

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Reactive Groups, Spacer Groups and Functional Groups in Macromolecular Design

Otto Vogl^a; Yoshio Okahata^a; Donald A. Bansleben^a; John Muggee^a; Mark Purgett^a

^a Polytechnic Institute of New York, Brooklyn, NY

To cite this Article Vogl, Otto , Okahata, Yoshio , Bansleben, Donald A. , Muggee, John and Purgett, Mark(1984) 'Reactive Groups, Spacer Groups and Functional Groups in Macromolecular Design', *Journal of Macromolecular Science, Part A*, 21: 8, 1217 – 1235

To link to this Article: DOI: 10.1080/00222338408056599

URL: <http://dx.doi.org/10.1080/00222338408056599>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Reactive Groups, Spacer Groups and Functional Groups in Macromolecular Design

Otto Vogl

in cooperation with
Yoshio Okahata, Donald A. Bansleben,
John Muggee and Mark Purgett

Polytechnic Institute of New York
Brooklyn, NY 11201

ABSTRACT

Several aspects of modern design of macromolecular architecture are discussed: the influence and importance of functional groups which often dominate the characteristics of the macromolecular structure; the importance of the spacer groups that provide flexibility and allow the functional group to act independently from the main chain when the functional group is attached to the main chain.

Examples are given for the synthesis of reactive, telechelic polymers, for polymerizability of monomers whose polymerizable group is separated from the functional group by a flexible methylene spacer, and the reactivity of functional groups separated from the main chain by a spacer group.

PREAMBLE

Polymers with functional groups have been known throughout the development of polymer science. When our last U.S.-Japan Seminar on

Polymer Chemistry [1], the second of the series, was planned, it was recognized that functional polymers had started to play a very important role in the development of polymer science. In 1974 at the steering committee meeting at the first U.S.-Japan Seminar at the Fujiview Hotel at Kawaguchi-Ko, we selected "Functional Polymers" as the theme of the second Seminar [2]. The selection of this title inspired, more in Japan than in the U.S., work on functional polymers: what type and how functional groups should be introduced into conventional polymers and how those exotic polymers should be designed. The second U.S.-Japan Seminar on Polymer Chemistry, "Functional Polymers," was held in 1978 at Pingree Park, Colorado. Agreement was reached for the third seminar to be held in Osaka, under the title of "Reactive Polymers," a specialty of Functional Polymers. For the proposed fourth seminar, "Specialty Polymers," the main theme is expected to emphasize more the properties of individual polymers with more emphasis on their use rather than the principle of their design by macromolecular architecture and engineering.

INTRODUCTION

Polymers with functional groups have become of major importance in the development of modern polymer science [3]. These macromolecules are often tailor-made to perform specific functions and are sought for these properties rather than for the mechanical bulk properties of the polymers. Such macromolecules may have groups that impart onto the polymer properties such as chemical reactivity, spectral or biological/medical properties, they may be photo-, thermally, or catalytically active.

In this article we will discuss three aspects of functional polymers: (a) End-reactive Polymers: the discussion of simple methods to make reactive telechelic polymers and attempts to develop simple crosslinking reactions under mild conditions; (b) Flexible Spacer Groups: (i) the use of spacer groups to separate

functional and polymerizable groups in monomers for subsequent polymerization; (ii) reactions on polymers whose functional group is in the side chain separated by flexible spacer groups from the main chain.

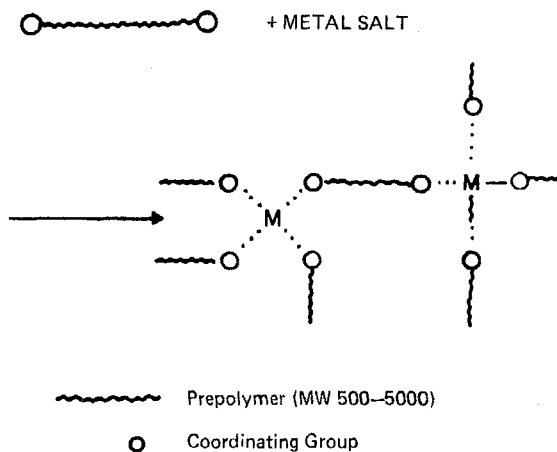
Selected End-Reactive Macromolecules

Polymers, usually of moderate molecular weight, whose reactive groups are at the ends of the polymer chains are called telechelic or end-reactive polymers: Very important reactive groups in telechelic polymers are acrylates, hydroxyl, carboxyl, sulfoxyl, and amino groups. Perhaps the most important end groups of the telechelic type are isocyanate groups, which are the basis of polyurethane technology, and are now used for the reaction injection molding (RIM) technology [4]. For high-temperature use, nitrile groups or acetylene groups have become important end groups for telechelic polymers.

