and acrylic monomers are involved, but also heterocyclic ones, such as ethylene oxide, butyrolactone, thiocyclanes²¹, or even cyclic dimethylsiloxane-trimer or tetramer.

Similarly it is possible to synthesize BAB triblock-copolymers by using a bifunctional initiator (such as naphthalene sodium, in which case the initiation is an electron transfer process to the monomer, followed by dimerization¹⁸) to initiate polymerization of monomer A. After completion of the polymerization, the obtained bifunctional living polymer A is reacted with monomer B, thus yielding a triblock-copolymer.

In both cases, adequate characterization of the block-copolymer is possible, and it was confirmed that if the experimental conditions are well chosen, the homogeneity in composition of the sample is satisfactory and the corresponding molecular weight distribution is narrow²².

Several attempts were made to carry out similar syntheses using cationic initiators and adequate monomers. But since transfer reactions often occur in cationic polymerization processes, most of these attempts were unsuccessful: chain ends do not retain active sites²³. However, a very nice method of preparation of styrene-tetrahydrofuran block-copolymers should be mentioned here: cross-termination between 'living' carbanionic polystyrene and a 'living' cationic polytetrahydrofuran results in block-copolymer formation with rather good yields²⁴.

Another method was recently described: living anionic polystyrene is reacted with a small amount of *p*-divinylbenzene and quickly deactivated with a proton donor: the molecular weight is unchanged but some double bonds remain pendant at the end of the polystyrene chain. The species obtained can then be copolymerized through these double bonds by any method applicable to styrene: free radical, cationic or anionic polymerization. The best results so far have been obtained anionically⁴⁵.

Another possible way to synthesize block-copolymers is to start with homopolymers A and B, both fitted with reactive end groups, and to have them reacted selectively on each other. A recent example for this type of process is the reaction of polyoxyethylene glycol with large excess of toluene diisocyanate, yielding no increase of the molecular weight. In a second step, the remaining isocyanate functions, at chain end, are reacted with the terminal

OH functions of a polyester whose preparation involved a slight excess of the glycol²⁵.

A similar method was used to prepare BAB triblock-copolymers of styrene and ethylene oxide, the PEO block being the central A block. Living polystyrene is reacted with an excess of phosgene to yield acid chloride end groups. The latter are then reacted on to the terminal OH functions of a polyoxyethylene glycol chain²⁶. One can also start from a living AB block-copolymer and react it with a difunctional deactivator to yield ABA triblock-copolymers²⁷.

(2) Graft-copolymers—To synthesize graft-copolymers using anionic polymerization techniques two different paths can be used, namely grafting via carbanionic initiation, and grafting via carbanionic deactivation²⁰.

(a) *Grafting via carbanionic initiation*

A polymer chain is fitted with organometallic sites distributed at random, and these sites are used to initiate the polymerization of an adequate monomer. Several examples of such reactions have been described, leading to graft-copolymers^{28, 29}. However, the number of grafts is usually lower than the number of sites; their length is not experimentally accessible and may fluctuate quite a bit within the sample (cf. ref. 20, review article).

The main difficulty of grafting reactions carried out via anionic initiation is of course to find ways to get organometallic sites on a polymer chain. Several methods have been used to perform this:

(i) Direct metallation of polymers containing vinyl-aromatic monomer units: vinyl-fluorene, vinyl-biphenyl, vinyl-naphthalene. In the two latter cases, however, the initiation process for vinyl monomers involves electron transfer, instead of addition³⁰. Therefore only ethylene oxide can be grafted here; with vinyl monomers homopolymers are formed, solely.

(ii) Polyvinylfluorene and poly-3,3-diphenylpropene can be metallated by naphthalene-sodium²⁸. The organometallic sites formed may initiate the polymerization of various monomers, yielding graft-copolymers.

(iii) Exchange reactions between halogen and metal can take place on to poly-*p*-bromostyrene, yielding *p*-lithiophenyl sites, which are rather active as initiators. Butyl-lithium³¹ or naphthalene-lithium³² have been used as metallating agents.

(iv) Though polystyrene itself is rather hard to metallate this was achieved recently by using a butyl-lithium complex with *N*-tetramethylethylene diamine³³. The same reagent was also used successfully to yield anionic sites on a poly-(2,6-dimethyl-1,4-phenylene oxide) chain³⁴. Metallation takes place both on the benzene rings and on the methyl side groups, but the latter isomerize yielding the former species.

