

Editors H. Höcker and W. Kern

New Developments on Polymer Structure and Morphology

**Lectures presented at the
IUPAC Symposium on
Macromolecules. Bucharest 1983**

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Hüthig & Wepf Verlag Basel · Heidelberg · New York

CIP-Kurztitelaufnahme der Deutschen Bibliothek

New developments on polymer structure and morphology :

lectures presented at the IUPAC Symposium on Macromolecules, Bucharest 1983 / ed. H. Höcker and W. Kern. — Basel ; Heidelberg ; New York : Hüthig und Wepf, 1984.

ISBN 3-85739-007-7

NE: Höcker, Hartwig [Hrsg.]; International Symposium on Macromolecules <30, 1983, Bucuresti>; International Union of Pure and Applied Chemistry

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FUNCTIONAL POLYMERS

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ABSTRACT

Functional polymers have become of major importance in the development of polymer science (1). These polymers have as their primary characteristics the properties of the functional groups and not so much the macromolecular properties. Functional polymers have become of interest in biology and medicine, in energy production and conservation, in agriculture, in food production and preservation, in nutrition and health care. They are prepared by homo- and copolymerization involving functional monomers or by substitution reactions on already formed reactive polymers. Conventional methods and novel approaches are being used to accomplish new designs in macromolecular architecture and to tailor-make multipurpose new polymeric structures.

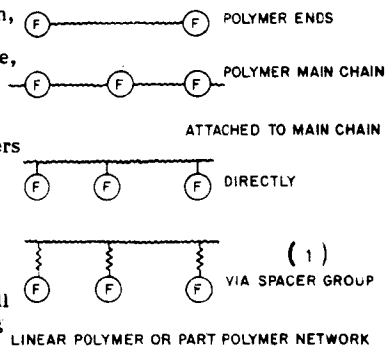
INTRODUCTION

Polymers with functional groups have been known since the infancy of polymer chemistry, but the modern era of "Functional Polymers" did not gain momentum, until very recently, when the expression "Functional Polymers" became generally accepted. Many polymers are now being synthesized, tested and used not so much for their macromolecular properties, the bulk properties of the polymers, but for the properties of the functional groups (2). Functional polymers need to be tailor-made with special attention to the type of functional groups and the position of these groups in the macromolecule. A very important type of functionality is a reactive group which can be used, when desired, for substitution or polymerization reactions.

Functional groups may impart on the polymer chemical, spectral, or biological/medicinal properties; they can be photo-, thermally or biologically active, or they might have utility as drugs, or catalysts, special uses are as ultraviolet absorbers, antioxidants or flame retardants.

Functional groups may be permanently attached to the polymer chain or they may be temporarily attached, to be removed by degradation or hydrolysis; in such cases the released low molecular functional groups are then responsible for the activity. The groups might be attached to a polymer in order to avoid volatilization or leaching from the polymer (Figure 1).

Many years ago, essentially all important addition polymers were homopolymers whose only structure anomalies were fragments introduced from initiation, termination and chain transfer. Later, copolymers were developed, to accentuate, improve or optimize special properties of the polymers.



A few examples where copolymers were useful in solving the problem of weakness in the polymer structure should illustrate the point: To increase thermal stability of a polymer and to avoid degradation to monomer, a suitable comonomer that would act as zipper-jammer was introduced in relatively small amounts into the polymer chain, resulting in products with higher thermal stability. For poly(methyl methacrylate), n-butyl acrylate, for polyoxymethylene, about 2% ethylene oxide (oxyethylene units) were introduced. Poly(α -methylstyrene) with a low ceiling temperature of 61°C cannot be melt fabricated as a homopolymer, consequently, α -methylstyrene can only be used in alternating copolymers (for example with acrylonitrile). Oxymethylene homopolymer, as prepared by anionic homopolymerization, has unstable hemiacetal endgroups which are the origin of thermal degradation to monomer; it is stabilized by acetate endcapping.