Relatively few reactions of telechelic polymers are known that can be carried out at room temperature. Among the curing reactions to give crosslinked networks at room temperature, especially used for dental impression materials, are the reactions of polymers with mercaptane end groups crosslinked with lead dioxide or silane-terminated low molecular weight polysiloxanes which are allowed to react with orthosilicates. A more recently developed system for chain extending or crosslinking involves also polysiloxanes. Siloxanes endcapped with Si-H groups are capable of adding to a carbon-carbon double bond, for example, an acrylate with platinum compounds as the catalysts. Another crosslinking reaction involves telechelic aliphatic polyesters endcapped with aziridino groups; the latter were then polymerized by cationic polymerization.

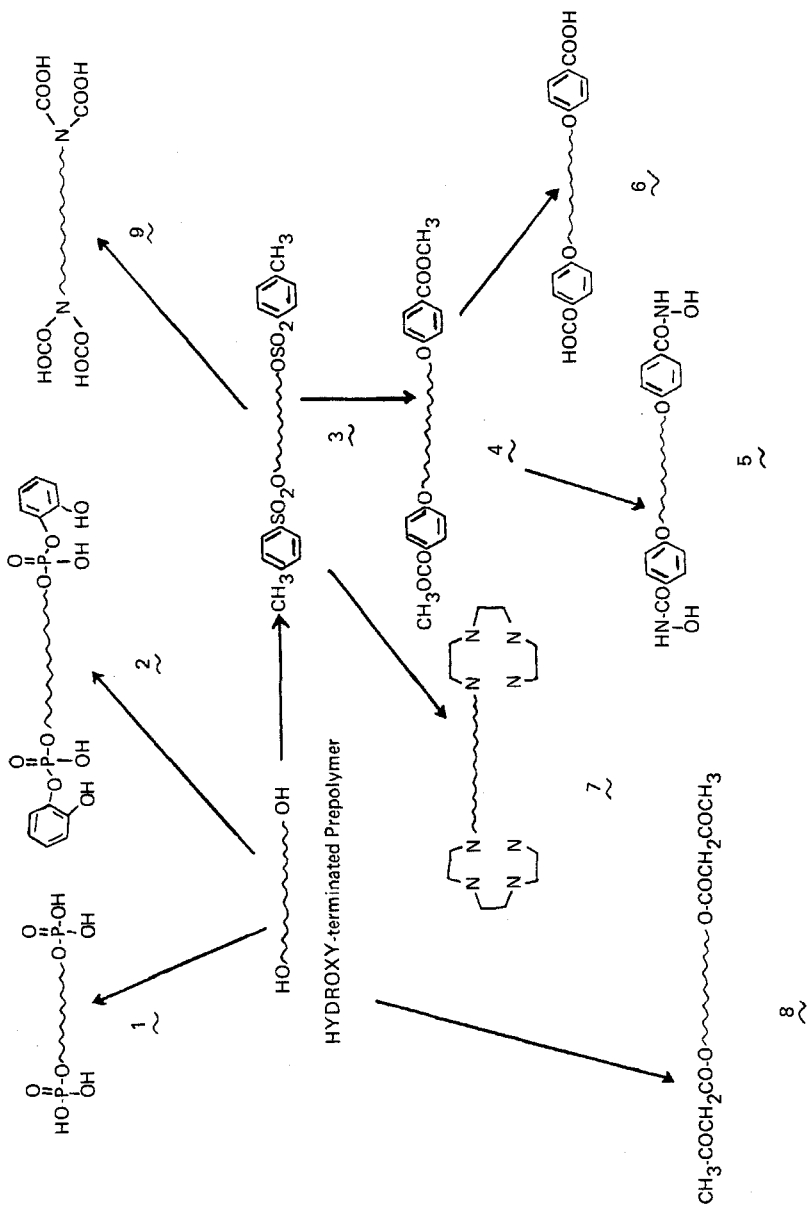
Most of these reactions are curing reactions in the bulk without solvents. This means that the reactions of the end-reactive groups are carried out with the polymer backbone chain being the actual solvent, and its polarity or solvent power dictates the progress of the reaction. Since the molecular weights of most of

the telechelic polymers are in the range of 2000 to 5000 and the molecular weights of the reactive end groups are about 100, we are speaking of reactions of 2-5% solution of the reactive end group with the polymer chain being the solvent (Equation 1).



