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APPLICATIONS OF ANIONIC POLYMERIZATION TO MACROMOLECULAR ENGINEERING

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ABSTRACT

The development of "macromolecular engineering" owes much to living anionic polymerizations. When carried out under conditions preventing spontaneous transfer and termination reactions, and with efficient initiators, these processes are well suited to the synthesis of model macromolecules of various kinds. Functionalizations at chain end can be achieved upon induced deactivation; macromonomer synthesis, end-to-end cyclization, and chain extension processes can be achieved; and end-linking reactions yield model networks. The use of anionic polymerization processes to synthesize well-defined block copolymers exhibiting low heterogeneity in molecular weight and in composition is of major importance because of the various specific applications of such materials. New efficient bi- and multifunctional metal–organic initiators have been developed. Recently, progress in star polymer synthesis, including core-first methods, has been achieved. Amphiphilic star-block copolymers have been made, as well as heterostar copolymers, whose cores carry two different kinds of arms (of different chemical natures) in roughly equal numbers. All these novel species have attracted wide interest because of their controlled structure and potential applications.

INTRODUCTION

Anionic polymerizations carried out under proper conditions in aprotic solvents with efficient metal–organic initiators [1] have been applied in many instances to synthesize model macromolecules [2]. The reaction scheme of living polymerizations comprises initiation and propagation, with no spontaneous termination or transfer reactions [1, 3]. The number of active sites in a batch is constant and equal to the number of initiator molecules introduced at the onset of the reaction. As a consequence, the number-average degree of polymerization is determined by the mole ratio of monomer converted to initiator used. Furthermore, the molecular weight distribution within a sample prepared under such conditions is rather narrow (Poisson) [4].

In such termination-free processes, once the polymerization reaction is completed, the sites remain living, granting opportunities to functionalize the chain ends upon induced deactivation or to initiate the polymerization of a second monomer to yield block copolymer.

CRITERIA OF LIVINGNESS

These ideal conditions are only fulfilled in a limited number of cases. It is necessary, therefore, to discuss the criteria of livingness.

1. *The number-average degree of polymerization DP_n is proportional to monomer conversion x:*

$$\mathrm{DP}_n = \frac{\Delta[M]}{[I]} = \frac{[M_0] - [M]_t}{[I]_0} = x\,\frac{[M]_0}{[I]_0}$$

2. *The rate of polymerization is first order in monomer concentration* because the number of sites stays constant throughout the process:

$$-\frac{d[M]}{dt} = k_p[M^-][M] = k_p[I]_0[M]$$

Integration of this equation leads to

$$\ln\frac{[M]_0}{[M]_t} = k_p[I]_0 t = -\ln\ (1 - x)$$

Possible limitations to livingness and their consequences on the above two criteria will now be reviewed briefly (Fig. 1).

CASE 1. No Termination, Some Transfer

The first-order plot of ln $([M]_0/[M])$ versus time is unaffected because the number of active sites $[M^-]$ remains constant. A plot of DP_n vs conversion exhibits a downward curvature until it eventually reaches a plateau value determined by the k_p/k_{tr} ratio. The molecular weight distribution (MWD) broadens. If the probability of transfer is high enough to affect all molecules formed during the process, the MWD tends toward a Flory-Schulz (most probable) distribution [5].

In ring-opening polymerizations, *reshuffling* occurs whenever the active site at the chain end is able to react with a function connecting two mers in the chain. If the reaction is intermolecular (*scrambling*), the number-average molecular weight M_n remains unchanged but the molecular weight distribution tends toward a Flory-Schulz distribution. If intramolecular reshuffling (*backbiting*) is also involved, cy-