Endreactive (telechelic) polymers are some of the most important functional polymers: These polymers have reactive endgroups which can undergo addition or polymerization reactions: Well known examples require the endcapping of terminal hydroxyl groups of medium molecular weight glycols with diisocyanates to polymeric diisocyanates, (used as intermediates for the formation of polyurethanes); the capping and oligomerization of bisphenols with epichlorohydrin to form terminal glycidyl ethers (which represent the most important family of epoxy resins). Other telechelic polymers are endcapped with acrylate or methacrylate groups, which can then be polymerized, for example, by ultraviolet light. Some phenol-, urea-, or melamine/formaldehyde first stage prepolymers can also be classified as endreactive polymers, but, (depending on the actual type) they are also chain reactive polymers. The best, known chain reactive polymers are the oligomeric unsaturated polyesters, whose unsaturations are used as "comonomers" in copolymerization with styrene or methyl methacrylate.

In the last twenty years, fabrication techniques of plastics materials have been tremendously improved. Larger and more sophisticated injection molding and extrusion machines have been developed for fabricating thermoplastic resins; some require significant amounts of energy, and, for large and complicated pieces, the mold cavity cannot always be filled properly. For applications, where melt fabrication is not suitable, other fabrication techniques such as reaction injection molding (RIM) have become important. RIM requires the rapid mixing of two endreactive polymers of low viscosity which react with each other to form high molecular weight and sometimes network polymers. Presently, intense studies are being undertaken to identify polymers, other than polyurethanes, that could possibly be fabricated by RIM techniques. A number of telechelic polymers with the functional groups, which also have the proper reactivity for use in such fabrication techniques are being

developed. A very special case, where rapid curing at room temperature is essential, is the use of endreactive polymers in dental impression materials. The development of materials that polymerize from low viscosity oligomers without stress and without imperfections are increasingly important as reliable insulation materials in the electrical industry.

Chemical postreactions of polymers to change polymer properties are used in a number of cases: Hydrolysis of poly(vinyl acetate) to poly(vinyl alcohol), acetalization of poly(vinyl alcohol) to poly(vinyl butyral) (or formal). Reactions involving functional groups on cellulose such as nitration, acetylation, methylation and cyanoethylation are important polymer modifications which change the polymer properties, but use one of the most important natural polymers. Probably the oldest postreaction on polymers is the sulfur vulcanization of natural rubber.

Before going into specific methods for the preparation of functional polymers, it is important to emphasize that it is apparent that research for the preparation, and utilization of functional polymers is the thrust of polymer research in the 1980's (3,4). Functional polymers, primarily functional synthetic polymers, are needed for applications in agriculture, medicine, food and nutrition, energy (oil recovery etc.), in various facets of handling, storage and retrieval, of information, in electrical and electronic applications to mention only a few.

In agriculture, the use of pesticides as functional groups on polymers, to be released, when needed, has been investigated extensively (5). Only cost, and, to some extent, the as yet limited reliability of the release of herbicides and pesticides for agricultural use is holding them back for large scale use. Not only synthetic polymers, but even more importantly, natural products as carriers for the attachment of agricultural chemicals such as wood chips and bark are being explored.

In medicine, there are two basic areas where functional polymers are important: medicinal biocompatibility and polymeric drugs (6). For biocompatibility, it is required that polymeric materials, both natural or synthetic, are accepted by the living system. Functionalization to achieve biocompatibility requires the chemical modification of the surface of the polymeric materials, but sometimes also the "mimicking" of the mechanical properties of the living system. In the area of polymers as drugs we must distinguish between functional polymers, whose drug functionality can be released as low molecular active component and where the entire polymer is active as a drug.

The ultimate objective in this field of polymeric drugs, although far from realization, is the multifunctional targeted drug, where several different functional groups are attached to the same macromolecule (7): The various functionalities could include drug functionality, a functionality to establish the proper solubility characteristic for the macromolecule, and a targeting group with the specific affinity to bring the complicated macromolecule to the site in the body where it is needed. The drug molecule may then be released by hydrolysis or by other means of degradation. This approach would avoid the danger of a drug overdose, especially in cases, where the drug toxicity is high, limiting the effectiveness of the drug.

In the food and nutrition area, the demand for effective polymeric (nontoxic and nonallergenic) antioxidants or food dyes is ever increasing.

In the energy field the enhanced oil recovery efforts demand the "ultimate" in the design of a combination of structure and functionality of fully or partially synthetic polymers. Simple modifications of the polymeric structures are often needed to adapt the polymers for the different requirements in the various oil fields.

Solar energy is considered the ultimate source of energy (8). Polymeric materials used for the equipment to collect solar energy have to be photostabilized by polymerbound photostabilizers and/or antioxidants. Effective polymerbound stabilizers are also needed in space applications, where the loss of stabilizer at the low pressure of space cannot be tolerated.