In the work reported here, we focus on chelating reactions of end groups as the curing reaction (Equation 1): hydroxy-terminated prepolymers such as polypropylene oxide (PPO) (MW: 425-~4000), polytetrahydrofuran (PTHF) (MW: 650-2000), poly(ϵ -caprolactone) (PCL) (MW: 640-1250), hydroxy-terminated polybutadienes (PB) (MW: 2800-3600), silanol- or carbinol-terminated poly(dimethyl siloxanes) (MW: 2400-22,000) were chosen for reasons of availability as the telechelic prepolymer; all materials had a low T_g . The hydroxy end groups of these polymers were converted to appropriate groups known to be good coordinating groups, such as phosphate, hydroxamate, carboxylate, tetramine, acetoacetate, and iminodiacetate [5-10]. The general structure and preparation scheme of the telechelic polymers which were prepared in this work are summarized in Equation 2.

Grafting of 5-vinylsalicylic acid onto PB (MW: ~3000) was also performed to obtain polymers whose chelating groups were attached to the polymer by grafting randomly along the polymer chain.



The following hydroxy-terminated polymeric glycols were used for our studies: PPO (MW: 650, 1000, 2000, 4000), PTHF (MW: 650, 1000), poly(ϵ -caprolactone) (ϵ PCL) (MW: 1250), PCL-triol (MW: 900), PB (MW: 2800), polysiloxane (PSi) (MW: 3200, 22,000), polysiloxane carbinol (PSiC) (MW: 2400). All hydroxy-terminated polymeric glycols had functionalities near 2.0 (Equation 2). The most extensively studied reaction was the phosphorylation of the polymeric glycols. Glycols, in chloroform solution, were treated with phosphorousoxychloride with triethylamine as the acid acceptor. Phosphorylation worked very well with the PPO's; a nearly quantitative reaction to phosphate-terminated polymers was achieved. PTHF and PCL glycols gave only 40-70% phosphorylation, and the reaction with PB glycol was very poor. The conversion to the phosphate-terminated PSi was from 60 to 80%. Phosphorousoxychloride had been used under reaction condition which might have caused some side reactions, especially diester or triester formation.

A better way of carrying out only monofunctional phosphorylations to monophosphoric acids is the use of *o*-phenylenephosphochloridate instead of phosphorousoxychloride. This reagent is readily prepared in good yields and reacts rapidly and quantitatively with most alcohols; it had been used exclusively as phosphorylation agent of nucleotides under mild conditions. The reaction was carried out as follows: The polymeric glycol in 1,4-dioxane solution was treated with *o*-phenylene phosphochloridate at room temperature in the presence of 2,6-lutidin. PPO and PTHF were *o*-hydroxyphenylphosphate-terminated in 90% conversion, the PCL-triol reacted to about 75%, and the PSi in much smaller conversion.

Acetoacetate-terminated polymers were prepared by transesterification of the glycol with ethyl acetoacetate. PPO was allowed to react in the presence of a small amount of lead oxide for two hours at 180°C and gave 80 to 85% yield of the acetoacetate-terminated PPO.

Regular esterification of terminal hydroxyl groups of glycols was carried out under mild conditions by treating the ditosylates of the polymeric glycols with methyl *p*-hydroxybenzoate and sodium

hydroxide in polar solvents; the ditosylates of all the glycols could be prepared in 80 to 90% yield. The conversion of the ditosylates to the methyl benzoate-terminated polymers of PPO and PTHF were from 80% to nearly quantitative. The methyl benzoate-terminated polymeric glycols served for the synthesis of carboxylate-terminated polymeric glycols and for the synthesis of hydroxamate-terminated polymeric glycols. Methyl benzoate-terminated PPO MW 650, 1000, 2000, and 4000 were hydrolyzed in 5% potassium hydroxide solution in ethanol:water (1:1) in 90-95% yield. For the synthesis of hydroxamate-terminated polymers, methyl benzoate-terminated polymers were treated with an alcoholic hydroxylamine solution (made from hydroxylamine hydrochloride salt and potassium hydroxide); the conversions were from 60 to more than 90% and gave a number of hydroxamate-terminated PO and THF polymers.