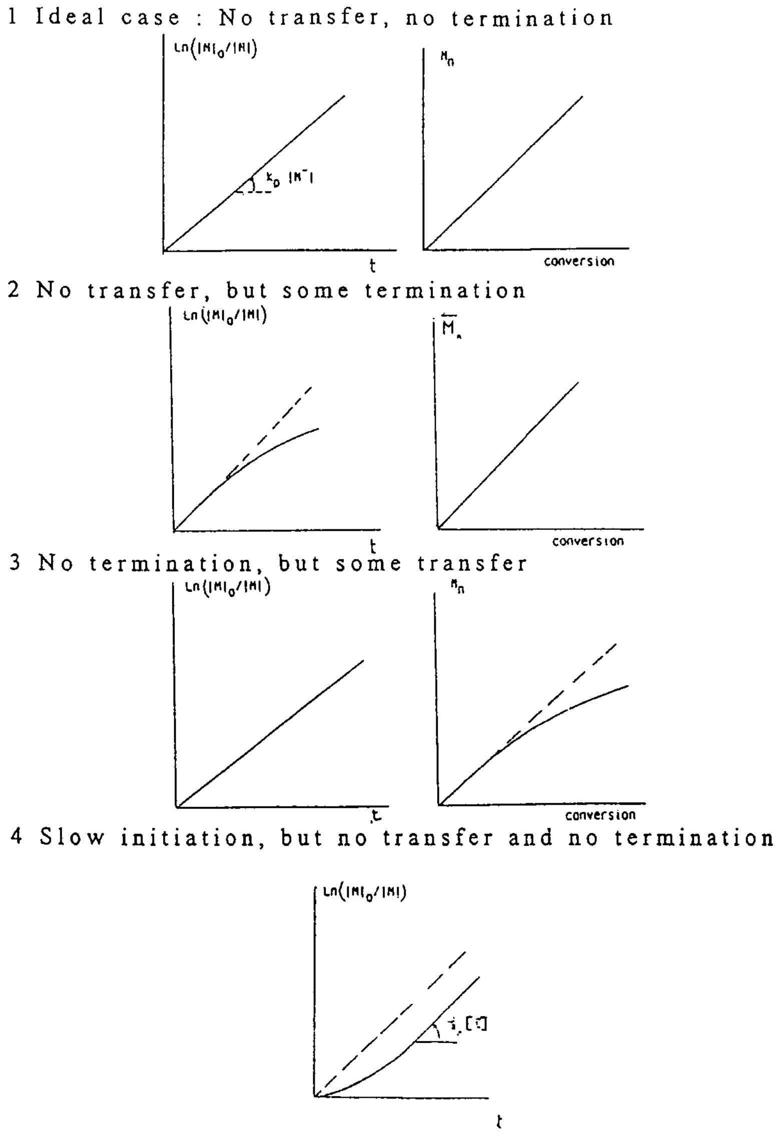


FIG. 1. Limitations to livingness in anionic polymerizations.

cles (unfunctionalized) are formed, whereupon the DP_n decreases. As the molecular weight distribution broadens, the linear chains still carry functions at the chain end.

CASE 2. No Transfer, but Some Termination

If propagation is in competition with slow termination, the number of growing sites slowly diminishes, following an exponential decay law. If the deactivation of the sites is very slow—a fraction of them still remaining after maximum conversion of the monomer—a plot of DP_n versus conversion remains linear, but the kinetic first-order plot—ln $[M]_0/[M]$ vs time—exhibits a downward curvature. The molecular weight distribution broadens and becomes dissymmetric, with a tail toward higher molecular weights. A "dead-end" polymerization occurs if all the sites are deactivated before the monomer is entirely converted.

CASE 3. No Transfer, No Termination, but Slow Initiation

If the active sites are not formed instantaneously, but once formed they remain living, their number increases with time until it eventually reaches its limiting value ($\equiv [I]_0$). The kinetic plot—ln $[M]_0/[M]$ vs time—exhibits an upward curvature, and eventually tends toward a straight line of slope $k_p\ [I]_0$.

If the monomer is polymerized quantitatively before initiation is completed, the kinetic plot never parallels the theoretical line. The number-average molecular weight is then given by

$$\mathrm{DP}_n = \frac{[M]_0}{[I]_0 - [I]_{\mathrm{fin}}}$$

where $[I]_{\mathrm{fin}}$ is the residual initiator concentration. The effect of slow initiation on the molecular weight distribution is less important than was anticipated [4].

CASE 4. No Termination, No Transfer, but Reversible Propagation

Propagation–depropagation equilibria are found in living processes whenever the free enthalpy of polymerization is low. α-Substituted vinylic monomers (α-methylstyrene) and 5- or 7-membered heterocycles [6–8] are typical examples. Below the equilibrium monomer concentration, $[M]_e$, which is strongly temperature-dependent, the polymerization cannot proceed. The rate of monomer conversion can be expressed as

$$-\frac{d[M]}{dt} = k_p[M^-]([M] - [M]_e)$$

which upon integration yields

$$\ln \frac{[M]_0 - [M]_e}{[M] - [M]_e} = k_p[M^-]t$$

If the number of active sites is constant, this plot is linear. The degree of polymerization varies linearly with conversion, the equilibrium monomer concentration $[M]_e$ setting the limit of chain growth:

$$\mathrm{DP}_n = \frac{[M]_0 - [M]_e}{[I]_0}$$

However, the consequences of propagation–depropagation equilibria on the molecular weight distribution are important. If the reaction is conducted far from the equilibrium conditions—i.e., at low temperature or to low conversions—a Poisson-type molecular weight distribution is obtained. If, on the contrary, equilibrium has been reached, the molecular weight distribution is of the Flory–Schulz type.

In spite of all these frequently encountered limitations, anionic polymerizations are quite efficient in macromolecular engineering. Slow initiation and reversible propagation can be accounted for. Minute transfer or termination do not markedly affect conversion or molecular weight, but the polymolecularity is broadened and the functionalization yields are lowered. In model-polymer synthesis it is necessary to be aware of these limitations in terms of *shelftime* [9, 10]: The lifetime of the active sites had to be compared to the time required to polymerize quantitatively the monomer *and* to have the active sites subsequently engaged in the desired synthetic applications.

CHARACTERISTICS OF ANIONIC POLYMERIZATIONS

Ionic chain growth proceeds by nucleophilic attack of the active site (carbanion or oxanion) onto an electrophilic monomer (i.e., a monomer carrying an electron-withdrawing substituent).

Monomers

To be polymerizable anionically, a monomer must be able to react with the anionic site derived from it. In other words, the nucleophilicity of the anionic site should match the electroaffinity of the monomer to be polymerized. A *vinylic monomer* should thus carry an electron-withdrawing substituent, but it should not contain functions that would deactivate the sites. In some cases, potentially damaging functions (proton-donating or highly electrophilic) can be hidden through chemical modification. These "protected" monomers are suitable for anionic polymerization, and the functions are subsequently regenerated [11].

There are no general rules concerning the ring-opening polymerization of *heterocyclic monomers*. Some of them grow cationically, others anionically, and epoxides can be polymerized both ways. Reversible growth is often encountered because the polymerization of 5- and 7-membered heterocycles does not involve a large gain of free energy [12].