(v) Another way of getting metallated sites on a polymeric chain is addition of butyl-lithium on to some pyridine rings of a polyvinylpyridine chain³⁵, or by reaction of butyl-lithium on to vinyl-naphthalene units³⁶. In both cases graft-copolymers could be obtained.

(b) *Grafting via carbanionic deactivation*

The second path for anionic grafting proceeds by carbanionic deactivation. It is well known that carbanionic sites do react with various electrophilic

functions such as halogenides, acid chlorides, esters, nitriles, and anhydrides^{18, 20}. If a living polymer A is reacted with electrophilic functions linked to a polymer chain B, graft-copolymers are obtained: the grafts which are attached to the main chain are randomly distributed, and they are, to a first approximation, of the same length. Though on reacting living polystyrene on to polymethylmethacrylate³⁷, only a small proportion of the ester functions do react—because of problems of accessibility—the graft-copolymers obtained are entirely characterizable. Side reactions sometimes occur, leading to ungrafted polymer A, but separation of this polymer is usually rather easy. Polymethylmethacrylate³⁷, polyvinylchloride³⁷, permethylated xylenes³⁸ and even polyvinylpyridine³⁹ served as backbone, i.e. as polyfunctional deactivators. Polystyrene, polyisoprene, polyvinylpyridine, were used as grafts, but not polymethylmethacrylate, because of insufficient reactivity.

This method of anionic grafting is restricted to a small number of cases, but it is one of the preferred methods to synthesize graft-copolymers for morphological investigations, since characterization of the structure of the molecule is easy: the length of the backbone, the number and the average length of the grafts are experimentally accessible; furthermore the random distribution of the grafts and the low level of fluctuations in composition within a sample have been established.

It should be mentioned that one example of cationic deactivation grafting process was published recently⁴⁰: grafting of cationic polystyrene on to poly-2,6-dimethoxystyrene, the cationic polymerization of styrene being carried out in the presence of the latter polymer. Yields are moderate, but characterization of the obtained graft-copolymers is not very easy.

II. BRANCHED HOMOPOLYMERS

It is well known that some industrial polymers of major importance, such as polyethylene, polyvinylacetate and acrylic polymers exhibit a certain number of branch points in their macromolecules. Branching affects the solution properties of the polymers as well as their mechanical behaviour. But to investigate systematically and efficiently the influence of branching on behaviour, model macromolecules must be used. Various methods have been developed to build up macromolecules of precisely known structure.

The first branched macromolecules to be investigated were polycondensates. If in a polyesterification of an acid-alcohol a small proportion of an acid-dialcohol (or of an alcohol-diacid) is added, the copolycondensation of the latter monomer results in the formation of branch points, which are more or less randomly distributed. These polycondensations can never yield networks (in contrast with reaction of a glycol with a diacid containing some triacid). But the polydispersity of the samples is high, and the average number of effective branch points per molecule is not known precisely. These randomly branched macromolecules, though of great interest, cannot be considered as model polymers.

More recently major interest has been devoted to branched molecules of rather simple molecular structure. Two types of branched model macro-

molecules have been investigated in great detail in several laboratories around the world: comb-like polymers and star-shaped polymers. The methods of preparation of these two model structures will be described below:

(A) Comb-like polymers

These are in fact graft-polymers in which grafts and backbone are of the same chemical nature. It is quite understandable therefore that the methods of anionic grafting should have been used to synthesize such model molecules. Since the methods using anionic initiation from a metallated backbone do not lead to well characterizable polymers, we shall not go into the details of such methods, which have been applied nevertheless to polystyrene and to polyvinylpyridine comb-polymers, but we shall describe two methods of grafting via carbanionic deactivation.

(1) The first method⁴¹ uses as a backbone a random copolymer of styrene and methylmethacrylate, the content of the latter monomer being of the order of ten per cent. Such copolymers are obtained using radical initiators, and care is taken to stop the reaction at rather low yields, in order to avoid fluctuations in composition within the samples obtained. Their polydispersity is, however, rather high. The ester functions of the backbone can be used in a second step as electrophilic deactivators for an anionically prepared 'living' polystyrene. This second step leads thus to a comb-like polystyrene, the polystyrene grafts being randomly distributed along the polystyrene backbone. A small proportion of ester functions remains untouched, but this is not important. A small proportion of ungrafted polystyrene has to be removed by fractionation, which is relatively easy, since grafts are usually not too long. But this method has two disadvantages: (i) the grafts are attached to the main chain by means of a carbonyl group which is quite sensitive to photochemical oxidation. As a matter of fact, prolonged exposure to bright light will yield chain scissions and free grafts; (ii) The molecular weight distribution of the samples thus obtained is as broad as that of the backbone itself, because the number of grafts is proportional to the length of the main chain. Therefore fractionation of the sample has to be undertaken with great care, prior to investigation of any physical property of the comb-polymers.