In one case, PPO (MW: 1000) ditosylate was allowed to react with triethylenetetramine, which was an attempt to prepare triethylenetetramine-terminated polymers. Reactions of the ditosylate with triethylenetetramine gave the polymer in 80% recovery but with only a 35% reaction conversion. Similarly, iminodicarboxylate gave in only 10-20% reaction conversions iminodiacetic acid-terminated polymers. When polysiloxane glycols were used for the attempted conversion of the hydroxyl group to other reactive telechelic end groups, the problem of hydrolytic stability of the silicon bonds to, for example, the phosphate groups became a problem. After normal work-up in the presence of water, the Si-O-P bond usually was completely hydrolyzed.

The principle of all the curing reactions with metal salts: oxides, hydroxides, etc., were based on the fact that the end groups would act as a bifunctional ligand and the transition metal would act as hexa-coordinate central metal atom for the complex, or that the whole metal salt in its solid state acted as an at least "trifunctional" crosslinking agent.

The effective curing of some of the end-reactive polymers depended on several factors: degree of substitution and type and extent of curing (some functional groups cured as such, others re-

quired that the acid group be first neutralized (usually with KOH) to form the anions).

The curing ability of individual telechelic polymers did not seem to depend so much on the structure of the polymer chain, but on the purity of the bifunctionality which should, of course, be near 100%. For the curing experiments, telechelic chelating group terminated polymers were mixed with the metal compounds on a glass plate. Phosphate-terminated PPO gave effectively cured polymers after neutralizing the phosphoric acid end group with one equivalent of potassium hydroxide and then with metal hydroxide, such as cobaltic chloride, nickel chloride, or quaternized tetramines. Other polymers (PCL, PTHF, PSi) with low conversion of the initially hydroxy-terminated polymer to phosphate end groups did not cure well. *o*-Hydroxyphosphate-terminated polymers did not cure in the acid form with any metal compound.

Hydroxamic acid-terminated polymers cured reasonably well with ferric chloride in spite of the fact that the telechelic polymers had only 75-95% of the hydroxyl groups converted to the hydroxamic acid end groups. Hydroxamic acid groups cure only in acidic medium. This is well known from the coordination of ferric compounds with hydroxamic acids.

Acetoacetate-terminated PPO gave good cures when mixed with potassium hydroxide and metal oxides such as oxides of copper, iron, nickel, or even calcium and barium. The best-cured elastomer was obtained in the PPO family when a PPO of MW 4000 was used.

All other end-functionalized polymers did either not cure because of the low functionality of the end-reactive groups or the chelate-forming reaction did not work as expected, or a combination of both (tetramine-terminated, iminodiacetic acid-terminated, or simply carboxylate-terminated).

5-Vinylsalicylic acid grafted on PB, especially on 1,2 PB, gave a cured polymer when mixed with metal compounds, but only when about 15 mol % of 5-vinylsalicylic acid was grafted onto the PB's.

Spacer Groups Between the Polymer Main Chain and the Functional Groups of the Side Chain

Functional groups directly attached to the backbone chain of high polymers are often less reactive than if these groups were not attached to a polymer. This reduced reactivity is caused by steric hindrance or by the fact that all or part of the polymer chain interferes with the reactivity of the individual functional group. Some cases have been recognized, and now more and more are being recognized in which the reactivity (or activity) of a functional group is unaffected by its neighboring group or more importantly by the polymer main chain. In such cases, the reactive or functional groups are separated from the polymer main chain by a "spacer" group. Most frequently, this spacer group is flexible; for example, a few methylene groups, but even such groups as a rigid phenylene group, are effective in separating the functional group from the polymer backbone chain.

In the past, some spacer groups had been placed between the polymer backbone chain and the functional groups to influence the reactivity of the functional groups in the polymer. Most of this work has been done without a full understanding of the importance of the spacer group effect. Spacer groups could be designed to be flexible or stiff, a most important capability to design macromolecular architecture by modern polymer synthesis. In some isolated examples in the past, spacer groups have been introduced to bring out specific polymer properties. Poly(vinyl alcohol) was allowed to react with ϵ -caprolactam followed by the attachment of aminoacids and enzymes, or by direct reaction (as anion) with long-chain aliphatic groups to change solubility characteristics. We now know that some of these reactions are incomplete and give poorly defined polymeric structures. The problems of polymer reaction to introduce functional groups via a spacer group into polymers where the spacer separates the functional from the polymerizable group vs. preparation of polymerizable monomers which can then polymer-

ize or copolymerize has recently been amply discussed and demonstrated [3].