Lactams (and Leuchs anhydrides or oxazolidinediones) are subject to activated monomer polymerization [13]. The active sites at chain end are acyllactam functions. Propagation involves addition of the lactam salt (deprotonated lactam) onto the acyllactam site. Proton exchange takes place, and the next growth step can occur.

Initiators

To be efficient, an initiator should react rapidly and quantitatively with the monomer. Its nucleophilicity has therefore to be considered with reference to the electrophilicity of the monomer chosen. If it is too weak, initiation may not take place at all or it will be slow. If it is too high, side reactions are likely to occur.

Factors affecting the nucleophilicity of an anionic site include: the kind of substituents it carries, the nature of the counterion, the solvent used, and the presence of solvating additives. Carbon—metal bonds may exhibit a covalent or ionic character. Winstein's scale can be used to schematize the increasing charge delocalization occurring as the size and the solvation of the cations increase. This is illustrated by the proportions of free ions, solvated ion-pairs, and contact ion-pairs in the system. Metal-free anionic polymerizations in which the metallic cation is replaced with tetrabutyl ammonium cations have been performed with acrylic monomers [14].

Difunctional initiators are required to synthesize polymers fitted with active sites (or functions) at both chain ends, cyclic macromolecules (via end-to-end cyclization), triblock copolymers (especially thermoplastic elastomers), and networks via end-linking processes.

In *polar solvents* [1], difunctional anionic initiators are readily accessible upon reaction of alkali metals with α-substituted vinylic monomers: 1,1-diphenyl ethylene or α-methylstyrene. Alternately, radical-ionic species, such as potassium dihydronaphthylide, initiate the polymerization of monomers by electron transfer to the monomer, followed by radical dimerization. Chain growth then proceeds at both chain ends. Electron transfer initiation requires cation solvating solvents.

In *nonpolar solvents*, the problem is more difficult. Attempts have been made with the butyllithium adducts of bis-unsaturated monomers. Isopropenyl-substituted benzenes have been addressed because of their high equilibrium monomer concentration at room temperature. Thus, the diadduct of diisopropenyl benzene [15] acts as a difunctional initiator. The adducts of BuLi onto α,ω-bis(isopropenylphenyl) alcanes or similar compounds [16] have been employed as well. The solubility of these adducts is low, as a consequence of the tendency of carbon—metal bonds to associate. Furthermore, the adduct formation is not always quantitative, and small amounts of species of higher functionality have been found in the medium.

Polymeric initiators are living anionic polymers that are able to initiate the polymerization of suitable monomers. For good efficiency and fast initiation, the nucleophilicity of the carbanionic site should match the electroaffinity of the monomer.

An important consequence of the above statement is that random copolymers cannot be made anionically. If a mixture of two monomers, A and B, is reacted with an anionic initiator, the more electrophilic monomer, say B, will homopolymerize since carbanions arising from monomer B are unable to attack monomer A. Systems of monomers exhibiting almost the same electroaffinity (dienes, alkyl methacrylates, . . .) are the only exceptions to that rule. Even then, the compositional heterogeneity may be large.

END-FUNCTIONALIZATION OF POLYMER CHAINS

ω-Functional polymers are of great interest. They allow accurate molecular weight determinations, provided the function at chain end can be determined quantitatively by spectroscopic or analytic methods; they can be used as valuable intermediates in block-copolymer synthesis; they can induce specific properties, such as fire-resistance (phosphonic esters), hydrophilicity, adhesion, ...

Anionic living polymerizations have been applied widely to the synthesis of ω-functional polymers, using two different methods.

1. A functional initiator can serve to initiate the polymerization of a monomer. Care must be taken to prevent side reactions between the metal-organic sites and the function. Several functional initiators have been described recently:

Amine-containing organometallics such as $(CH_3)_2N-(CH_2)_3-Li$ efficiently initiate the polymerization of various vinylic monomers [17].

Caprolactone has been polymerized using functional zinc dialkoxide initiators to yield polyesters fitted quantitatively at the chain end with functional alkoxide groups [18].

The polymerization of oxirane can be initiated with the K-alkoxide derived from *p* vinylbenzylic alcohol [19]. Since alkoxides do not attack styrenyl unsaturation, a poly(ethylene oxide) macromonomer is obtained.

2. Induced deactivation of metal-organic sites by means of a functional electrophile is far more common as a functionalization method. To prevent side reactions involving the function, it is advisable to lower the nucleophilicity of the sites by an intermediate addition of 1,1-diphenylethylene (a monomer that does not polymerize) or even of oxirane (under conditions preventing its polymerization). An excess of functional deactivator is sometimes required to avoid attack of the function by the remaining active sites. A few examples are presented in Table 1.

Functional derivatives of 1,1-diphenylethylene (DPE) have also served to fit polymers with functions at the chain end. Because DPE does not homopolymerize, the addition of one molecule of functional DPE, followed by protonic deactivation, yields the functional polymer [20].

Polymers bearing fluorescent (or fluorescence quenching) groups have been synthesized either by anionic initiation or by induced deactivation [21]. A combination of both methods has served to synthesize telechelic polystyrene macrozwitterions: Li-dimethylamide was the initiator and propanesultone the deactivator [22].

