

ON NEW CHEMICAL REACTIONS OF POLYMERS

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INTRODUCTION

Three major areas of work present themselves to a chemist who is concerned with polymer materials namely: synthesis and degradation of polymers; structure analysis of natural and synthetic polymers; and chemical transformations of polymers. Although these three fields are very closely related, I wish to concern myself only with the last of them.

Reactions with natural or synthetic polymers have played an important role in technology for a number of decades. I need only mention the nitration and acetylation of cellulose, the sulphochlorination of polyethylene, which leads to Hypalon, or, to give a more recent example, the use of reactive dyes. Chemical transformations of macromolecules are also of great importance in connection with basic research in polymer chemistry. I wish especially to call attention to the fact that many biochemical processes occur through reactions in dissolved macromolecules or on polymer surfaces.

Due to the great significance of polymers with reactive groups, several papers are devoted to this subject at each IUPAC symposium. I need only mention the main lectures of Smets on analogous polymer reactions¹, of Overberger on biologically active polymers² and of Manecke on enzyme resins³ in Montreal, Prague and Tokyo respectively.

But in view of the great number of publications which appear annually on the subject, it is not possible to present a comprehensive survey within the compass of a single lecture and I shall be obliged to restrict myself to certain aspects. I have chosen topics which have not been treated at previous symposia and to which our group in Mainz has been able to make contributions. I wish to discuss the following items:

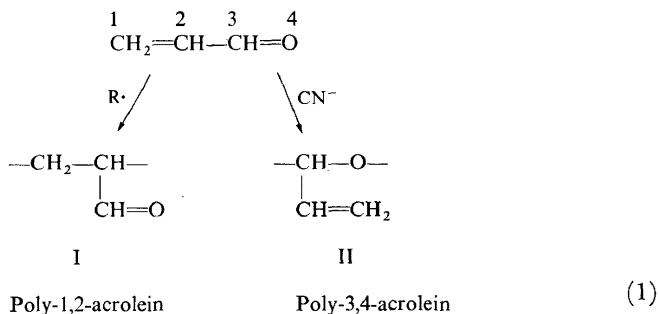
1. New reactions on polyacroleins
2. Reactions on polymers with anhydride groups, carbonate groups or lactone groups
3. Isomerizations on macromolecules
4. Asymmetric syntheses on polymers
5. Polyradicals

Certain other important aspects will be considered in detail by Professor Sakurada.

REACTIONS ON POLYACROLEINS

Under the influence of free-radical initiators on acrolein, only the vinyl group is polymerized, and polymers with aldehyde groups in the side chains

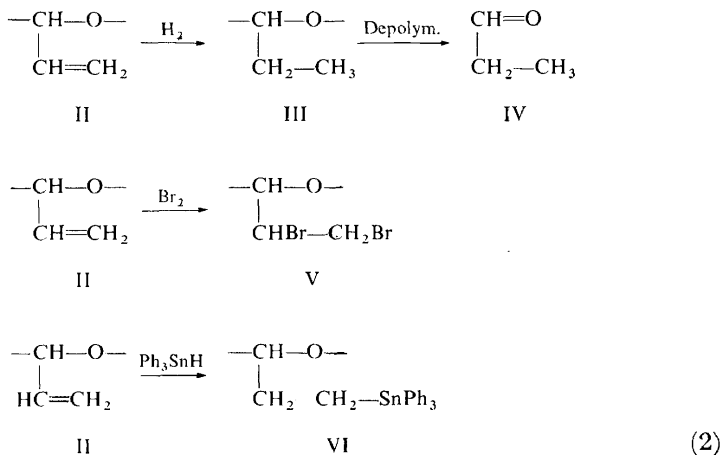
are obtained⁴. [I, equation (1)]



These aldehyde groups, although not in a free form, are nevertheless highly reactive. The numerous reactions which are possible with this type of polyacrolein were extensively reported on at an earlier IUPAC symposium^{5,6}. We have since been able to show that in the case of alkali cyanides at low temperature, polymerization takes place exclusively at the carbonyl group of acrolein. Polyacetals with vinyl groups in the side chains are obtained⁷ (II). We call this polymer poly-3,4-acrolein. The physical and chemical properties of this polyacrolein are of course quite different from those of polyacrolein obtained by free-radical polymerization.

Poly-3,4-acrolein softens at about 90°C and is soluble in various organic solvents. The double bonds of this polymer are highly reactive; hence, upon storage in air for an extended period of time, chemical changes take place, which lead to cross-linking and insolubility. But in solution or at low temperatures these polymers can be kept unchanged for some time.

In order to study the chemical properties and the structure of the polymers, we carried out various reactions with the double bonds.



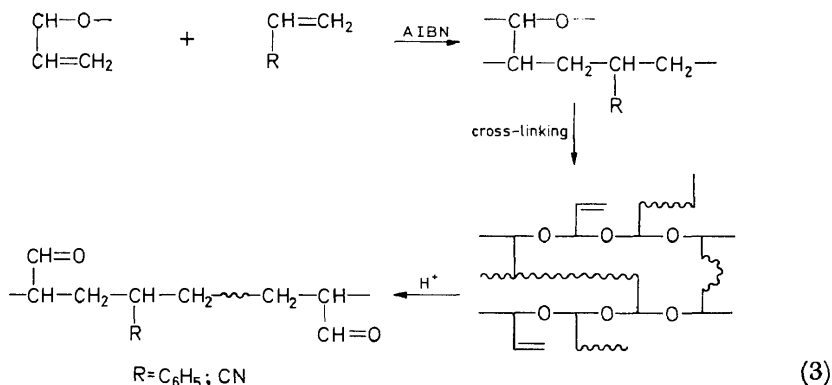
Hydration of poly-3,4-acrolein yields polypropionaldehyde (III). But the latter compound is very unstable and depolymerizes, in part, even during the hydration. The monomeric propionaldehyde (IV) formed in this way can

be trapped as phenyl hydrazone and identified by thin-layer chromatography. Thus the structure of the polymer is proved.

Bromine can be added to the double bonds under very mild conditions. This reaction proceeds with yields of over 95% and can be used for the quantitative determination of the vinyl groups. Although the polymer (V) can be isolated, it is not very stable, since it readily cleaves off hydrogen bromide.

Addition of triphenyltin hydride is also possible; the maximum tin content, however, is 5%⁸.

The vinyl groups in the side chains of poly-3,4-acrolein can undergo free-radical polymerization. If the polymer is dissolved in styrene or acrylonitrile and if AIBN is added, a grafting reaction takes place upon heating, which ultimately leads to cross-linking [equation (3)].



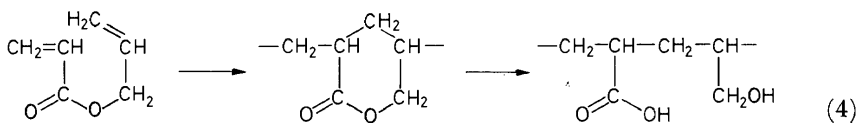
But the acetal links of the polyacrolein main chain can be cleaved by strong acids; hence it is possible to degrade the insoluble network hydrolytically and to isolate the network links of polystyrene or polyacrylonitrile. They are characterized by carbonyl groups⁸. From the molecular weight, the density of the network and the mesh size can be determined. However, these investigations have not yet been completed.

POLYMERS WITH ANHYDRIDE GROUPS, CARBONATE GROUPS OR LACTONE GROUPS

Anhydrides are highly reactive, but few polymers are known to contain this group. It was not till the discovery of cyclopolymerization⁹ that poly(acrylic anhydride) and poly(methacrylic anhydride) became readily accessible¹⁰. These polymers show the usual reactions of the anhydride groups; for example, they form poly(acrylic acid) or poly(methacrylic acid) when hydrolysed. However, it is found that polyacids prepared in this way are not identical with the corresponding polymers obtained from acrylic acid or methacrylic acid by free-radical polymerization. The intra-intermolecular propagation steps during cyclopolymerization give rise to a particular stereo-regularity¹¹; therefore the tacticity of the poly(acrylic acid) thus obtained differs from that of the conventional poly(acrylic acid).