One of the simplest, but at the same time most striking examples of the effect of spacer length on polymer properties is in the case of "side chain" crystallization. Years ago it had been noted that methacrylates with long normal aliphatic ester groups showed the peculiar phenomenon that the rate of polymerization was substantially enhanced when the aliphatic chain of the alcohol of the methacrylate reached a certain length. When the polymers were examined, it was found that these polymers were crystalline. The degree of crystallinity depended on the length of the normal aliphatic alcohol group of the ester [11]. In fact, no crystallinity was found in polymethacrylate esters whose alcohol group was less than n-dodecyl. In all cases, the stereochemistry of the backbone chain was not different from that of radically prepared poly(methyl methacrylate), clearly showing that crystallinity of the polymer was that of the paraffinic side chain.

Polyesters of terephthalic acid and 2,3-substituted 1,4-butanediols showed a similar behavior [12]. Side chain crystallization was found when the paraffinic groups in 2,3 position of the 1,4-butanediol were very long, as one would expect from the influence of a stiff backbone chain. From the quantitative measurement of the heat of crystallization of the aliphatic side chains in excess of the length necessary for the first observation of crystallizations occurring, it was found that the side chain length necessary for the paraffinic side chain crystallization of these poly(butylene terephthalates) was at n-dodecyl. The capability of the side chains to crystallize seems to be independent of the stereochemistry in the 2,3-substitution of the paraffinic long chain.

An even more interesting example of side chain crystallization was found in the case of higher aliphatic polyaldehydes of isotactic structure [13]. These polyaldehydes crystallize in a 4_1 helix with four polymer chains in the unit cell. When the polyaldehyde had only one methyl group as substituent of the polyacetal chain

(isotactic polyacetaldehyde), only one melting point of about 165°C was observed. Even with a side chain of an n-propyl group as in the case of the crystalline isotactic polymer of n-butyraldehyde, only one melting point of about 245°C was detected. From a side chain length of more than 3 carbon atoms, a dual melting point was found. The higher melting point could be assigned to the melting of the helical polyacetal backbone chain, but the second melting region is much lower; it was identified as the melting of the paraffinic side chain. Both melting regions are clearly identifiable and are separated by almost 100°C . Isotactic poly(n-heptaldehyde) was especially well studied and its crystalline structure established [14] (Figure 1). Isotactic polyaldehydes with normal paraffinic side chains of more than ten carbon atoms do not show the melting regions of the polymer backbone chain any more, indicating that there exists no crystalline phase of the polyacetal backbone any more and the entire crystallinity is due (as in the case of

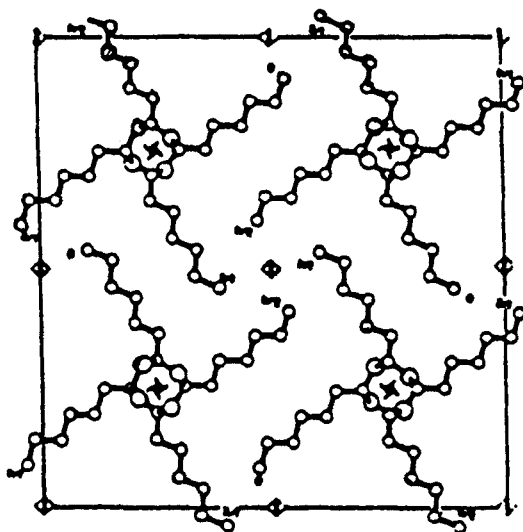


Figure 1

methacrylates and polyesters) to the paraffinic side chain crystallization. In the cases described above, the functionality of the side chain is crystallizability. Depending on the structure and rigidity of the backbone chain, the spacer group might be as short as a three methylene group to allow crystallization to occur, as we have seen in the crystallization of isotactic polyaldehydes.

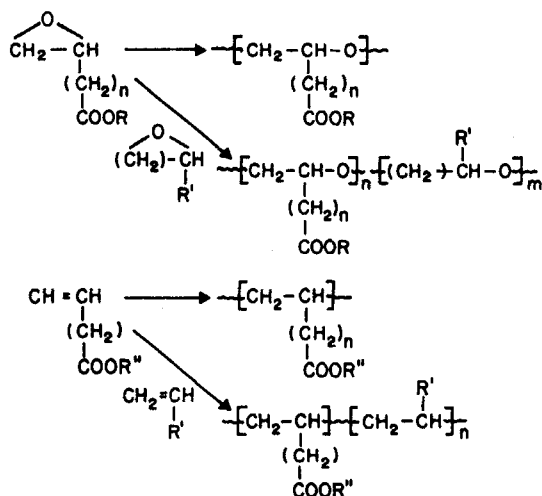
One of the characterization techniques of network polymers is the study of the swelling behavior of networks with flexible connecting groups. It was also found that penetration of solvent molecules, necessary for swelling, can occur only in the main part of the networks, but not near the branch points. It is now reasonably well established that no penetration of solvent molecules occurs nearer than 3 carbon (or other) atoms from the branch or crosslinking point, again indicating that there is a "magical" three- or four-atom region from the branch point which is strongly influenced by the polymer chain.