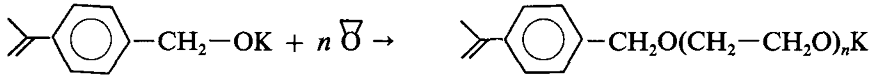
MACROMONOMERS

Macromonomers are polymers fitted at the chain end with a polymerizable unsaturation [23, 24]. They are valuable intermediates in graft copolymer synthesis. Their free-radical copolymerization with a low molecular weight comonomer yields graft copolymer, each macromonomer incorporated resulting in a graft. The synthesis of macromonomers derives from anionic functionalization and can be carried out in different ways.

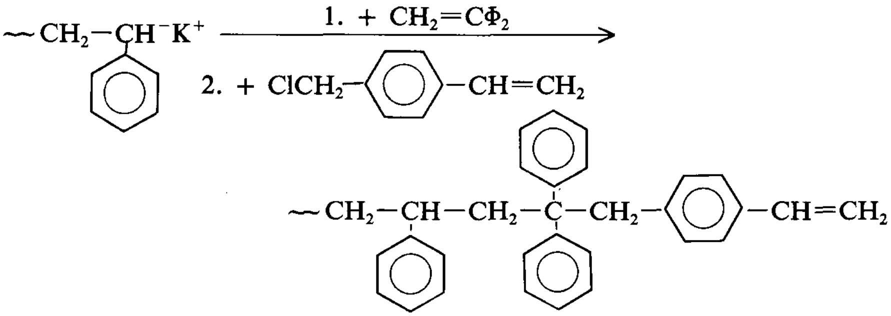
TABLE 1. End Functionalization by Deactivation

Functional deactivator	End groups produced
CO_2 (excess) or cyclic anhydrides	Carboxylic
Oxirane or aldehydes	Hydroxylic
Phosgene (excess)	Acid chloride
Chlorodimethylvinylsilane	Vinylsilane
Ketone (Mischler's ketone)	*t*-Alcohol
Methacryloylpyrrolidone	Acyllactam
Propane sultone	Sulfonic acid
Dialkyl chlorophosphonate	Phosphonic ester

Initiation by an unsaturated metal-organic compound [19], already mentioned:



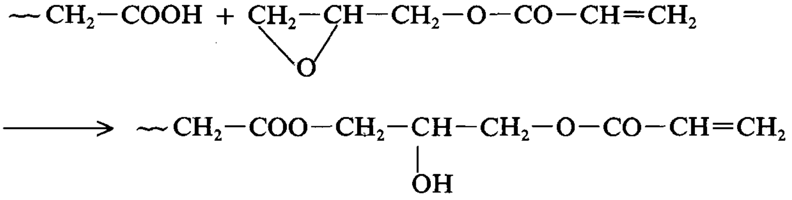
Use of an unsaturated deactivator to end-cap the living polymer [25]. If necessary, the nucleophilicity of the active sites is lowered to prevent side reactions affecting the unsaturation.



A large variety of macromonomers has been prepared by this method.

Two-step methods have been developed [26] starting from ω-hydroxy or ω-carboxylic polymer. The function at the chain end is reacted with an adequate unsaturated compound to introduce polymerizable unsaturation.

$$\sim CH_2{-}OH + Cl{-}CO{-}CH{=}CH_2 \longrightarrow \sim CH_2{-}O{-}CO{-}CH{=}CH_2$$



$$\sim CH_2{-}COOH + \underset{\text{O}}{CH_2{-}CH}{-}CH_2{-}O{-}CO{-}CH{=}CH_2 \longrightarrow \sim CH_2{-}COO{-}CH_2{-}\underset{\text{OH}}{\underset{|}{CH}}{-}CH_2{-}O{-}CO{-}CH{=}CH_2$$

The ability of a macromonomer M to undergo free radical copolymerization with a low molecular weight comonomer A has been studied extensively [27, 28]. Since the molecular weight of a macromonomer is rather high, the molar ratio of macromonomer to comonomer is usually very low. Consequently, the classical "instantaneous" copolymerization equation reduces to that of an "ideal" system:

$$\frac{d[A]}{d[M]} = r_a \frac{[A]}{[M]}$$

The reciprocal radical reactivity ratio of the comonomer, $1/r_a$, characterizes the relative reactivity of the macromonomer. The molecular weight of the macromonomer does not impede copolymerization. However, the incompatibility between backbone chains and macromonomers can affect the process. The solvent used in these copolymerizations may act as a compatibilizer and favor the incorporation of macromonomers [29].

CYCLIC MACROMOLECULES

Cyclic macromolecules have always attracted interest. In the past, **ring-chain equilibria** [30, 31] have been used to synthesize cyclic polymers. Such macromolecules are formed whenever a functional site at the chain end can react with a function connecting two mers of the same chain: transesterifications in polyesters, backbiting reactions in living cationic poly(oxolane), in living anionic poly(caprolactone), and in poly(dimethylsiloxane). The probability of cycle formation decreases as their size increases, in accordance with the predictions of Jacobson and Stockmayer [30]. Consequently, most cycles formed upon backbiting are small and their molecular weight distribution is broad.

End-to-end cyclization is far more efficient because it results from intramolecular coupling between the active chain ends of an α,ω-difunctional polymer [32–34]. The reaction of such a polymer with an appropriate difunctional electrophile, in stoichiometric proportions, yields well-defined cyclic macromolecules. It has to be carried out at very low concentration in order to favor the intramolecular reaction (cyclization) with respect to the intermolecular reaction (chain extension). Dichlorodimethylsilane and xylylene dibromide are efficient coupling agents. Cyclization yields are usually between 25 and 50%. It can be assumed that ring closure is unlikely once intermolecular coupling has occurred, since the probability of cyclization decreases rapidly as the molecular weight of the chains increases.