At this point I wish to call attention to a peculiarity of reactions with

cyclopolymers which has hitherto received little notice. Ring-opening reactions can produce 1:1 copolymers which frequently cannot be obtained by means of normal copolymerization. For example, by free-radical polymerization of allyl acrylate a cyclopolymer is obtained which, when hydrolyzed, yields a 1:1 copolymer of allyl alcohol and acrylic acid¹².

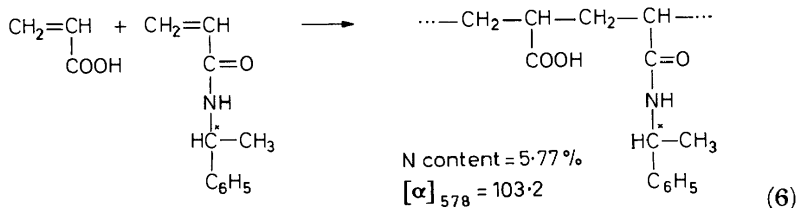
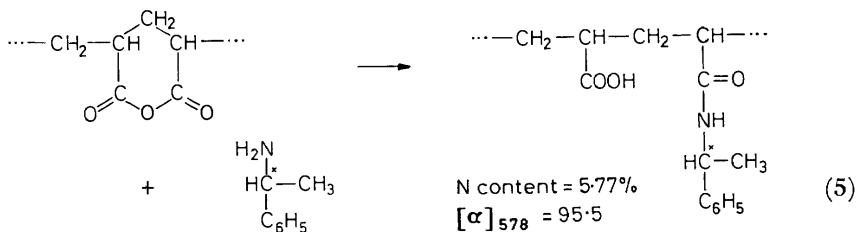


As can be seen from the copolymerization parameters of allyl alcohol or allyl acetate and acrylic acid, a copolymer of this type cannot be obtained by means of copolymerization.

Aminolysis of poly(acrylic anhydride) results in a copolymer consisting of monomer units of acrylic acid and acrylamide in a molar ratio which must necessarily be 1:1.

If it is true that ring opening always takes place in the same manner, an alternating copolymer results. This cannot, of course, be generally assumed; but even if the rings cleave at random and without neighbouring group effects, there cannot be more than two consecutive acid groups or amide groups. The maximum sequence length is thus 2. It is to be expected that such copolymers will differ from random copolymers.

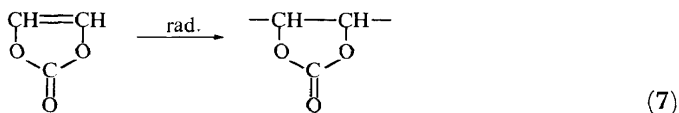
In order to test this conclusion we allowed poly(acrylic anhydride) to react with (—)-phenylethylamine; an optically active polymer with the calculated nitrogen content results (5). By copolymerization of acrylic acid and (—)-*N*-α-phenylethylacrylamide a copolymer with the same nitrogen content can be obtained (6); but it certainly has a different distribution of sequence lengths. The rotatory powers of the two optically-active copolymers are in fact distinctly different¹³.



In the well-known polycarbonates prepared with bisphenol A, the carbonate groups are located in the main chain. But there is also a polymer

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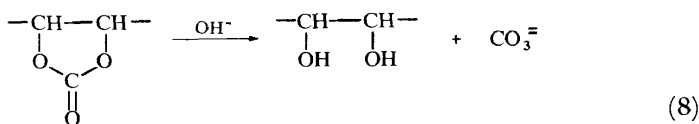
with carbonate groups in the side chains. It is obtained by polymerization of vinylene carbonate¹⁴ and has the following structure:



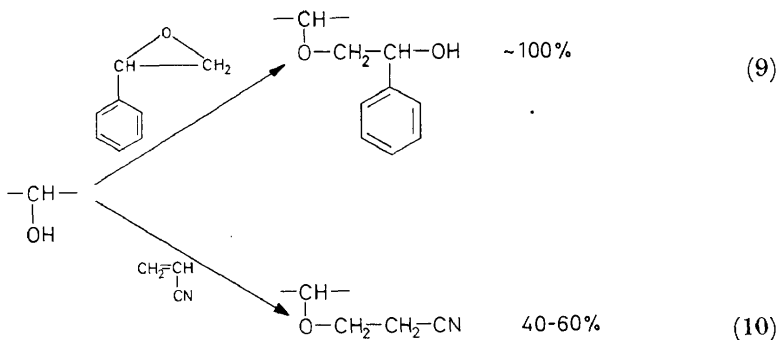
Melt-polymerization and polymerization in various solvents with free-radical initiators¹⁴⁻¹⁶ or with γ -rays¹⁷ have been thoroughly investigated by several authors. Cationic¹⁸ or anionic catalysts were found to be unsuitable.

Vinylene carbonate can also be copolymerized with various vinyl compounds and with acrylic acid derivatives¹⁸⁻²⁰. In most cases, however, only a small amount of vinylene carbonate is incorporated. Particularly favourable parameters were found for the system vinylene carbonate-vinylisobutyl-ether²¹, namely $r_1 = 0.16$ and $r_2 = 0.18$. It follows that for a monomer feed ratio of 49:51 an azeotropic copolymerization occurs.

Both the homopolymers and the copolymers can be readily hydrolysed in an alkaline medium. From the homopolymer a polymer is obtained which consists solely of secondary hydroxyl groups and is therefore called polymethylol.



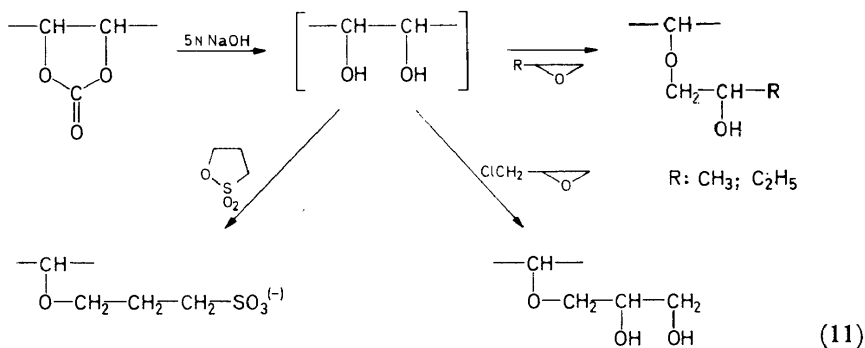
Polymethylol of high molecular weight is completely insoluble in the usual solvents, presumably because of strong hydrogen bonding. Reactions with the OH-groups of this polymer are therefore extremely difficult to carry out, and frequently only low yields result^{15,22}. We found, however, that during the reaction with styrene oxide in an alkaline medium almost all OH-groups are alkylated (9)¹⁷.



The resulting polymer is readily soluble in DMF, DMSO and chloroform.

Cyanoethylation (10) proceeds only up to a conversion of about 60%; but in this case no soluble products are obtained.

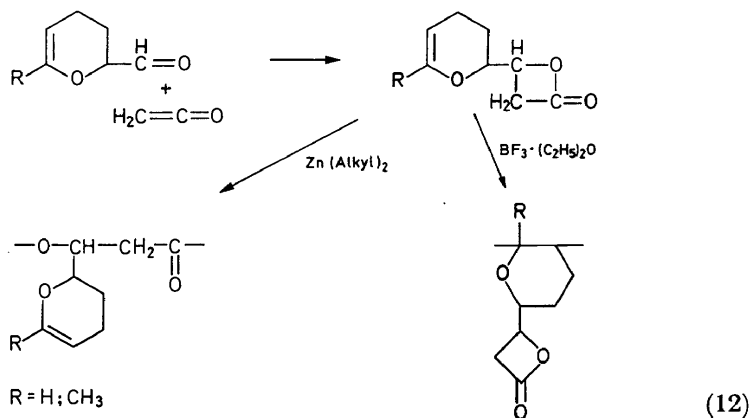
It was then found to be far more advantageous to carry out such reactions not with polymethylol itself as starting material but directly with poly(vinylene carbonate). For if it is saponified with 5N NaOH at room temperature, the resulting polymethylol remains in clear solution; it is not isolated, but the homogeneous solution is used for further reactions. Poly(vinylene carbonate) also reacted with various other epoxides in the same manner¹⁷.