Few polymers obtained by polymerization of functionally substituted monomers have been accessible in the past that do not have the functionality directly attached to the polymer chain. Those are acrylates or methacrylates as homo- and copolymers, or the important copolymers of the free acids (methacrylic or acrylic acids) with ethylene which produced the most important family of ionomers. All acrylic monomers can be homopolymerized with radical initiators or copolymerized with comonomers capable of radical copolymerization. Examples are copolymers of methacrylic acid (10-30 mol %) with ethylene under conditions of free radical "high-pressure ethylene polymerization."

Styrene-type monomers are another category of monomers that polymerize well with radical initiators. The benzene ring of the polystyrene can later be used for substitution reactions, or substituted styrenes (p-chloromethylstyrene) could be used directly for homo- or copolymerization which can then be used for further displacement reactions. The formation of ion-exchange resins of the tertiary amine or quaternary ammonium category or the use of these p-chloromethylstyrene-containing resins in the Merrifield peptide syn-

thesis are typical examples. In these cases, not only the functionality but also (because the resins are crosslinked) the crosslinked density and/or the swellability in the appropriate solvents plays an important and significant role in their reactivities and effectiveness. Styrene-type monomers have as the "spacer" group a phenylene group that is stiff and can readily separate the polymer chain from the functional group. An advantage is that styrenes (as do the acrylates) readily undergo radical polymerization and copolymerization.

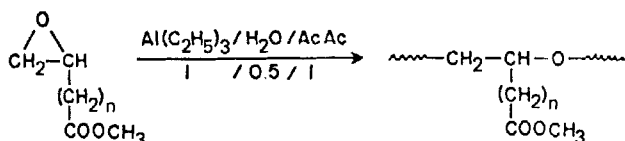
Our goal for the preparation of functional polymers was to develop methods for the polymerization of olefins or epoxides (oxiranes) with functional groups (for example, ester or nitrile groups). We have now accomplished the homopolymerization of functionally substituted epoxides and olefins and their copolymerization with selected cyclic ethers or with α -olefins (Equation 3).



Functionally Substituted Epoxide Monomers: Functionally substituted epoxide monomers were synthesized from methyl ω -alkenoates by epoxidation with *m*-chloroperoxybenzoic acid. When the epoxidation step was studied as a function of the number of methylene groups between the double bond and the carbomethoxy group, it was

already recognized that the rate of epoxidation was not the same for all ω -alkenoates. The position of the carbomethoxy group, an electron-withdrawing group, and the degree of separation played a significant role in the rate of epoxidation [15]. It was very slow when the carbomethoxy group was directly attached to the olefin group to be epoxidized (methyl acrylate). As methylene groups were inserted between the olefin double bond and the carboxylate group, the olefin double bond became more and more reactive, and when three methylene groups were placed between the olefin double bond and the carbomethoxy group the rate of epoxidation reached a maximum and remained essentially constant as further methylene groups were inserted. It is interesting to note that the value of the ^{13}C NMR chemical shift of the methine carbon atom also became constant, indicating a constant electron density in the olefin double bond and no more electronic influence of the carbomethoxy group.

Polymerization experiments with methyl ω -epoxyalkanoates were successfully carried out with specially prepared triethylaluminum/water/acetylacetone (1.0/0.5/1.0) initiator system [16,17] (Equation 4). This reaction mixture provided an anionic coordinative



initiator system, but 5 mol % of aluminum must be used to polymerize the functional epoxide; even at this high "initiator" concentration, polymers of 5×10^5 molecular weight were obtained, indicating that the actual initiator is only a small percentage, perhaps 0.1% to 1.0 mol % of the initiating system.

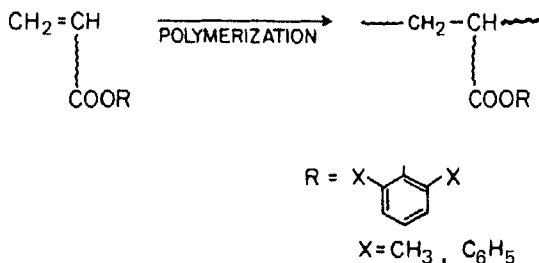
We have no doubt that only a part of this system acts as initiator and that another part of the initiator system is used for coordination of the functional epoxide; apparently, no chemical reaction occurred between aluminum alkyl groups of the initiator system and the carbomethoxy group of the monomer as the carbometh-

oxy group was always found unchanged after polymerization and work-up with methanolic hydrogen chloride. It is not unreasonable to believe that similar systems slightly different from the stoichiometry of 1.0/0.5/1.0 might also be active for polymerization of functional epoxides. When the initiating system was made in a similar manner with triethylaluminum/water/acetylacetonone (1.0/0.3/0.5), the initiator formed was quite inferior in activity [18].