(2) The second method^{42, 43} is more rigorous. An anionically prepared polystyrene sample—of sharp molecular weight distribution—is chloromethylated cationically under experimental conditions chosen so as to avoid any coupling or degradation process⁴⁴. The degree of chloromethylation is limited to values of the order of five to eight per cent. The chloromethylated groups are selectively located in para position to the phenyl groups. These functions are used in a second step as electrophilic functions to deactivate 'living' monocarbanionic polystyrene. This deactivation is unambiguous, because no elimination reaction is possible when benzylic chlorides are used. Some authors⁴³ have claimed that exchange reactions between metal and halogen may take place, but later results have shown that these side reactions can be neglected if adequate experimental conditions have been chosen⁴². The grafting reaction is not far from being quantitative, and the comb-polymers thus obtained can be considered to be real model macromolecules. The polydispersity is very low, the grafts are identical, to a first approxima-

tion, and randomly distributed on a backbone which can be characterized by itself.

(B) Star-shaped polymers

These are characterized by one single p -functional branch-point connecting p chains of identical length; they have been synthesized in various laboratories, two main experimental techniques being used:

(1) The first method uses polyfunctional electrophilic derivatives to react with a monocarbanionic polymer. The deactivators used are various polyhalogen derivatives such as SiCl_4 ²⁷, tri- or tetrachloromethylbenzenes^{46, 47}, the trimer of phosphonitrilic chloride⁴⁶; more recently triallyloxytriazine⁴⁸ gave good results. A slight excess of living polymer, with respect to stoichiometry is introduced; it has to be separated carefully afterwards by fractionation. The main disadvantage of this method is that it may only lead to star-molecules with three, four or at most six branches. Furthermore, the reaction is not always quantitative; with tetrachloromethylbenzene⁴⁹ it yields approximately equal amounts of stars with three and four branches, mixed with some of the initial polystyrene. Quantitative separation of these constituents is a hard job.

(2) The other method which was developed in recent years proceeds by anionic block-copolymerization of a vinyl monomer and a divinyl monomer, the latter being used in small amounts⁵⁰. If the polymerization of styrene is carried out with an effective monofunctional initiator, it yields a living polymer, with active sites located at the chain end. Addition of a small amount of divinylbenzene (say three moles per living end) results in formation of small polydivinylbenzene nodules, each of them being connected, surrounded and protected by the p -polystyrene chains which participated in initiation of the DVB of the central nodule. As a matter of fact, much greater amounts of DVB can be used without gelation of the reaction medium, so effective is the protection of the nodule by the surrounding chains. But for model molecules it is better to use very small proportions of DVB, to keep the central nodule as small as possible. It was found that the value of p is determined by the concentration of the reaction medium, and, to a lesser extent, by the amount of DVB added. Star-molecules with six to twenty branches could be obtained thus.

The polydispersity of the samples obtained is merely the problem of the fluctuations of p within a sample, the branches being to a first approximation identical. To study the distribution of numbers of branches within a sample, careful fractionation had to be undertaken. The standard precipitation fractionation method is of no interest for that purpose, since differences in solubilities between molecules differing only by the number of branches are very small. Elution chromatography using a column fitted with cyclic variation of temperature⁵¹ was sensitive enough to yield satisfactory fractionation. It was found that the fluctuations of p around its average value are rather small, provided the experimental conditions are adequate. It is thus established that this method of preparation of star-shaped macromolecules yields well characterizable model macromolecules, and that the homogeneity of the samples is satisfactory. Because of their simple structure and of their high degree of symmetry, these star-shaped molecules are of

particular interest for investigations on the effect of enhanced segment density on the morphological and thermodynamic properties of branched macromolecules^{5,2}.

It should be mentioned briefly here that the same preparation technique, carried out with an efficient bifunctional initiator, yields model networks^{5,3} in which the average distance between two successive branch points is more or less constant within a sample and can be known in advance, by a proper choice of the styrene-to-initiator ratio, i.e. the molecular weight of the dicarbanionic polystyrene precursor. If the experimental conditions are satisfactory, the gels obtained are homogeneous. From their swelling behaviour^{5,4} it was established that these model gels are very close to 'ideal' gels, in which all chain ends are linked to a branch point.

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