A conversion of up to 70% was obtained, the percentage depending on the experimental conditions. In most cases the reaction products were readily soluble in water.

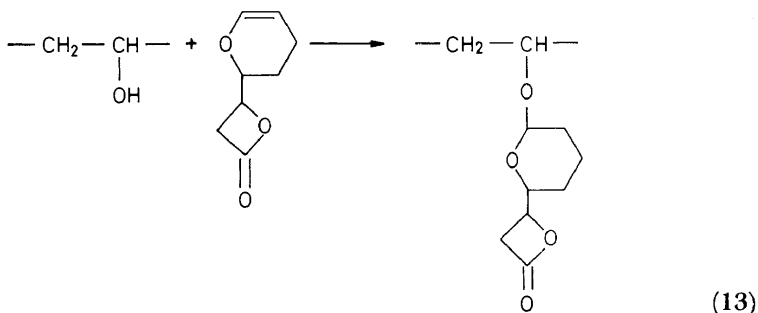
When polymers containing OH-groups are treated with sulphones, polymeric sulphonic acids are obtained²³. This reaction too can be applied to polymethylol under the conditions described above¹⁷. The conversion can be determined from the sulphur content or by titration and amounts to as much as 35%. The free acid and its alkali salts are soluble in water; they exhibit the viscosity behaviour which is characteristic for polyelectrolytes. The alkaline-earth salts and the lead salts are insoluble. [For further reactions of poly(vinylene carbonate) *see* ref. 69].

Recently polymers have been described which contain β - or γ -lactone groups along the main chain²⁴. An example of the preparation of such polymers is shown in equation (12).

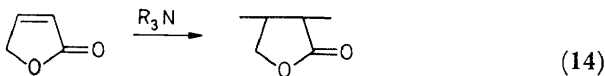


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The starting material is the acrolein dimer or the methacrolein dimer, to which ketene is added. The resulting β -(2,3-dihydropyranyl-2)- β -lactone has two different groups which are capable of polymerization, namely the β -lactone group and the vinyl ether group; both can be polymerized selectively. Upon initiation with BF_3 -etherate, polymers with β -lactone groups in the side chains are obtained. A second method of synthesis is based on the addition reaction of dihydropyran to the hydroxyl groups of a polymeric alcohol (Eq. 13).



Polymers with γ -lactone groups can be obtained by base-catalysed polymerization of the lactone of γ -hydroxycrotonic acid.



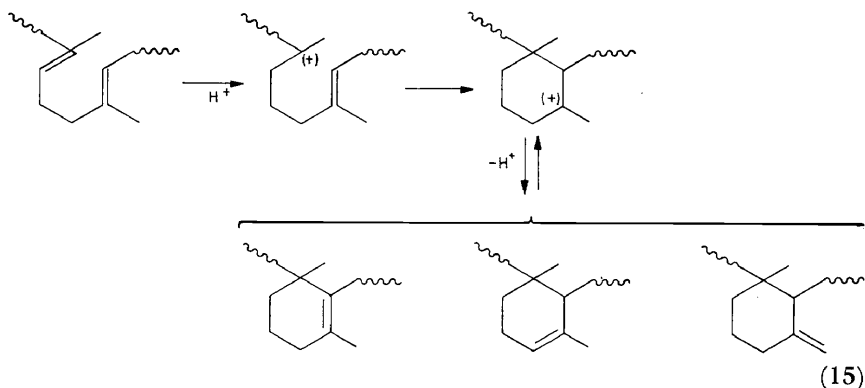
Both the β - and the γ -lactone groups are highly reactive and add water, alcohols, amines, acids etc. under ring opening and formation of the derivatives of the corresponding β - or γ -hydroxyacids.

ISOMERIZATIONS IN MACROMOLECULES

The work of Kennedy²⁵ has shown that in a number of cationic polymerizations isomerization can take place during the propagation reaction through hydride shifts or rearrangements. Therefore polymerizations of this kind are also called 'isomerization polymerizations'. But since isomerization here takes place only at the growing chain-ends, these investigations do not come within the scope of this paper. I wish to deal only with isomerizations which occur in previously-prepared polymers.

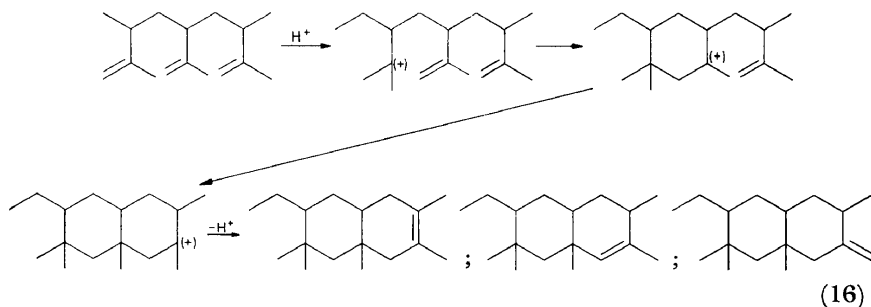
Cyclization reactions in natural rubber, polybutadiene and polyisoprene were the first to be observed and have been studied most thoroughly^{26,27}. These reactions are also carried out on a technical scale because the resulting 'cyclo-rubber' is particularly suitable for certain uses²⁸. It was not till recently that it was possible, with the help of i.r. and n.m.r. spectroscopy, to elucidate the exact structure of the cyclized polymers.

An example of cyclization of *trans*-1,4-polyisoprene initiated with sulphuric acid is shown in equation (15)²⁹.



After completion of the reaction the cyclized polymer contains only 33% of the C=C double bonds originally present. Apart from the cyclization a shift of the double bonds must also be considered. But recent investigations with polyisoprene deuterated in the 3-position showed conclusively that this isomerization does not occur here^{30,31}. On the other hand, Blatz and Johnson³² have lately reported that, under the influence of acids, the isolated C=C double bonds of polycyclopentadiene shift in such a way that sequences of 3 to 6 conjugated C=C double bonds result.

Cyclization reactions of unsaturated polymers have also been investigated in connection with the preparation of double-strand polymers³³. Starting materials used for this purpose were, for example, 1,2-polybutadiene and 3,4-polyisoprene. The nature of the cyclization steps and their number of course depend on the experimental conditions and particularly on the tacticity of the polymers used.



At first it was believed that the cyclization reactions spread over many consecutive monomer units and that ladder polymers are formed in the process. But the most recent results of Angelo *et al.*³⁴ showed that sequences of 2 to a maximum of 5 anellated rings are found; in addition, in accordance with statistical theory, there are about 18% of isolated vinylidene groups which are left over and remain unchanged.

A further example of cyclization in a polymer is the well-known pyrolysis of polyacrylonitrile, although in this case dehydrations and cleavage reactions also occur.

The *cis-trans* isomerization of unsaturated polymers has received much attention and has been the object of many investigations²⁶, which were essential for the elucidation of the structure of natural rubber, balata and gutta-percha. When, by means of Ziegler-Natta catalysts, sterically homogeneous polybutadienes and polyisoprenes became available by synthetic methods as well, *cis-trans* isomerization was studied in their cases too. Golub²⁵ and Cunneen³⁰ have made fundamental contributions in this field.

It was found that the effect in question is caused by a true thermodynamic equilibrium. In the case of polybutadiene the equilibrium at 25°C corresponds to a *cis-trans* ratio of about 20:80, regardless of whether the reaction was begun with a pure *cis*-isomer or a pure *trans*-isomer³⁶. In the case of 1,4-polyisoprene at 140°C, an equilibrium with about 45% *cis* and 55% *trans* is reached. The isomerization is catalysed by ultraviolet light, γ -rays, sulphur dioxide (in the form of butadiene sulphone), disulphides etc. and doubtless proceeds according to a free-radical mechanism³⁷.