All methyl ω -epoxyalkanoates (MEA) gave homopolymers and also copolymers with selected cyclic ethers [19,20]. After a polymerization time of several weeks, the homopolymerization of MEA with the triethylaluminum/water/acetylacetonone (1.0/0.5/1.0) initiating system gave low polymer yield when n was 0 (methyl glycidate), slightly higher with $n = 1$ (methyl 3,4-epoxybutanoate), or even with $n = 2$ (methyl 4,5-epoxypentanoate). In the cases of the polymerization of MEA's with $n > 4$, the polymer yields were high and polymers were obtained relatively more rapidly. In addition, the molecular weight of MEA polymers of $n = 0-2$ was low and the molecular weight distribution was broad. For polymers of MEA's of $n > 4$, the molecular weights were high as judged by the inherent viscosity; the molecular weight distribution $\overline{M}_w/\overline{M}_n$ was much narrower, < 1.7 , which suggests one single type of initiator site. The coordinative polymerization of these functional epoxide monomers might even have similarities with living polymerization. The fact that coordinative anionic polymerization has living character has been demonstrated by S. Inoue [21] for aluminum alkyl systems complexed with porphyrin ($\overline{M}_w/\overline{M}_n$ of < 1.2 have been found for propylene oxide polymerization). It is concluded from this work that for effective polymerizations of substituted functional epoxides at least 2, preferably 3 methylene groups are necessary between the polymerizable epoxide (oxiran ring and the carbomethoxy group to establish maximum yield and optimum molecular weight of the polymer. Similar conclusions have also been found by other workers more recently for the polymerization of ω -epoxyalkanonitriles [22].

Functionally Substituted Olefins: Functional olefins can polymerize by radical mechanisms, when the polymerizable olefin group

is directly attached to the carboxylate or nitrile group (acrylic acid derivative) or a phenyl group (styrene derivative). As soon as there is a carbon atom with a hydrogen substituent positioned in alpha position to the polymerizable olefin group, hydrogen abstraction to form allylic radicals proceeds readily. In the presence of these stable radicals, propagation to high molecular weight polymers does not proceed. Consequently, ω -alkenoates have not been homopolymerized. It has become clear that homo- and copolymerization with other olefins or with ethylene could only be accomplished by Ziegler-Natta-type coordination polymerization (Equation 5).



In our work approach [23] we have restricted our choice of initiators to those systems whose components are easily available and which are already well known for the polymerization of propylene. TiCl_3 modified with AlCl_3 and acetylacetone of various grain size and surface area were studied.

It was found that polymerization of 10-undecenoate could be accomplished if the monomer was precomplexed with diethylaluminumchloride or di-sec-butylaluminum chloride. Complexation occurred at room temperature rapidly but not instantaneously. When a solution of the complexed monomer was added to the freshly prepared initiator system, polymerization proceeded smoothly and a good yield of polymer was obtained. Eight to ten moles of complexing agent per mole of functional group were needed; similar results were obtained with 7-octenoate. With 5-hexenoate, the yields of polymer were lower. Best results in our polymerization experiments were obtained with the 2,6-dimethylphenyl or the 2,6-diphenylphenyl ester of the corresponding ω -alkenoic acids.

These functional monomers (alkenoates) could be copolymerized with α -olefins with the same polymerization initiators that gave good yields of homopolymers. The ease of incorporation of the alkenoates undoubtedly depends on the copolymerization ratio between the α -olefin and the alkenoate. With 1-dodecene as the comonomer for the copolymerization with 10-undecenoate, good incorporation of the 10-undecenoate was achieved; even when 1-hexene was used as the α -olefin comonomer, 10-undecenoate was readily incorporated. It was, however, difficult to incorporate more than 10 mol percent of 10-undecenoate into a copolymer with propylene; under more forcing copolymerization conditions, the molecular weight of the copolymer dropped rapidly. Under our reaction conditions we have achieved incorporation of up to 5 mol percent of 10-undecenoate into copolymers with ethylene. A previous patent claimed an incorporation of up to 2 mol percent into ethylene; no homopolymerization experiments had been reported at this time [24].