One of the problems, that face the development of functional polymers is the fact that this area of polymer science has only recently been recognized as a special entity, consequently, many questions have either not been properly asked or the answers are often not yet available.

In the next part of the paper we will describe the different types of polymer structure, capable of attachments of specific functional groups, and the modes of preparation of functional polymers.

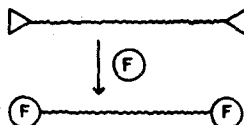
FUNCTIONAL GROUPS AS END GROUPS

Polymer endgroups are different from the monomer units of the main chain. In chain reaction polymerization they are introduced as a result of initiation, termination or chain transfer (Figure 2). In step reaction polymerization they are simply residual functionality of the bifunctional monomer; for example, amine and carboxylic acid groups in polyamides, or hydroxyl groups and carboxylic acid groups in polyesters. Sometimes these groups undergo further reactions: isocyanate groups can be hydrolyzed to amino endgroups and carbon dioxide and can thus become the cause of color formation.

Some polymers, obtained by chain reaction polymerization, have endgroups that can be the origin of lower thermal stability; in poly(methyl methacrylate), it is the vinyl endgroup (9), and in polyoxymethylene, it is the hemiacetal hydroxyl endgroup where thermal degradation can start. In poly(methyl methacrylate) this fault, although inconvenient, is not essential and does not always need to be remedied. In polyoxymethylene, the unstable hydroxyl endgroups must be capped for the polymer to be sufficiently stable for melt fabrication (10). Alkyl capping (with trimethylorthoformate or dimethylsulfate) makes the polymer stable to base, acetate capping (with acetic anhydride), on the other hand (easier performed rapidly and quantitatively), renders the polymer thermally but not base stable.

In other cases, endcapping of lower and medium molecular polymers with reactive endgroups, for example hydroxyl endgroups, allows in a simple way the introduction of two functional (but nonreactive) endgroups. Such functionalities, for example stabilizers, can be useful when low molecular weight functional compound needs to be blended into a polymer, but is either too volatile or is not sufficiently compatible.

END CAPPING



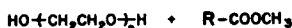
CHAIN TRANSFER

(2)

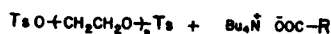


Endcapped oligomers are poly(ethylene oxide) glycols capped with ultraviolet absorbing groups, such as *N,N*'-dimethyl-aminobenzoate or salicylate (12) (Figure 3).

a) DIRECT REACTION



b) ACTIVATION PRIOR TO REACTION



(3)



Endcapping is a technique to introduce reactive endgroups into low to moderate molecular weight polymers; very often hydroxyl terminated polymers are used. Diisocyanates when allowed to react with polyester- or polyether glycols give isocyanate capped polymers which can be "chain extended" with glycols or diamines to polyurethanes (13). When multifunctional polyols, either in polymeric form or as low molecular additives with glycols are used, cross-linked networks are obtained. The epoxy groups of the polymeric glycidyl ethers of bisphenols are cured by polymerization with diamines and carboxylic acid anhydrides.

Chain transfer with monofunctional but still reactive groups especially in step reaction polymerization is also used to introduce other reactive groups as endgroups into low to moderate molecular polymers. Prominent among these are polymers with acrylate and methacrylate endgroups; through these groups, network formation can be achieved by ultraviolet curing.

Polymers with functional groups have also been used for macromolecular engineering by cationic mechanism. Polymers with tertiary halide, when allowed to react with metal alkyls, for example, diethylaluminumchloride, give polymeric carbenium ions that can be used as initiators for cationic polymerization (14). By using the proper polymeric halides (for example in poly(vinyl chloride)) not only block but also branched polymers can be made.

Various functional groups in terminal positions are used for crosslinking reactions rather than chain extension or polymerization: isocyanate terminated polymers are cured by base catalyzed trimerization to isocyanurates, nitrile terminated perfluorocarbon ether polymers are trimerized to triazines, and some high molecular weight, high temperature polymers can only be made from acetylene terminated high temperature oligomers by trimerization reaction of the acetylene groups to predominantly benzene rings.

Other types of "curing" not used for the formation of sigma bonds, but also using end functionality of telechelic polymers are effective for the formation of ionic clusters, typical for ionomers, for the formation of a glassy, a crystalline or even a liquid crystalline phase.