Although the chemical composition obviously remains unchanged during these isomerizations, very considerable changes occur in the physical properties. Hence these transformations are of particular interest for the elucidation of the relationship between structure and properties³⁶.

Cis-trans isomerizations are also possible in the case of unsaturated polyesters of maleic, fumaric or citraconic acids as starting material; such isomerizations have been thoroughly investigated³⁸.

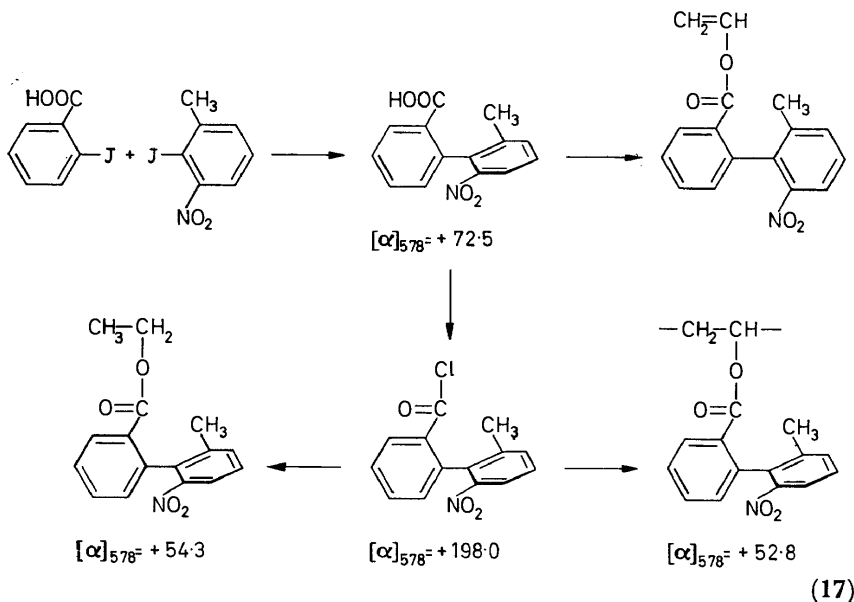
In connection with the study of tactic polymers the question presented itself as to what extent the configuration of the tertiary carbon atoms in the main chain of vinyl polymers is stable. Braun, Hintz and Kern³⁹ showed that the tacticity of isotactic polystyrene is not perceptibly altered by mechanical degradation through the effect of aluminium chloride or even by metallization at the α -carbon atom. Thus it was found that the configurational stability of this polymer is considerably higher than that of comparable low-molecular-weight model compounds.

As has already been mentioned, the isomerization of polymers can best be demonstrated by physical methods. I now wish to report on some experiments in which we determined the rate of isomerization by measuring the optical rotations. It is the purely thermal racemization of an optically-active polymer that here concerns us.

For our experiments we chose a polymer whose monomer units are molecularly asymmetric because of hindered rotation and are therefore optically active⁴⁰. The synthesis of a monomer which seemed suitable is shown in equation (17). By Ullmann condensation of *o*-iodobenzoic acid and 2-iodo-3-nitrotoluene, 2-methyl-6-nitrobiphenyl-2'-carboxylic acid is obtained in 50% yield. When allowed to react with vinyl acetate it yields the corresponding vinyl ester. But, although a variety of conditions were tried, it was not possible to obtain homopolymers or copolymers with styrene from this compound because of the strong inhibiting effect of the aromatic nitro-group.

We therefore introduced the biphenyl groups by reaction with a polymer.

For this purpose the quinidine salts of the acid were separated into the antipodes, and from the dextrorotatory form the acid chloride was prepared. From it the desired polymer can be obtained through Schotten-Baumann reaction with polyvinyl alcohol. Esterification with methanol, ethanol or



1,4-butanediol yields the low-molecular-weight model compounds which we need for reference measurements. The conversion, as determined by the nitrogen content of the polymer, was found to be 97% by weight; in accordance with this value, the rotations of the polymer also amount to 95% of the molar rotations of the model compounds. This polymer, it should be noted, is the first example of an optically-active polymer without asymmetric carbon atoms.

It is known that atropisomeric biphenyl derivatives racemize when heated. At elevated temperatures the restriction of free rotation is reduced, and when the phenyl rings can rotate freely the optical activity disappears. The racemization can be readily observed by following the gradual decrease of the rotations at elevated temperatures. This is a first-order reaction; the length of the half-life depends on the reaction medium and on the kind of substituents. The results are shown in *Figure 1*. The ethyl ester as well as the methyl ester racemize exactly according to first-order kinetics. At 120°C in dioxane the half-life is 24 hours in solutions of 1% as well as of 0.1%.

The polyvinyl alcohol ester, on the other hand, shows a totally different behaviour. In 1% solutions a curved line results, i.e. there are distinct deviations from first-order kinetics. Presumably this is due to disturbances caused by cross-linking reactions. In 0.1% solutions these deviations do not occur: racemization here proceeds according to first-order kinetics but at a considerably lower rate than in low-molecular-weight model compounds. It

might be objected that the ethyl ester represents only one monomer unit and is therefore not an adequate model. But the racemization of the diester of butanediol proceeds with the same half-life; hence no neighbouring-group effect occurs here.

We also checked for a possible effect of the viscosity of the polymer solutions. By adding poly(vinyl acetate) we raised the viscosity of the reaction medium by a factor of 100. This does not influence the racemization of the model compound perceptibly⁴¹.

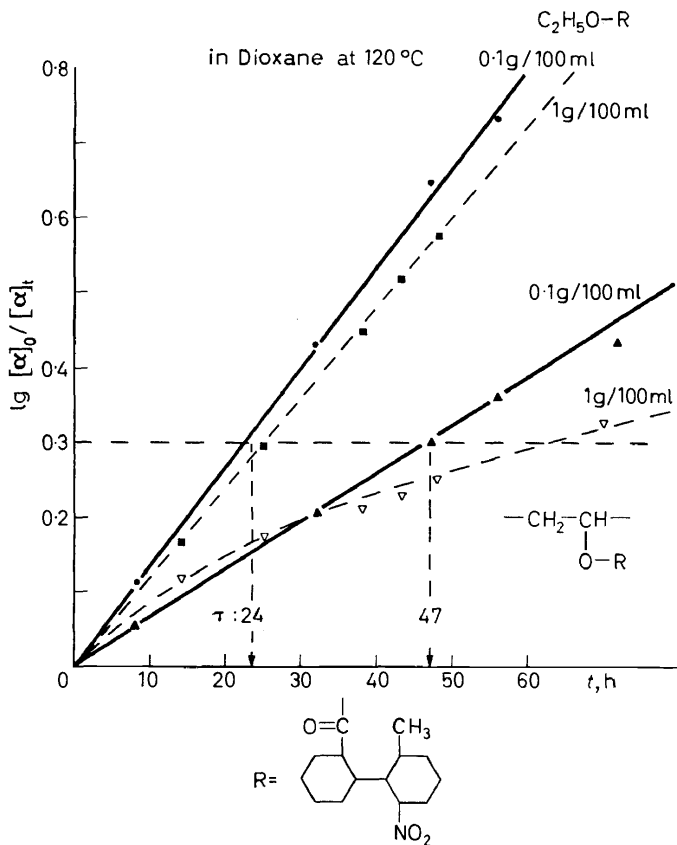


Figure 1. Kinetics of racemization of atropisomeric esters of ethanol and polyvinyl alcohol