Separation of the cyclic constituent from the crude reaction product is achieved by fractionate precipitation. Advantage is taken of the large difference in molecular weight between the cyclic molecules and the "polycondensate" resulting from chain extension.

The method [32–35] grants free choice of the molecular weight of the cycles, and the possibility of comparing a cyclic polymer with its linear homologue (i.e., the precursor, sampled before the introduction of the coupling agent). It is reliable with polystyrene up to molecular weights of 200,000–300,000. End-to-end cyclizations have also been achieved with poly(2-vinylpyridine), with polydienes, and with poly(oxyethylene). In the latter case the cyclic molecules are difficult to isolate because of the high tendency of PEO to crystallize when it is unsolvated.

END-LINKING REACTIONS

The occurrence of intermolecular coupling competing with end-to-end cyclization has already been mentioned. **Chain extension** is obviously dominant at elevated concentrations. Under proper conditions, a living dicarbanionic precursor polymer can undergo polycondensation with various difunctional electrophiles [36]; dichlorodimethylsilane, xylylene dibromide, diesters, dinitriles, ... With stoichiometric amounts of functions of either kind, and in the absence of side reactions, high degrees of polycondensation have been attained since the molecular weight of the polycondensate is 5 to 10 times that of the living precursor. **Tri-block copolymers** can also arise from coupling reactions, as will be shown below.

Network synthesis can be performed by end-linking processes involving multifunctional deactivators [37]. A living difunctional polymer is reacted with a stoichiometric amount of a deactivator exhibiting *f* electrophilic functions. Each such compound becomes a branch point as it connects several (f) chain ends. Each precursor molecule becomes an elastically effective network chain, i.e., a chain joining two branch points of an infinite network. The structural characteristics of such *model networks* [37] can be chosen at will: Number ν and average length of the elastic chains, functionality f, and number $2\nu/f$ of the branch points. Such networks may, however, exhibit structural defects: *loops* (one chain attached by both ends to the same branch point); *double connections* (two branch points connected twice); *loose chain ends* or dangling chains (a precursor chain attached to the network by one end and the other end loose).

BLOCK COPOLYMERS

The major application of anionic polymerization is in the synthesis of block copolymers with incompatibility between the chemically different blocks [38]. Intramolecular phase separation results, yielding mesomorphic structures. Owing to the resulting properties (optical birefringence and mechanical anisotropy), block copolymers have found numerous uses; as thermoplastic elastomers, as compatibilizers in polymer blends, as adhesives, as surface modifiers, ... Neither free radical polymerization nor any process involving propagating sites with short lifetimes can be used to synthesize well-defined block copolymers. Conversely, living polymerizations are efficient for such syntheses. Three different approaches have been used.

1. Sequential Addition of Monomers

Once the living anionic polymerization of monomer A is completed, active sites A^- remain at the chain end. A new A-monomer addition results in extension of the existing chains. If, instead, another appropriate monomer B is added to the solution of living poly(A), a block copolymer results. It exhibits narrow molecular weight distribution and low compositional heterogeneity [39, 40], provided certain conditions are satisfied: Monomer B should be polymerizable anionically and its electroaffinity should be higher than that of monomer A to allow the living sites A^- to initiate its polymerization efficiently. If the nucleophilicity of the carbanionic sites A^- is too high and could induce side reactions with the electrophilic monomer B, an intermediate addition of 1,1-diphenylethylene is helpful because the resulting diphenylmethyl anions are resonance stabilized and less nucleophilic [39].

This method has been applied successfully to a large number of systems in both polar and in nonpolar solvents, the latter being required whenever polydiene blocks with high 1,4-unit contents are desired [41].

Triblock Copolymers

If the A^- sites are able to initiate the polymerization of monomer B, the B^- sites are usually unreactive toward A monomer, as stated previously. Therefore, BAB triblock copolymers cannot be prepared by sequential monomer addition unless a difunctional initiator is used to make the central poly-A block first. The active sites A^-, located at both chain ends of the precursor, subsequently initiate the polymerization of monomer B to build the outer blocks. Monomer B should be more electrophilic than monomer A. The synthesis of poly(styrene)-*b*-poly(diene)-*b*-poly(styrene) triblock copolymers has been studied in great detail because of their applications [42]. It requires nonpolar solvents in order to obtain high 1,4-unit contents in the polydiene block.

Model Networks via Sequential Copolymerization

Model networks can arise from end-linking processes, but they can also be made by sequential anionic copolymerization [37, 43]. If the living sites of a difunctional polymer initiate the polymerization of a small amount of a suitable bis-unsaturated monomer (such as divinylbenzene or ethylene dimethacrylate), the precursor molecules become the elastically effective network chains. Each of the small cores formed (branch points) is connected with the *f* chains that have contributed to its formation. These model networks are constituted of a known number of elastic chains of known length, but no access is granted to the average functionality of the branch points.

2. Coupling Reactions

Block copolymers can also arise from the reaction between two ω-functional homopolymers carrying antagonist functions. These functional polymers can be made anionically or by other means. Here are some examples of coupling reactions between ω-functional polymers:

The mutual deactivation of living anionic poly(styrene) and living cationic polyoxolane (poly(THF)), involving formation of linkages between the blocks, is a striking example of polymer coupling [44].