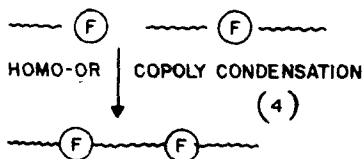
Ionomers with phosphate and sulfate groups have been prepared from telechelic polymers. These and other telechelic polymers with salicylate, pyrocatechol and other chelating endgroups have been made and chelated with transition metal salts (15). In other cases, the "functional endgroups" are short blocks of another monomer, as, for

example A-B-A triblock polymers. The A blocks provide the functionality to agglomerate and phase separate into a glassy phase (styrene/isoprene/styrene triblock) (16), or a crystalline phase (pivalolactone/isoprene/pivalolactone) or even a liquid crystalline phase.

FUNCTIONAL GROUPS AS PART OF THE MAIN CHAIN

Functional groups have been introduced into the main chain of polymers (Figure 4). Typical examples are nonreactive groups present in amounts of 1-3 mol percent that provide dye sites in polyesters.

Polyesters and polycarbonates with biologically active comonomers or antioxidants (bisphenols) in the chain have been made; these are examples of functional polymers, where the active component has to be released by hydrolysis. Other recently developed examples of condensation polymers using biologically active compounds as monomers are polybiurets: these polymers have been prepared by allowing diisocyanates to react with aliphatic primary amines, the primary amino group functioning as bifunctional monomer. The antimalarial compound primaquine and the antiviral agent aminoadamantane have been used as examples for the preparation of such polymers (17). Adenine and hypoxanthine have been incorporated into polymer chains by polymer reaction using bisorthoesters as polymer intermediates (18).



Salicylic acid has been condensed with formaldehyde to give polymers with chelating capabilities and antibacterial activity (19).

While for many years efforts have been made to make polymers stable at higher temperatures which require almost perfect rigid rod polymers, ladder polymers etc., recent interests seem to go the other way. It is indeed true, that maximum high temperature properties require ultimate properties; the price is intractability of the polymer and consequently high cost of fabrication or even the necessity of developing new fabrication techniques (for polytetrafluoroethylene and polyimides, sintering or rotational molding techniques). If only some of the characteristic properties are needed or can even be used, no need exists to strive for all possible polymer properties. As carbon or poly(p-phenyleneterephthalamide) fibers are imbedded in epoxy resin matrices to maximize the properties of the fibers while maintaining toughness of the material, dual purpose polymeric materials are being identified.

Regular copolyoxamides of aromatic diacids have been developed which are amorphous, have the toughness and high T_g based on the aromatic rings and a high concentration of amide groups which induce the formation of the morphology needed for channel type water transport (percolation principle) (20).

It has now become apparent that groups which impart highly desirable properties into the polymer but whose accumulation causes the formation of intractable polymers can be "diluted" to retain fabricability or to have their solubility properties modified. This can be achieved by introducing flexible spacer groups. The length of the spacer group can be varied and the maximum effectiveness determined.

Several types of polymers with a flexible spacer in the main chain have recently been developed. Introduction of methylene spacers between groups useful for the development of liquid crystalline behavior have lowered the thermotropic range and indeed extended the thermotropic range in liquid crystalline polyesters. It has been suggested that flexible links could very generally be used for polymers whose main characteristics are the solid state properties of otherwise intractable polymers. A critical size of the polymer unit, for example, in materials like polyacetylenes and other electronically active polymers, could be defined and utilized.

A number of reactive groups, suitable for polymerization or crosslinking reactions have been introduced into the backbone of polymers. Polyester oligomers with maleate and fumarate groups are used as comonomers for polymerizations with styrene or other monomers. Cinnamate groups, introduced into polyesters, provide photocrosslinking sites (to form polymeric truxilic acid derivatives).

Carbonyl groups introduced into polyethylene (polyethylene/CO copolymers) are used as points of photochemical attacks to render polyethylene photodegradable.

As indicated earlier, the butadiene unit in polymeric systems is a favored reactive group. The reactive part of the butadiene containing elastomers is the basis for vulcanization reactions. This unit is also effective for grafting/blending in high impact polystyrene or acrylonitrile/butadiene/styrene terpolymers.