We have also accomplished the terpolymerization of 10-undecenoate with ethylene and propylene. With the titanium initiator system, a crystalline terpolymer was prepared when a 12/1 ratio of propylene/ethylene was used as the feed of the olefin component. The terpolymers had a 5 to 10 mol percent of 10-undecenoate incorporated and showed two melting endotherms about 15 to 20°C lower than the melting endotherm that could be assigned to the crystalline melting point of linear polyethylene (122°C instead of 136°C) and isotactic polypropylene (145°C instead of 165°C). With vanadium initiators, an amorphous terpolymer with a similar incorporation of 10-undecenoate was obtained similar to what one would have obtained from regular ethylene/propylene copolymerization to amorphous elastomer.

Unlike the polymerization of functional epoxides, where three methylene groups were needed for good polymerization, polymerization of ω -alkenoates requires a spacer length of $n \geq 5$ to achieve good polymerizability.

In conclusion, several classes of polymers with functional groups have been investigated. Reactive telechelic polymers have

been prepared and network-forming crosslinking reactions with transition metal salts were studied. Phosphoric acid, hydroxamic acid, salicylic acid groups have been used as end groups in these telechelic polymers. For most effective and rapid setting, polymers with a functionality of 3 with arms of equal length are probably preferable. Functional epoxides with $n \geq 3$ and functional olefins of $n \geq 5$, where n is the number of methylene groups between the carboxylic ester and the polymerizable group, are needed for homo- and copolymerizations using the appropriate coordination-type initiators.

REFERENCES

1. U.S.-Japan Seminar on "Functional Polymers," Pingree Park, CO, 1978.
2. O. Vogl and J. Furukawa, "Ionic Polymerization: Unsolved Problems," Marcel Dekker, Inc., New York, 1976.
3. O. Vogl, Makromol. Chem., in press.
4. J. H. Saunders and K. C. Frisch, "Polyurethanes: Chemistry and Technology," Interscience Publishers, Inc., New York, NY, 1962, 1964.
5. C. K. Berninger, R. C. Degelso, L. G. Donaruma, A. G. Scott, and E. A. Tomic, J. Appl. Polym. Sci., 7, 1797 (1963).
6. T. A. Khwaja, C. B. Reese, and J. C. M. Stewart, J. Chem. Soc., (C), 2092 (1970).
7. H. A. C. Montgomery and J. H. Turnbull, J. Chem. Soc., 1963 (1958).
8. L. Zevras and I. Dilaris, J. Am. Chem. Soc., 77, 5354 (1955).
9. J. G. Moffatt and H. G. Khorana, J. Am. Chem. Soc., 79, 374 (1957).
10. L. A. Slotin, Synthesis, 1977, p. 737.
11. N. A. Platé, in "Reactions in Polymers," J. A. Moore, Ed., D. Reidel Publishing Co., Boston, MA, 1973, p. 169.
12. Z. Florjanczyk, B. Deopura, R. S. Stein, and O. Vogl, J. Polym. Sci., Polym. Chem. Ed., 20, 1051 (1982).

13. O. Vogl, *J. Polym. Sci.*, 46, 261 (1960).
14. I. Negulescu and O. Vogl, *J. Polym. Sci., Polym. Chem. Ed.*, 14, 2415 (1976).
15. J. Muggee, Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1982.
16. D. A. Bansleben, Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1982.
17. E. J. Vandenberg, U.S. Pat. 3,106,549 (1963).
18. D. Tirrell, O. Vogl, T. Saegusa, S. Kobayashi, and T. Kobayashi, *Macromolecules*, 13, 1041 (1980).
19. O. Vogl, J. Muggee, and D. Bansleben, *Polymer J. (Japan)*, 12(9), 677 (1980).
20. O. Vogl, P. Loeffler, D. Bansleben, and J. Muggee, in "Coordination Polymerization," C. C. Price and E. J. Vandenberg, Eds., *Polym. Sci. Tech.*, Plenum Press, Vol. 19, 1983, p. 95.
21. N. Takeda and S. Inoue, *Makromol. Chem.*, 179(5), 1377 (1978).
22. S. E. Cantor, G. D. Brindell, and T. J. Brett, Jr., *J. Macromol. Sci., -Chem.*, A7(7), 1483 (1973).
23. M. Purgett, Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1982.
24. Farbwerke Höchst., French Pat. 1,498,009 (1967); CA 69, 67923w (1968).