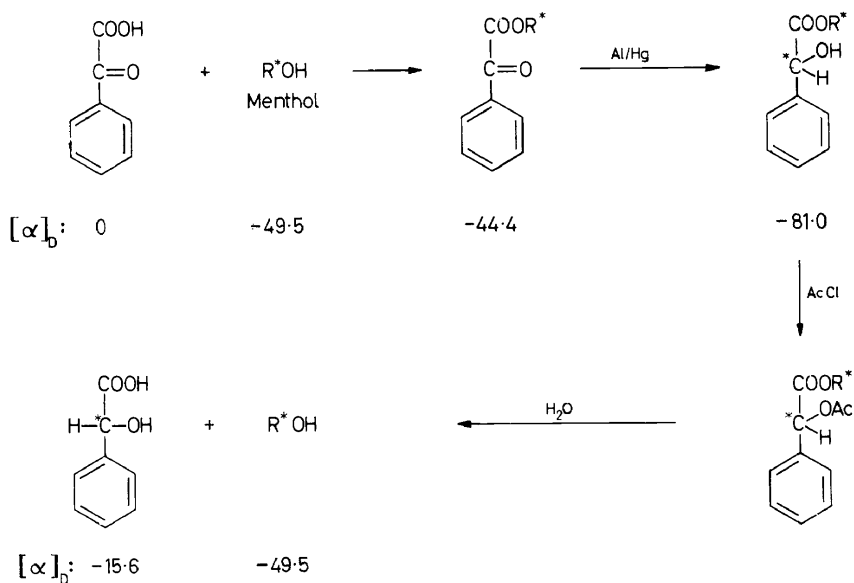
We therefore conclude that the low rate of racemization of the poly(vinyl ester) is a result of its macromolecular structure. The free rotation of the phenyl rings is in this case impeded not only by the substituents but by the tight coil shape of the macromolecules as well.

We have since extended our investigations to polymers in which the atropisomeric groups are located in the main chain⁴². Without going into details I merely wish to state that the measurement of optical rotations is a useful method of studying certain isomerization reactions in polymers.

ASYMMETRIC SYNTHESIS ON POLYMERS

In an asymmetric synthesis a new asymmetric centre is formed in the molecule, the reaction proceeding in such a way as to cause preferential formation of one of the antipodes. This means that from a symmetric optically-inactive compound used as starting material an asymmetric optically-active product is obtained. Ideally only one of the antipodes should be formed at all, as a pure product. But in most cases the other antipode is also formed to a greater or lesser extent. The ratio of the optical rotation of the mixture to that of the pure antipodes is the so-called optical yield. In the case of low-molecular-weight compounds numerous asymmetric synthesis have already been described⁴³. It is not necessary here for me to enter into a discussion of the steric, kinetic and thermodynamic problems; there are detailed reports and reviews on these subjects^{44,45}. Recently Ugi and Ruch have also set up a mathematical model for calculating asymmetric syntheses⁴⁶.

The following example is intended to illustrate the principle and the chemical process involved in an asymmetric synthesis⁴⁷.



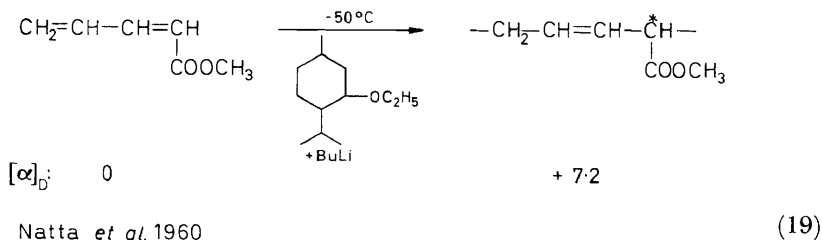
(18)

Phenylglyoxylic acid, an optically-inactive compound, is esterified with (–)-menthol and then reduced. After the reduction menthol is cleaved off hydrolytically and mandelic acid is obtained, which contains an excess of the laevo-rotatory form. The optical yield is in this case 10%. Menthol here serves only as an auxiliary substance whose purpose is to influence the reduction sterically. Other optically-active compounds can also serve as auxiliary materials; they are frequently employed as catalysts or as solvents⁴³. But in each case they are removed when the asymmetric synthesis has taken place.

In polymer chemistry two different kinds of asymmetric syntheses can

be distinguished. In the first kind the propagation steps during polymerization of unsaturated compounds are affected in such a way that a monomer without asymmetric centres is converted into an optically-active polymer. Synthesis by this method were first attempted by Marvel and his coworkers in 1943⁴⁸. Later a number of other authors also dealt with this problem, but in no case did the asymmetric synthesis of a polymer succeed in the respect detailed above⁴⁹.

It was not until 1961 that Natta⁵⁰ was able to report on the first successful synthesis of macromolecules.



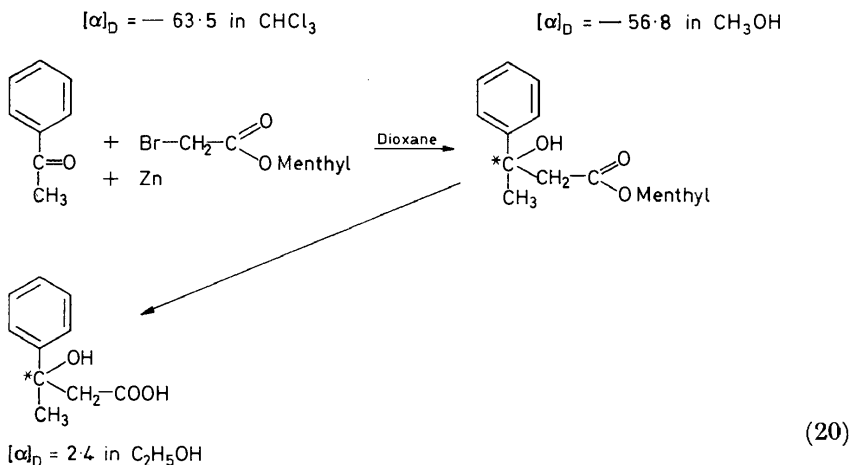
An example of this reaction is illustrated in equation (19). β -Vinylacrylic acid esters contain no asymmetric carbon atoms. But during 1,4-polymerization the α -carbon atom becomes asymmetric. If stereospecific catalysts are used together with asymmetric cocatalysts to effect the propagation steps in such a way that *one* of the configurations of this asymmetric carbon atom is preferred in all monomer units, an optically active polymer results. It was possible to show that the optical activity is not the result of built-in catalyst fragments. Through ozonolysis of these polymers, optically-active di- or tri-carbonic acids are obtained⁵⁰; this proves conclusively that we have here an asymmetric synthesis of macromolecules.

Another example is the polymerization of benzofuran with cationic catalysts which are complexed with optically-active compounds⁵¹. If (–)- β -phenylalanine is used as the asymmetric catalyst, a laevo-rotatory polymer results; if (+)- β -phenylalanine is used, a dextro-rotatory polymer is obtained.

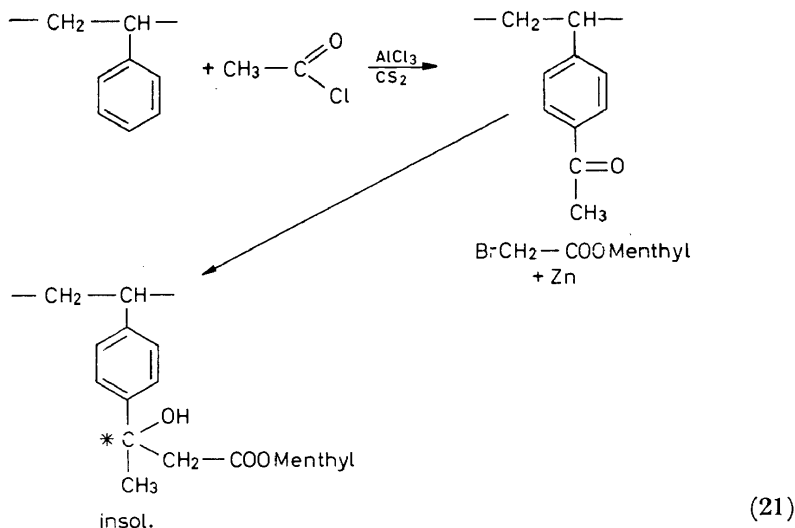
Thus in the cases described so far the asymmetric synthesis depends on the sterically-controlled propagation reaction during the formation of the macromolecules. But in the case of polymers there is yet another kind of asymmetric synthesis. It involves the formation of asymmetric carbon atoms through reactions on functional groups of a previously-prepared optically-inactive polymer. As nothing has yet been published on this problem, to our knowledge, I would like to report on the work we have done so far in this field.