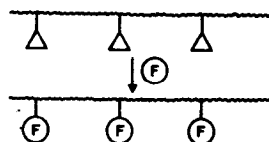
FUNCTIONAL GROUPS ATTACHED DIRECTLY TO THE POLYMER CHAIN

Most functional polymers have the functional groups directly attached to the polymer chain. These polymers are made by polymer reactions or by homo- or copolymerizations of a monomer which has the functional group attached to the polymerizable group (Figure 5). In the case of addition polymers each of these two basic methods has advantages and disadvantages; to achieve maximum effectiveness both basic methods should be carefully evaluated.

Polymer reactions require that suitable polymers or copolymers that have reactive groups attached to the polymer chain are available. Polymer reactions might be carried out directly on a reactive group or an activating group must first be introduced (Figure 6).

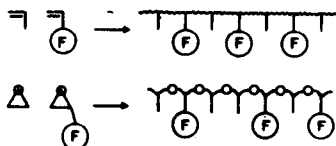
Advantages of polymer reactions are that a suitable polymer of the right molecular or molecular weight distribution is already on hand. The polymer reaction can be allowed to proceed to a limited extent or to completion. Disadvantages are that not many polymers are available for polymer reaction and often the right kind of polymer is unavailable.

A. POLYMER REACTION



(5)

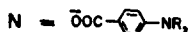
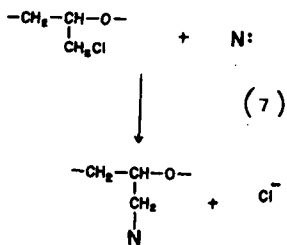
B. POLYMERIZATION AND COPOLYMERIZATION



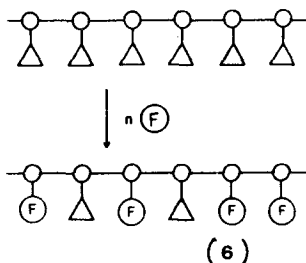
Very often a polymer reaction cannot be carried out to completion because of the interference of the polymer backbone. Most important, however, is the fact that few chemical reactions are quantitative. When reactions on low molecular weight compounds are carried out, the reaction products can be purified by distillation, crystallization or chromatography to remove the byproducts of the reaction. In most cases of polymer reactions, the by-product becomes part of the polymer chain; it causes the introduction of undesirable functionality into the polymer chain, one of which is color formation.

Polymers used for polymer reactions, already have functional groups in the polymer chain. For example, polymers with carboxyl groups can be used as polymeric carboxylate initiators for anionic pivalolactone polymerizations. Radicals can be generated by photolysis of the carbonyl linkage of poly(vinyl ketones). Cationic polymerizations can be carried out with carbon-chlorine bonds in poly(vinyl chloride) using aluminum alkyls to generate the polymeric cation. Tetrahydrofuran or other cationic monomers could be used for this branching reaction.

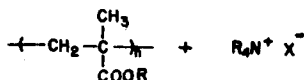
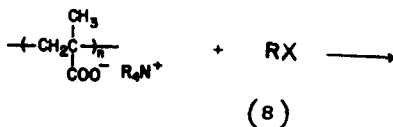
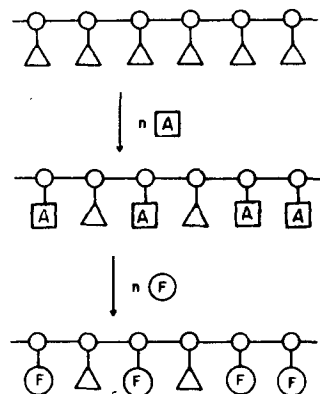
Excellent examples for reactions on polymers are those using homo- or copolymers of epichlorohydrin (21,22) (Figure 7) as reactive polymers. Many nucleophilic reactions have been demonstrated. They include reactions with carboxylate to form polymeric esters (23), and reactions with aliphatic amines thiocyanate, thiolate and alkoxides to form polymeric amines, thiocyanates, ethers or thioethers. Polymers and copolymers of methacrylic and polyacrylic acids were the subject of numerous polymer reactions (Figure 8), for example, esterification with alcohols, diazomethane, and (as salts) with dimethyl sulfate and alkyl halides (24). Selected hydrolysis of poly(acryl amides) to copolymers of acrylamide and acrylic acids have produced polymers for tertiary oil recovery (25).



