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Abnormal Groups in Vinyl Polymers*

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ABSTRACT

The more important structural abnormalities occurring in vinyl polymers of commercial interest are outlined. Possible mechanisms for the formation of these abnormal groups and their effect on polymer properties are discussed.

INTRODUCTION

The commercial manufacture of vinyl polymers was commenced nearly 50 years ago, at about the time Staudinger first published the concept of polymers as organic entities of high molecular weight. In the intervening years there have been tremendous developments in the manufacturing of vinyl polymers and in the elucidation of their molecular structures. Although the overall structure of most polymers is now well established, there is still the challenge of detecting and characterizing certain anomalous structural units within the polymer molecule. There has been a growing realization among Polymer Chemists that the presence of these abnormal groups, often

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*This review is based on the text of the lecture given by Dr. Solomon in November 1978 following his award of the Australian Polymer Medal by the Polymer Division of the Royal Australian Chemical Institute.

in statistically-insignificant proportions, can greatly affect the properties of vinyl polymers [1]. It is the aim of this review to describe some recent advances in our knowledge of the origin and consequences of these structural abnormalities.

Originally, chemists had considered the known polymers (e.g., celluloses, natural elastomers, and the early condensation polymers) to consist of micellar aggregations of molecules having low molecular weight. Staudinger showed that their structure was more probably macromolecular. In the case of a vinyl polymer such as polystyrene, he postulated that the monomer units were connected by covalent bonds without rearrangement of the carbon skeleton, the terminal valencies being satisfied by the formation of a large cyclic structure as shown in Fig. 1 [2].

In the Staudinger model all the monomer units are in the same chemical environment, each being flanked by similar chemical entities. The modern view is that vinyl polymers are not normally large cyclic structures, but are essentially linear molecules in which the terminal valencies are satisfied by endgroups which differ from those of the repeating units. In addition, side reactions during polymerization can result in structures containing nonterminal groups which differ from those of the ideal structure of Fig. 1. Because of these foreign or abnormal groups, all the monomer residues in the polymer chain are not in the same chemical environment. For the purposes of this review an abnormal group is defined as one which does not have the basic carbon skeleton of the monomer (i.e., a foreign molecule or a rearranged monomer unit) or one which is not flanked on either side by a normal repeating unit. Polymer tacticity will not be considered here, although it can give rise to different environments along the molecular chain.

Many of the physical and chemical properties of polymers can be adequately explained in terms of an idealized structure, which may

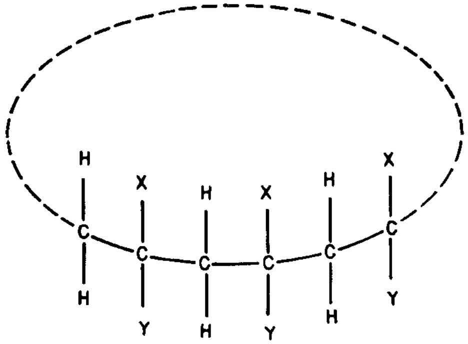


FIGURE 1.

account for more than 99.5% of the chain units of some polymers. This structure, however, does not explain or predict important properties of a number of widely used materials, particularly those of some of the thermoplastics. It is this observation, together with the scientific challenge of the quantitative determination of these structural abnormalities and explanation of their origins, which are the compelling reasons for our present interest in abnormal groups.

SOME IMPORTANT DEGRADATION MECHANISMS INITIATED BY ABNORMAL GROUPS

The manner in which a small number of abnormal groups dictates the properties of a polymer can be illustrated by consideration of the degradation processes undergone by a polymer molecule containing an abnormal group.

Unzipping

Polymers derived from 1,1-disubstituted ethylene molecules are often susceptible to radical chain depolymerization, and on pyrolysis can revert to monomer in high yields; a typical example is poly(methyl methacrylate), Fig. 2. This chain depolymerization depends on the formation of a polymer radical and is usually initiated at an abnormal group (1) (Fig. 2). Other familiar examples of polymers which undergo efficient thermal depolymerization are poly(vinylidene cyanide), poly(α-methylstyrene), and poly(methacrylonitrile).