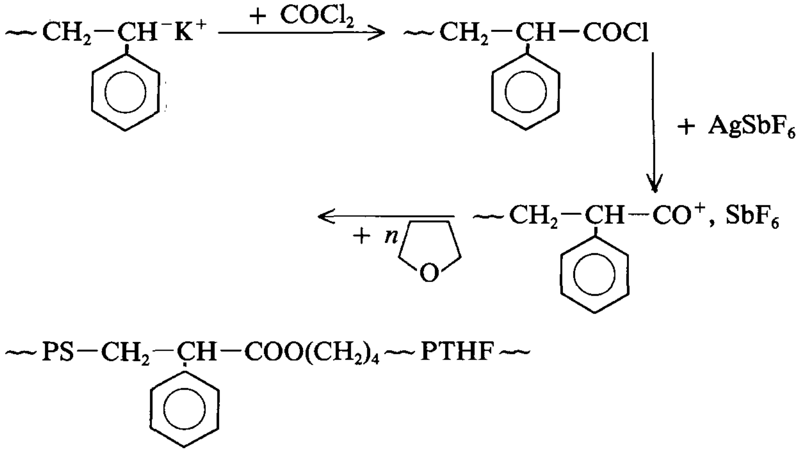
Coupling by hydrosilylation of polymer chains fitted with terminal silane and vinylsilane functions, respectively, has been widely used. Poly(dimethylsiloxane) carrying terminal silane functions is obtained either by anionic or cationic polymerization of the cyclic siloxane oligomers D3 or D4. Polystyrene fitted at one chain end with a vinylsilane function arises from induced deactivation with chlorodimethylvinylsilane. The hydrosilylation is performed in the presence of a catalyst (H_2PtCl_6). Initially heterogeneous, the reaction mixture becomes homogeneous as soon as some block copolymer—acting as a compatibilizer—is formed [45].

Coupling can also be applied to synthesize triblock copolymers from a living diblock copolymer by using a stoichiometric amount of a suitable coupling agent [46]. The method can be extended to the synthesis of multiblock copolymers.

3. Site Transformation Techniques

If one of the monomers (say, B) of the expected block copolymer cannot be polymerized anionically, a site transformation can be carried out on the living poly-A to allow its polymerization [47, 48]. These methods have been initiated by Richards [47]. A few examples follow.

Polystyrene-b-Polyoxolane) Block Copolymer [49]. A living poly(styrene) is treated with excess phosgene to obtain acid chloride functions at the chain end. After removal of the excess reagent, the functional polymer is reacted with silver hexafluoroantimonate. The resulting oxocarbenium salt is an efficient cationic initiator for the polymerization of THF. The high yield of the site transformation (anionic to cationic) prevents the formation of homopolymers of either kind.



Polyisobutene-b-Polybutadiene Block Copolymer. Isobutene is polymerized cationically using the Inifer technique, the chains carrying chlorinated end groups. Dehydrochlorination followed by metalation with *n*-butyllithium/lithium *t*-butoxide yields anionic sites. The subsequent polymerization of butadiene yields the desired block copolymer. This is a case of cationic to anionic site transformation [50].

Polydimethylsiloxane-b-Polyamide Block Copolymer. Hexamethylcyclotrisiloxane (D3) is polymerized anionically using a lithium silanolate. The resulting living poly(dimethylsiloxane) (PDMS) is reacted with chlorodimethylsilane. The terminal SiH functions then undergo hydrosilylation with an unsaturated acylactam. Subsequently, the polymerization of caprolactam is initiated by the acyllactam functions in the presence of a "lactam salt."

Unfortunately, the PDMS undergoes chain scissions in the presence of the metalating agent ($LiAlH_4$) usually employed. To overcome this difficulty, a metalating agent of lower nucleophilicity was used: lithium dialkoxydihydroaluminate [51]. In this case the growth mechanism is different and involves a concerted electron migration.

GRAFT COPOLYMERS

Graft copolymers are constituted of a polymer backbone carrying a number of polymeric side chains (grafts) of different chemical natures, distributed at random. The morphology and the properties of these species are profoundly influenced by the incompatibilities among the backbone chain and the grafts. Intramolecular phase separation tends to yield micellar conformations, especially in the presence of a solvent exhibiting preference for the grafts. Graft copolymers have been applied as compatibilizers in polymer blends, as additives, and in coatings. They are also used as emulsifiers, as surface modifiers, as adhesives, as moisturizers, and as water repellents. The anionic synthesis of graft copolymers can be carried out in various ways.

Grafting from Methods [52–54]. A polymeric backbone is fitted with initiating sites which will subsequently initiate the polymerization of another monomer, whereupon grafts grow. This process yields macromolecules which are not well defined. The metalation of a polymer backbone is difficult to perform and induces insolubility. The average length of the grafts is not accessible experimentally. The samples are polydisperse because of fluctuations in the number of grafts.

Grafting onto Methods [55–58]. A living anionic polymer is reacted with the electrophilic functions of another polymer backbone. These methods are efficient and reliable, but they apply to a limited number of systems. The graft copolymer, the backbone, and the individual grafts can be characterized separately. The grafting yield can be evaluated, and the distribution of grafts along the backbone is random. The molecular weight distribution of the graft copolymer reflects that of the polymer backbone (provided the degree of grafting is not too high): The number of grafts is proportional to the length of the backbone [55].