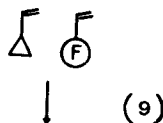
a) DIRECTLY



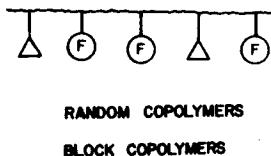
b) WITH ACTIVATING GROUP



When copolymerization of a functional monomer is chosen for the preparation of functional polymers other problems have to be faced. Once the functional monomer has become available, it could be polymerized with a number of comonomers, often in the amounts of comonomers similar to the feed ratio of the comonomers.

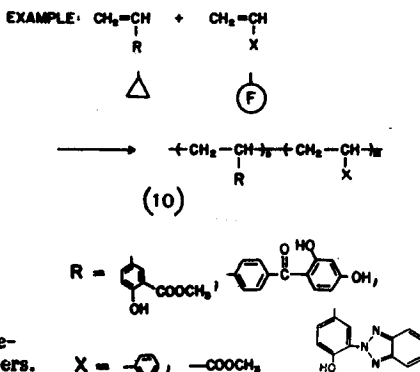


A number of disadvantages also exist when copolymerization of functional monomers is chosen as the method for the preparation of functional polymers. First, it might not be possible to synthesize the functional monomer; if synthesized, the functional monomer might not polymerize or copolymerize with the desired comonomer. Sometimes this problem can be overcome by choosing a copolymerizable monomer followed by polymer reaction. The copolymerization of the functional monomer might not lead to the polymer of desirable molecular weight or molecular weight distribution. The copolymerization might not lead to the desirable copolymer composition (blockiness rather than randomness) (Figure 9).



A few examples might illustrate the use of copolymerization using functional monomers and particularly, without avoiding the discussion of its disadvantages. One of the most important functional groups introduced by copolymerization is the carboxylic acid group, which after salt formation can lead to the important ionomers: Copolymerization of ethylene with 10 to 20 mole percent of methacrylic or acrylic acid lead to copolymers which, when partially or completely neutralized, gave the polyethylene based ionomers. Another example for the preparation of ionomers is the copolymerization of ethyl glycidate with trioxane or oxiranes followed by hydrolysis; this gives ionomers with polyoxymethylene or polyoxyethylene rather than with a polyethylene backbone chain.

homo- and copolymers of other functional monomers were aimed at the development of polymeric photostabilizers (26). As functional monomers were synthesized methyl 3-(4-, 5-) vinylsalicylate, 4'-vinyl-2,4-dihydroxybenzophenone, 4-methacryloxy(acryloxy)-2-hydroxybenzophenone, 4-vinyl- α -cyano- β -phenylcinamate (27), 2(2-hydroxy-5-vinyl(isopropenyl)phenyl)21-benzotriazole (28,29), 2(2-hydroxy-5-methylphenyl)-4-vinyl-21-benzotriazole (30), 2(2-hydroxy-4-methacryloxy(acryloxy)phenyl)21-benzotriazole (31) and others. As comonomers methyl methacrylate, n-butyl acrylate and styrene were used (Figure 10).



Not only vinyl or acrylate groups, but also oxirane groups have made functional groups polymerizable. Two events have made this development possible: First, oxiranes can now be prepared readily and in a general way by epoxidation of vinyl groups with *m*-chloroperoxybenzoic acid and, second, it has been demonstrated that certain acetylacetone modified aluminumalkyl initiator systems can readily polymerize oxiranes with functional groups. Based on this experience, copolymers of propylene oxide and methyl epoxyethylacetyl-salicylate have been prepared (32).

Polymeric antioxidants primarily based on 4-vinyl(isopropenyl)-2,6-ditertiarybutylphenol as the monomeric antioxidant were prepared by polymerizing it with styrene, methyl methacrylate, butadiene and isoprene. The copolymer of butadiene or isoprene could be hydrogenated to the corresponding copolymer of the polymerizable antioxidant with ethylene or ethylene/propylene (33). (Like other styrene derivatives 4-vinyl-2,6-ditertiarybutylphenol does not normally copolymerize with ethylene or α -olefins, even with coordination initiators.)

Copolymers with styrene and acrylonitrile were also prepared with polymerizable fire retardants, acrylates and methacrylates of 1,2-dibromopropanol, 2,4,6-tribromophenol and pentabromophenol (34,35).