We studied the Reformatsky reaction between acetophenone and menthyl bromoacetate⁵² (*see* Eq. 20). In this reaction an asymmetric carbon atom is formed. Menthol again serves merely as an auxiliary material and is cleaved off after the reaction. An optically-active β -hydroxy- β -phenylbutyric acid is obtained whose specific rotation is $[\alpha]_{\text{D}}^{25} = 2.384$. This corresponds to

an optical yield of 30%, which is in accordance with published data.

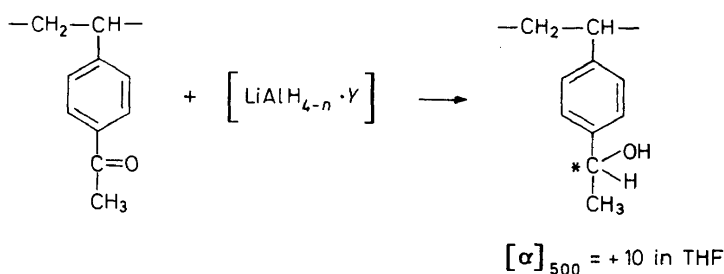
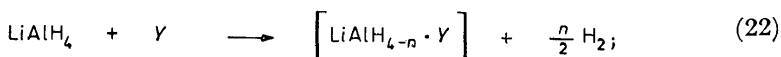


After analogous preliminary experiments we applied the same reaction conditions in the case of polyvinylacetophenone⁵³.



In dioxane at 90°C it was in fact possible to carry out a Reformatsky reaction. In the infrared spectrum the bands for the OH-groups and ester groups appear. But the highly reactive zinc-organic intermediates lead to cross-linking of the polymer. Although the reaction conditions were varied, our attempt to obtain a soluble polymer was not successful. Therefore it was not possible to measure the optical rotations or to determine the optical yield. Nor was the application of the Reformatsky synthesis to poly(methyl vinyl ketone) successful.

We therefore studied the reaction conditions for an asymmetric reduction of the keto groups. The reduction of polyvinylacetophenone with lithium aluminium hydride has long been known and results in good yields of the corresponding secondary alcohol⁵⁴. On the other hand, it is also known that low-molecular-weight ketones can be asymmetrically reduced if the lithium aluminium hydride has been previously exchanged with an equivalent amount of an optically-active alcohol. Certain glucose derivatives⁵⁵ or quinine⁵⁶ are suitable for this purpose (22). The structure of the complexes has not yet been elucidated. For instance, optically active α -phenylethanol is obtained from acetophenone. The optical yield amounts to 15 per cent or 48 per cent, depending on the experimental conditions.



Y: Chinin, $n=1$; 1,2 Dicyclohexyliden-D-glucofuranose, $n=3$;

(23)

We applied this reaction to polyvinylacetophenone (23)⁵³. But because of the solubility properties of the polymer the reaction conditions must be somewhat altered. Nearly all keto-groups were reduced, and readily-soluble polymers resulted. It was possible to separate quantitatively the asymmetric auxiliary agent, i.e. the glucose derivative or the quinine, by reprecipitation or by dialysis. The polymers prepared and carefully purified in this way were in fact optically active. When the glucose derivative is used, a laevo-rotatory polymer results. But the reduction with lithium aluminium hydride-quinine proved to be more advantageous. The polymer resulting from this reduction is dextro-rotatory; for instance, at 500 $m\mu$ in THF $[\alpha]$ amounts to $+10^\circ$ ($C = 1.404$). If it is assumed that the optically-pure polymer has the same specific rotation as (+)- α -phenylethanol, the resulting optical yield should be 15 per cent. This yield is lower than those of the model reactions; possibly it can be yet increased. In any case, this shows for the first time that asymmetric syntheses can also be carried out with macromolecules. We plan to investigate whether other asymmetric syntheses from the chemistry of low-molecular-weight compounds can likewise be adapted to polymers.

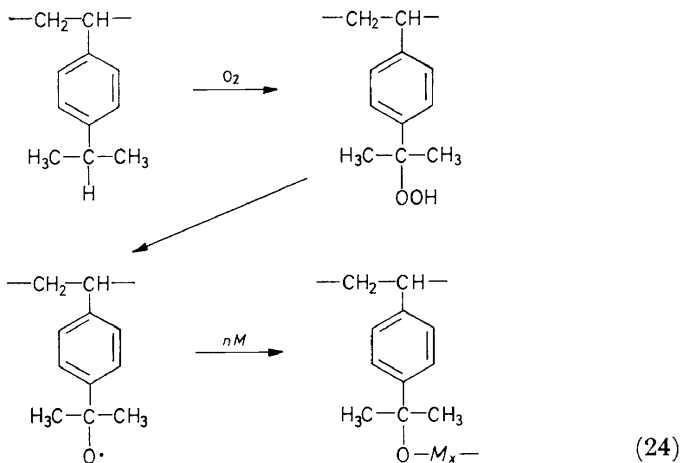
MACROMOLECULES WITH NUMEROUS ODD ELECTRONS ALONG THE CHAIN [POLY-RADICALS]

Polymers with a positive or a negative charge at each base unit—as for example polyacrylic acid or polyvinyl pyridinium chloride—are called polyanions or polycations respectively. Consequently, polymers with unpaired electrons in the side chain have to be labelled as “poly-radicals”.

These poly-radicals should be distinguished from growing chain-ends in radically-initiated polymerizations; they carry a free electron, but they are termed “macro-radicals” because they contain just *one* radical position per macromolecule. In the following I should like to treat only uncharged poly-radicals, i.e. macromolecules with many unpaired electrons along the main chain.

A well-known reaction to generate O-radicals is based on the homolytical scission of peroxides. Free radicals are also formed by a redox-reaction of hydroperoxides and reducing agents. Application of this reaction to polymers with hydroperoxide side-groups should result in poly-radicals.

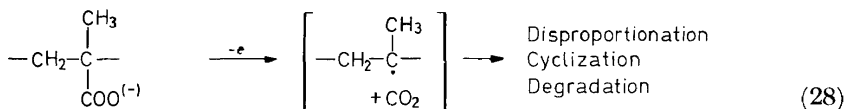
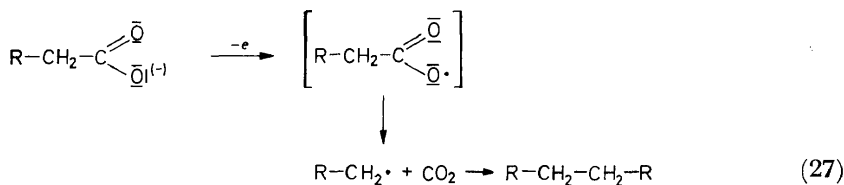
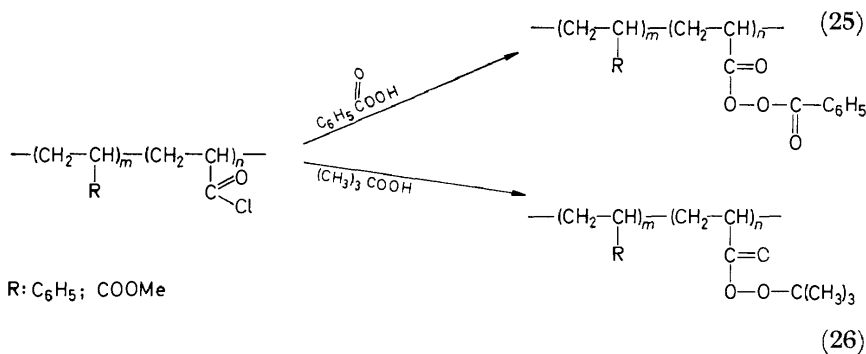
In 1955 such polymers were prepared by Hahn and Lechtenböhrer⁵⁷ and by Metz and Mesrobian⁵⁸.