Poly(methyl methacrylate), poly(vinyl pyridine), and poly(vinyl chloride) have been used as backbone chains. Electrophilic functions can also arise from appropriate chemical modifications. A typical example is the chloromethylation of polystyrene, a reaction that proceeds smoothly and yields randomly distributed benzylic chloride functions [57]. In order to be grafted, living polymers must be able to react efficiently with these electrophilic functions. Grafting of poly(oxyethylene) onto chloromethylated polystyrene [57] yields amphiphilic graft copolymers.

Grafting through Methods [59]. *p*-Diisopropenylbenzene can be polymerized anionically to linear chains carrying one dangling unsaturation per monomer unit (low conversion, low temperature). Such a backbone chain can be used subsequently in two different ways: Either it is reacted under selected conditions with a stoichiometric amount of butyllithium and the sites formed are used to grow the grafts (this is a "grafting from" process), or the dangling unsaturations may participate in the polymerization of another monomer. The difficulty is to prevent crosslinking.

STAR-SHAPED POLYMERS AND COPOLYMERS (Fig. 2)

The interest in branched polymers arises from their rather compact morphology and from their enhanced segment density compared to their linear counterparts of the same molecular weight. The mutual interpenetration of their molecules is expected to be lower. Two types of branched model polymers have been studied extensively: *Comblike polymers* and *star-shaped macromolecules*. The former species are actually graft copolymers in which the grafts and backbone are of the same chemical nature. Their synthesis [60] derives from that of graft copolymers.

Homopolymeric star-shaped polymers have a "core" carrying *f* identical branches. The core can be polymeric in nature or it can arise from a multifunctional

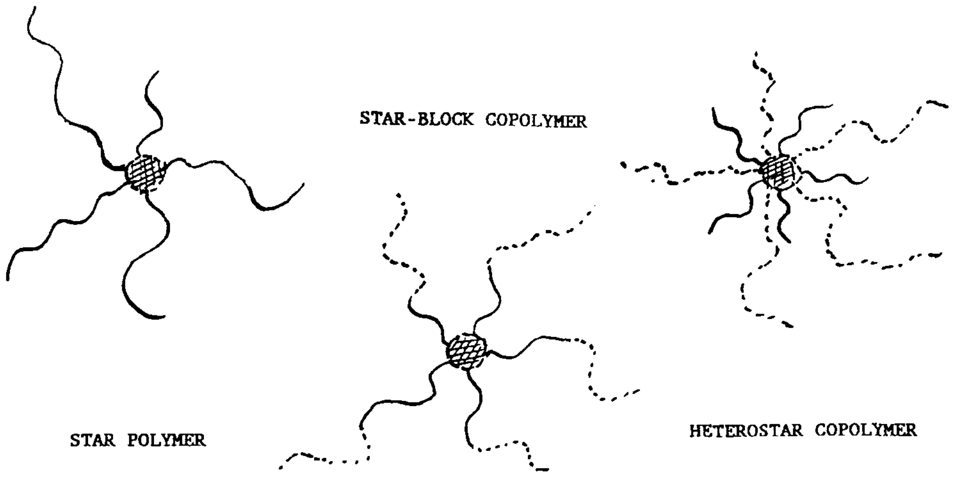


FIG. 2. *Various types of star-shaped macromolecules.*

linking agent. In a **star-block copolymer** each branch is constituted of two homopolymeric sequences. The core of a **hetero-star copolymer** carries homopolymeric branches of two different kinds. The synthesis of star-shaped polymers requires specific methods.

1. Arm-First Methods

There are two kinds of arm-first methods. One of them involves the stoichiometric reaction of living precursor chains with a multifunctional electrophilic deactivator, establishing links between them. The deactivation should be fast, quantitative, and free of side reactions. Multifunctional electrophilic substances include chloromethylated benzenes [61], triallyloxytriazine [62], and silicon tetrachloride; deactivators with 6, 12, 18, and even 36 functional Si—Cl linkages have been developed by Fetters [63, 64]. High reaction yields have been attained, and star polymers with a known number of branches of known length have been made available. The method can also serve for the synthesis of star-block copolymers, each branch being a polystyrene-*block*-polydiene block copolymer [64]. Even if the number of branches is slightly lower than the functionality of the deactivator, this process is reliable, at least with living precursors of high nucleophilicity.

In the second kind of arm-first methods [65, 66], the living precursor is used to initiate the polymerization of a small amount of a bis-unsaturated monomer (divinylbenzene or ethylene dimethacrylate). Small crosslinked nodules (the cores) are formed, each of them being connected with the f precursor chains that have contributed to its initiation. The length of the individual branches can be chosen at will. The average number of branches per core is given by the ratio of the molecular weight of the star molecules to that of the precursor, account being taken, if necessary, of the weight fraction of the core [67].

A few remarks have to be made at this point. The number of branches per core depends upon several factors: proportion of bis-unsaturated monomer per living site, overall concentration, nature of the solvent, ... Fractionations showed that the molecular weight distribution within a star polymer is not very broad [68]. The size distribution of the grafts does not contribute to the polydispersity of the star polymer sample.

The protection exerted by the branches on the crosslinked cores is efficient. It is illustrated by the fact that no gelation has been observed, even when the amount of divinylbenzene added is large (40% of the total mass of the star molecules). In such "porcupine" polymers [67], coupling between cores is prevented by the solvated branches surrounding each of them.