A number of copolymers of vinylsalicylic acids were prepared which were found to be effective antibacterial agents. Many homo- and copolymers prepared by cyclopolymerization gave polyanions with anticancer activity (36). Functional polymers were also used to prepare water soluble polymers and polyampholytes with specific properties.

FUNCTIONAL GROUPS ATTACHED VIA A SPACER GROUP TO THE POLYMER CHAIN

When functional groups are attached directly to the polymer main chain, their effectiveness or reactivity is greatly influenced by the polymer chain. It had been recognized that under many circumstances it would be desirable to have functional groups attached to the polymer chain, yet, to have the functional group behave as if it did not know that it was part of a polymer chain. This can be achieved by attaching the functional group via a spacer group to the polymer chain. The early work in this field was done intuitively and empirically. Most of this work includes the preparation of monomers and polymers where the spacer group is attached to a conventional functional monomer of the methacrylate family for example hydroxyethyl methacrylate and dimethylaminoethyl methacrylate. Functional styrene derivatives have also been studied extensively; here, the benzene ring can be considered the (very stiff) spacer group. Typical examples of styrene type functional monomers are chloromethylstyrene, styrenesulfuric acid, the amines and ammonium salts based on reactions of chloromethylstyrene polymers with secondary and tertiary amines. In these cases, the advantages are that the methacrylate and styrene derivatives can undergo radical polymerization very similar to that of the parent compounds; these functional monomers can also undergo copolymerization with many comonomers. The functional groups can be introduced by polymer reactions that are basically reactions of esters or benzene derivatives.

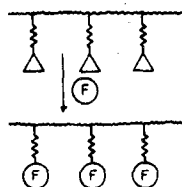
Spacer groups have also been introduced by polymer reactions. Good examples are reaction on poly(vinyl alcohols) with ϵ -caprolactam or ϵ -caprolactone to make polymeric acetals.

An extreme case of a functional group is the paraffin side group. The paraffin group when sufficiently long can crystallize (side chain crystallization) in a polymer backbone that is adequately polar. Examples have been shown for polymethacrylates, polyesters and polyaldehydes (37).

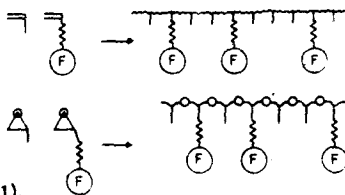
Very recently, a deliberate effort has been made to prepare polymers that have a polyethylene or a polyoxyethylene backbone and functional groups, attached to the main chain via a flexible spacer group of several methylene groups. This work required the development of new initiating systems for the coordination polymerization of ω -alkenoates (38) and ω -epoxyalkanoates (39,40). ω -Alkenoates could be polymerized and copolymerized with essentially all α -olefins including ethylene with titanium based initiating systems. In spite of the fact that the functional ester groups have the tendency to complex with the coordination initiator systems with partial deactivation, polymerization to high yield and high molecular weight has been achieved. ω -Epoxyalkanoates were polymerized and copolymerized with other oxiranes with an triethylaluminum/water/acetylacetone (1.0/0.5/1.0) initiator system. While the polymerization of functional α -olefins (ω -alkenoates) requires at least three methylene groups for the homopolymerization to proceed, the oxirane ring opening polymerization with two methylene spacer groups proceeds quite readily.

The functional ester group influences the polymerizability of the olefin bond or the oxirane ring by a.) withdrawing electrons from the double bond or the ring, b.) immobilizing the polymerizable group by complexing the functional group with parts of the initiator system. As the methylene spacer group reaches a critical length those factors become less important. It should also be pointed out that the polyoxyethylene chain is more flexible due to the additional flexible oxygen atoms in the polymer chain, (as compared to the polyolefin backbone chain). As a consequence, the number of methylene groups needed for the polymerization ω -epoxyalkanoates need not be as large as the number of methylene groups needed for polymerization of ω -alkenoates (Figure 11).

A POLYMER REACTION



B POLYMERIZATION OR COPOLYMERIZATION



Polymers and copolymers of functional α -olefins and epoxides with various lengths of flexible methylene groups that have become available, have been hydrolyzed very readily to the corresponding ionomers and polymeric acids. They will be used as valuable intermediates for the preparation of other functional polymers by polymer reaction; the rates of reaction are expected to be studied as a function of the number of methylene groups as spacer groups (41,42).