Autoxidation of poly-*p*-isopropyl styrene yields a polymer with 1–4 per cent hydroperoxide groups, from which, by the action of heat or reducing agents, O-radicals are produced. They are very unstable and cannot be isolated in this form. However, intermediate radical formation can be proved with a highly-sensitive method: these polymeric peroxides initiate radical-chain polymerization of vinyl- or acrylic monomers. Thus, graft copolymers are formed confirming the intermediate existence of poly-radicals.

Hahn and Fischer⁵⁹ and more recently, Smets *et al.*⁶⁰ also prepared polymers with perester side groups. The reactions of copolymers containing 10 per cent acrylic acid chloride with tertiary butyl hydroperoxide (26) or benzoic peracid (25) have been studied. These polymers, too, yield poly-radicals on thermocracking; Smets and his coworkers studied the kinetics of the peroxide decomposition and the graft copolymerization.

ON NEW CHEMICAL REACTIONS OF POLYMERS

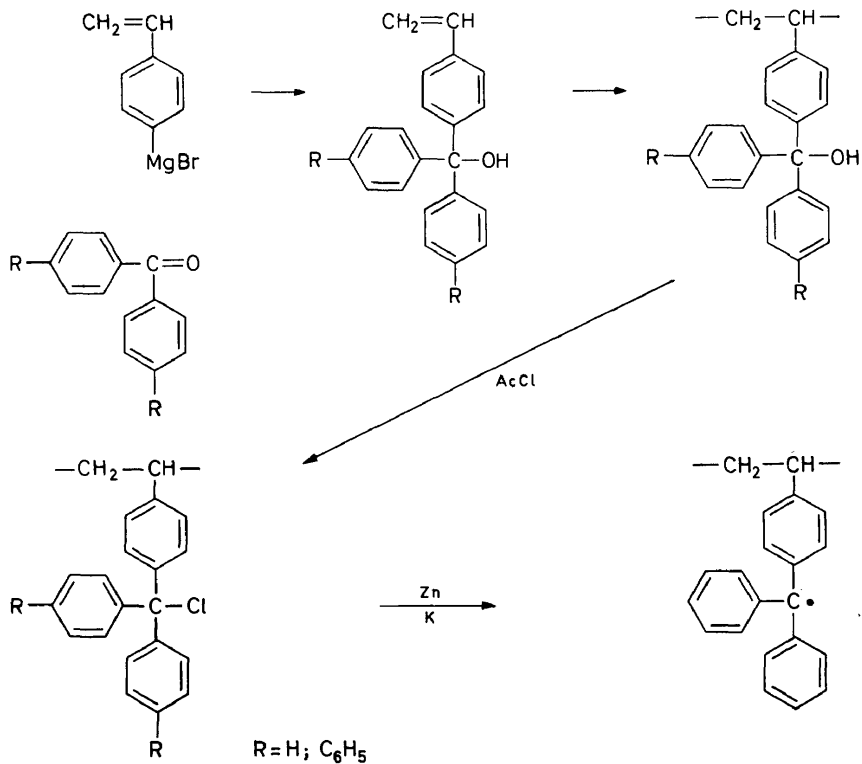


Another, well-known method to create radicals is the so-called Kolbe-synthesis (27). Smets⁶¹ has transferred this reaction to polymethacrylic acid (28). The reaction process can be followed by carbon dioxide formation. Obviously, intermediate poly-radicals do exist; however, due to numerous side-reactions, insoluble and non-uniform polymers are formed.

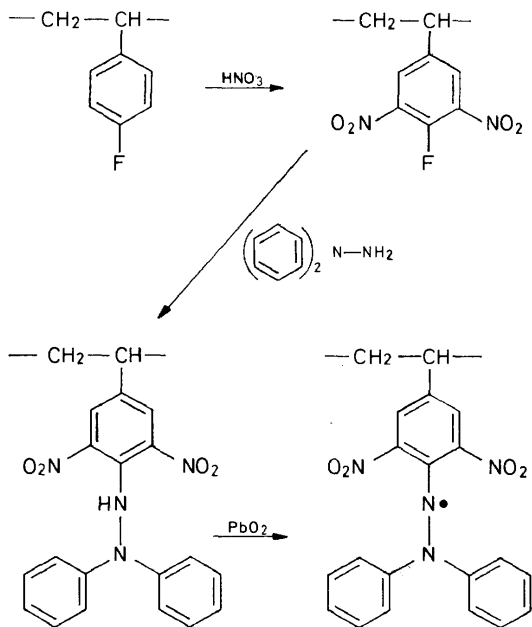
Recently, Braun and Faust⁶² described a polymer carrying the Gomberg triphenylmethylradicals as side-groups (29). From *p*-vinylphenyl-Mg-bromide and benzophenone the corresponding carbinol is obtained. It is easily polymerized by free radicals. Copolymerization with styrene is also possible. The hydroxy-groups of the polymer are chlorinated by acetyl chloride. Reaction with zinc powder or metallic potassium yields poly-radicals. Intermolecular dimerization leading to cross-linking can be circumvented by working in dilute solution (for example 5 g/l.). The e.s.r.-spectra show indeed that free radicals are present. Quantitative determination revealed on the average 100 unpaired electrons per macromolecule. With a molecular weight of ca. 30 000 this means 1 radical per 3-4 base units. Naturally, the poly-radical is extremely sensitive towards oxygen as is its parent monomeric radical.

Most of the radicals with the unpaired electron located at C- or O-atoms, are unstable. Certain N-radicals, however, are known for high stability, as for example DPPH. Braun *et al.*⁶³ were also able to introduce this group into a macromolecule and they obtained a completely stable poly-radical. The synthesis is shown in equation (30).

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(29)

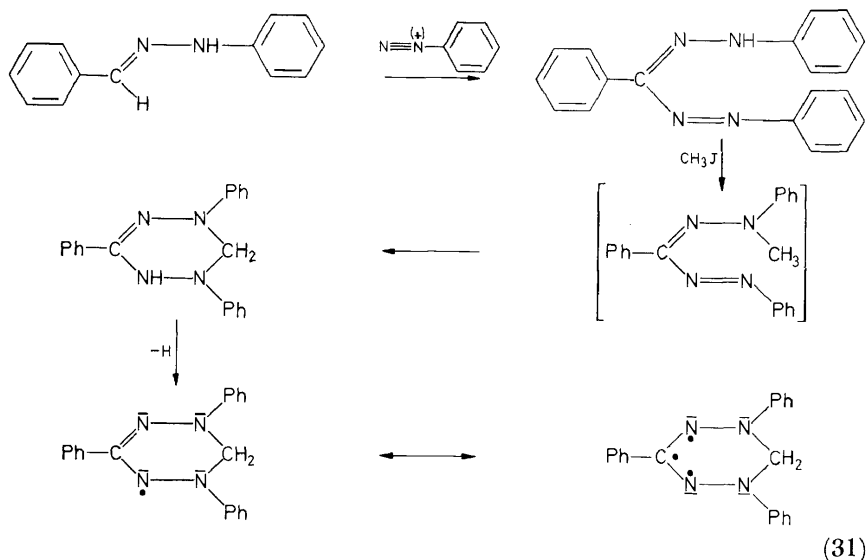


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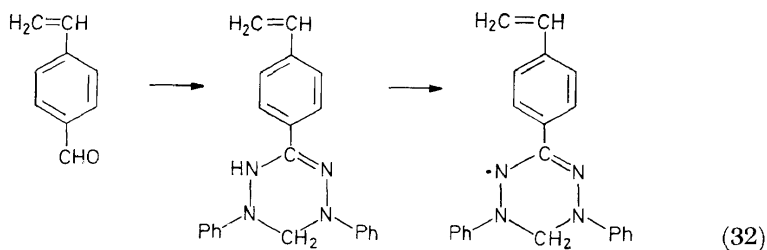
By nitration of poly-*p*-fluoro-styrene the fluorine atom becomes highly activated and nucleophilic substitution of asymmetric diphenyl hydrazine is possible. On shaking with lead dioxide, a dark-purple solution is obtained, from which the poly-radical can be precipitated as a black powder. It is soluble in several organic solvents and quite stable in air and humid conditions. The absorption and the e.s.r spectra are consistent with the low-molecular-model compound. The radical character, determined after different methods amounts to 20–30 per cent. For further poly-radicals see ref. 64.