The method has been extended to the synthesis of star-block copolymers [64, 65]. A living diblock copolymer is used to initiate the polymerization of a small amount of a bis-unsaturated monomer.

2. Core-First Methods

If a multifunctional metal-organic compound is used to synthesize star-shaped macromolecules, several difficulties have to be overcome. Such compounds are not easy to prepare, and they tend to precipitate out of the reaction medium. Burchard [69] was the first to succeed in making multifunctional anionic initiators upon reacting butyllithium with divinylbenzene, at a very low concentration, in a nonpolar solvent (cyclohexane). The very fine suspension of active cores subsequently served to initiate the polymerization of a monomer such as styrene. Star molecules of extremely high molecular weights ($> 10^7$) resulted.

A decisive step was performed by Lutz [70], who applied the same basic principle but optimized the reaction conditions. Tetrahydrofuran was used instead of cyclohexane, and initiation was performed by electron transfer instead of by addition. Under such conditions, and provided the mole ratio of divinylbenzene to initiator is low enough (1.5 to 2.5 DVB per active site), multifunctional cores are obtained. Each site of the core can initiate the polymerization of an appropriate monomer (styrene, dienes, vinylpyridine, ethylene oxide, alkyl methacrylates). Branches are grown and star polymers result.

It is reasonable to assume that the molecular weight of the individual branch is determined by the ratio of the weight of monomer added to the total number of sites available, provided initiation is fast and no deactivation has taken place. A drawback of the core-first method is the broad molecular weight distribution of the samples, arising from large size fluctuations of the cores.

In the early stages of the core-first synthesis of poly(oxyethylene) star molecules in THF, the reaction medium is heterogeneous because alkoxide sites are associated. These associations do not affect the process: As the PEO chains grow, they increasingly contribute to cation solvation and the reaction medium becomes homogeneous again [71, 72].

The possibility of functionalization of the branches at their outer end is a specific advantage of the core-first method. It can be performed by deactivation of the metal-organic sites located at the outer end of the branches with an adequate electrophilic compound.

Star-block copolymers [70, 73] can be made by the core-first method provided the monomers constituting the branches are added in the order of increasing electroaffinity. Styrene/diene, styrene/methyl methacrylate, styrene/2-vinylpyridine, and styrene/ethylene oxide are typical examples. In the latter case, the materials obtained exhibit amphiphilic behavior.

3. Synthesis of Heterostar Polymers

In the search for better control of the structure of star-shaped macromolecules, an attempt was made to combine the two methods described above. Each core resulting from a sequential copolymerization process contains a number of active sites *f* which is equal to the number of chains that have participated in its formation. The novel idea is to use these sites for the core-first polymerization of a second monomer. Thus it should be possible to control—to some extent—the average functionality of the cores (which arises from the first step) and to have second-generation branches grow from these cores, which are functionalizable at their outer end.

Funke [74] was the first to work along this line. He established that even very short first-generation branches suffice to provide a rather satisfactory homogeneity in molecular weight, and low fluctuations of the number of sites per core, within a sample. The cores are molecularly dispersed because of the protection exerted by the surrounding branches, and initiation of the second-generation branches proceeds homogeneously. Most of Funke's experiments were carried out in nonpolar solvents. Low molecular weight living poly(*p*-*t*-butylstyrene) was reacted with some divinylbenzene to make the cores.

A similar method was designed by Lutz [72] to make reasonably well defined poly(oxyethylene) star molecules. Experimental conditions were quite different from those of Funke; tetrahydrofuran was the solvent and cumylpotassium was selected as the initiator for the synthesis of the polystyrene precursor. The latter served to make the cores by the regular arm-first method. Subsequently, this *f*-functional living star polystyrene was used to initiate the core-first growth of rather long poly(ethylene oxide) branches. An advantage of this method is that the system remained homogeneous throughout the reaction, contrary to what happened in the first case mentioned above.

The same method has been applied to the synthesis of hetero-star copolymers [73, 75], i.e., star molecules in which the cores carry branches of two different kinds *and of similar length*; for instance, polystyrene and poly(oxyethylene), or polystyrene and poly(*t*-butyl methacrylate). If the operating conditions are satisfactory, and no deactivation has taken place, the number of branches of either kind should be the same, and the fluctuations in molecular weight—and thus in core functionality—within a sample should remain reasonably low.

CONCLUSION

Szwarc was the first to establish (in 1956) that some anionic polymerizations carried out in aprotic solvent exhibit a living character. This discovery had very large consequences on developments in polymer science. It became possible to synthesize well-defined macromolecules, exhibiting known structures, with molecular weights chosen purposely and with low polydispersities. These species also offer opportunities for further reactions thanks to the active sites that remain at the chain end once polymerization is completed. The availability of such tailor-made macromolecules has accelerated tremendously the investigation of structure/property relationships. Anionic polymerization methods have also opened new routes to well-defined polymer species that were not accessible before, such as block and graft copolymers and star-shaped macromolecules.

The main applications of anionic living polymerizations to the synthesis of various types of well-defined macromolecules have been reviewed briefly in this paper. It appears that the diversified contributions of these techniques have decisively accelerated the development of model macromolecules. Several other polymerization methods have been shown in recent years to exhibit living character when they are carried out under specific conditions. They have been applied successfully to the synthesis of tailor-made macromolecules of various kinds, thus enlarging the domain of model macromolecules to polymers originating from monomers that do not polymerize anionically.

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