In 1963 Kuhn⁶⁵ discovered a new stable radical which he named verdazyle. The synthesis and structure are given in equation (31).



Aldehyde phenyl hydrazine and diazonium salt solution form the well-known formazanes. On methylation a tetraaza-cyclohexane is formed. Oxidizing agents remove an H-atom and a solution of deep green colour is obtained from which black crystals can be separated. According to the e.s.r. spectrum, a free radical exists in solution and in the crystal. The unpaired electron might be distributed evenly on the 4 N-atoms.

Some years ago, starting from polyacrolein, we prepared a polymer with formazane side-groups⁶⁶. We thought it would be easy to methylate this and to prepare the polymer verdazyle by oxidation. Unfortunately, all attempts



failed. Too many side reactions occurred and radicals—if any were formed—were too unstable.

Therefore we prepared a verdazyle carrying a vinyl group at one of the benzenerings⁶⁷(32). This shows a typical absorption spectrum with a maximum at 720 m μ and 9 lines in the e.s.r. spectrum (Figure 2). However, being a strong radical-quenching agent, it cannot be polymerized radically. Polymerization with anionic catalysts is possible, but the investigations on

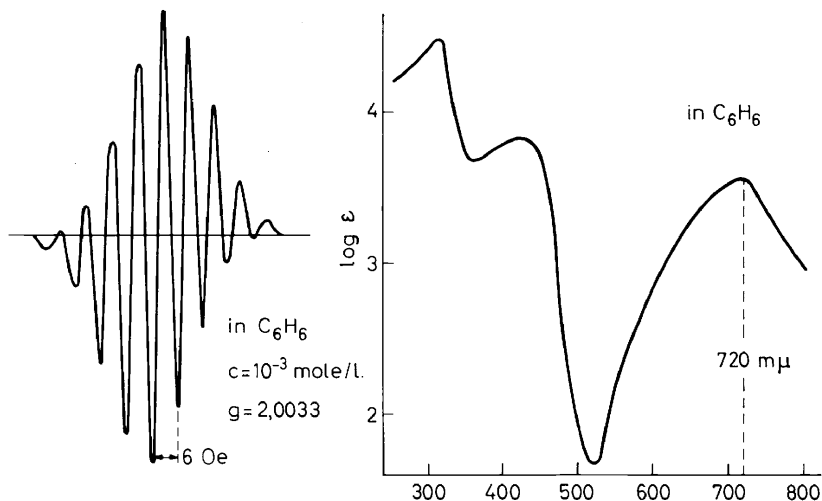
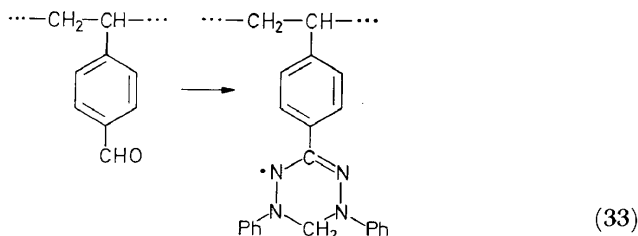


Figure 2. The e.s.r. and absorption spectra of monomeric vinyl verdazyle (see equation 32)

this topic are not yet finished. We then attempted the polymerization of the precursors, but here insoluble polymers resulted which did not react further. So we had to start with poly-*p*-vinyl benzaldehyde and conduct all steps of synthesis, one after the other, with the polymer. In this way it was possible to obtain a polymer with verdazyle radicals along the main chain.



Proof for the presence of free radicals comes from the e.s.r. spectra (Figure 3). The absorption spectrum reveals the agreement in chemical structure of the polymer radical with the low-molecular-weight verdazyle. From the spectra it is also possible to judge the radical-concentration. In our best samples it was *ca.* 45 per cent, that means each second to third base unit is a verdazyle radical.

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The polymer is a green powder, soluble in DMF and stable in air for many months. From the solution green films can be cast in which radicals are also found. A specific property of the verdazyles is the loss of the unpaired electron on the action of oxidizing agents, as for example chlorine or

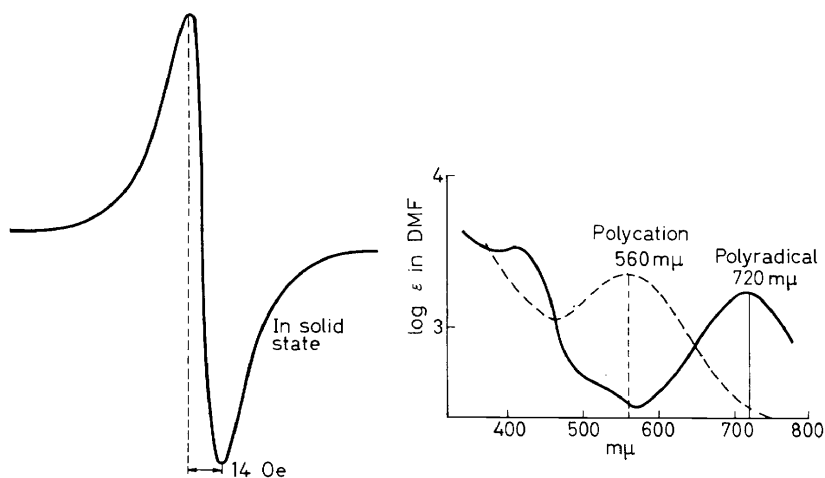
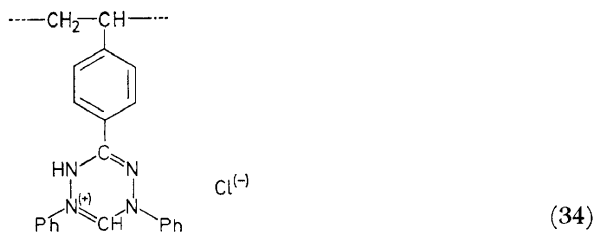


Figure 3. The e.s.r. and absorption spectra (solid lines) of polyverdazyle radical (see equation 33). Broken line: absorption spectrum of poly-cation (see formula 34)

bromine and creation of a purple cation. The maximum at 720 mμ disappears and a new one occurs at 550 mμ. The same reaction is also given by the polymeric verdazyle, in solution as well as in cast film. Again this reaction confirms the structure of the polymer and proves the nature of the poly verdazyle.



This has brought me to the end of my lecture. It is my hope that the examples I have selected are representative of the present stage of development. It was also my purpose to give you an impression of the diversity of chemical transformations of polymers. It is difficult to make predictions about future development in this area of polymer chemistry; but some major fields of interest may be expected to emerge:

1. The preparation of polymers with particularly reactive groups, for example new macromolecular metal-organic compounds.

2. The application of particularly selective reactions to polymers, for example new Redox reactions, complex formations, models of enzymatic reactions and further development of the so-called "matrix reactions"⁶⁸.
3. The application of selective reactions to biopolymers.
4. Researches about the relations between tacticity or secondary structure and reactivity of the polymers.

In conclusion, I wish to offer warm thanks to my coworkers for their industrious assistance and cooperation in the course of these investigations. Furthermore I am indebted to the "Deutsche Forschungsgemeinschaft" and to "Fonds der Chemischen Industrie" for supporting our research.

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