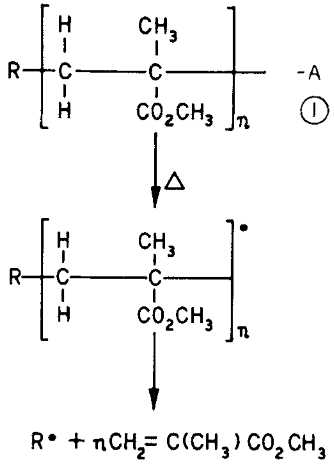


FIGURE 2.

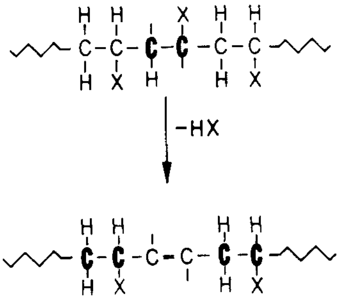


FIGURE 3.

Elimination

Some polymers derived from 1-monosubstituted-ethylene monomers eliminate simple molecules, e.g., hydrogen chloride from poly(vinyl chloride) (Fig. 3) or acetic acid from poly(vinyl acetate), and the elimination can be autocatalytic as the unsaturated species formed activate the adjacent groups. The first stage of the elimination, however, is likely to occur at, or adjacent to, an abnormal group (see later).

Cross-Linking

Where the activated polymer attacks or combines with another polymer molecule, a network structure can result. For example, if the active center generates a radical, intermolecular combination with a second polymer radical may occur, or the radical may react with unsaturated centers in the second polymer chain. An average of three or more such intermolecular links per polymer molecule is sufficient for the formation of a cross-linked polymer having markedly different rheological and mechanical properties.

The above examples show that even a small number of abnormal groups in the polymer can be of significance. In a polymer chain of 1000 units, not large in comparison with those of many commercial plastics, one abnormal unit could be sufficient to promote the depolymerization or elimination reactions shown above.

Not all abnormal groups constitute weak links in a polymer chain. In fact, copolymers are often preferred because a second, minor monomer component can act as a stabilizing group. For example, poly(methyl methacrylate) containing 0.5% of ethyl acrylate as a comonomer has a reduced tendency to undergo depolymerization. Abnormal groups can be beneficial in other respects, for example, in providing reactive sites for polymer modification or adsorption centers for dyes, and in some cases, when present in sufficiently high concentration, can improve mechanical properties.

Abnormal groups, especially rearranged monomer units, are known to be often present in large proportions in vinyl polymers prepared by cationic and, to a lesser extent, anionic polymerization processes. In contrast, the possibility of the formation of structural abnormalities is frequently overlooked in radical polymerization processes. Specific literature references are very sparse, and many papers on the structure of polymers or on initiating species refer only to the predominant structures present. In the past, detection of low concentrations of abnormal groups usually depended on chemical methods, for example, the dye-adsorption studies of endgroups, or the degradative fission at midchain abnormal groups. Recent advances in analytical methods,. particularly in magnetic resonance spectroscopy and data processing, coupled with an imaginative use of model compounds and radical trapping agents has allowed a new insight into unsuspected abnormalities which can occur in commercial polymers.

ORIGIN OF ABNORMAL GROUPS

Radical polymerization of vinyl monomers proceeds via the three stages shown in Fig. 4; namely initiation, propagation, and then termination by one of several alternate modes. This idealized mechanism requires that the reactions involved are 100% specific, which would be unusual for radical processes. In fact, as already mentioned, side reactions occur during polymerization, and these result in the incorporation of abnormal groups into the polymer chains. The individual stages of the polymerization process and the anomalous reactions which may accompany them will now be considered in detail.

Initiation

Most radical polymerizations are induced by the dissociation or decomposition of an added initiator or combination of initiators. The free radicals generated then add to monomer and are thereby incorporated as chain ends of polymer molecules. The predominant mode of addition is to the "tail" of the vinyl monomer, as shown in Fig. 4. Even this idealized initiation, by the present definition, results in the formation of abnormal groups and these are represented by the initiating and first monomer units. The initiating systems commonly used in polymer synthesis may result in the incorporation of a variety of abnormal groups, some typical examples of which are described below.

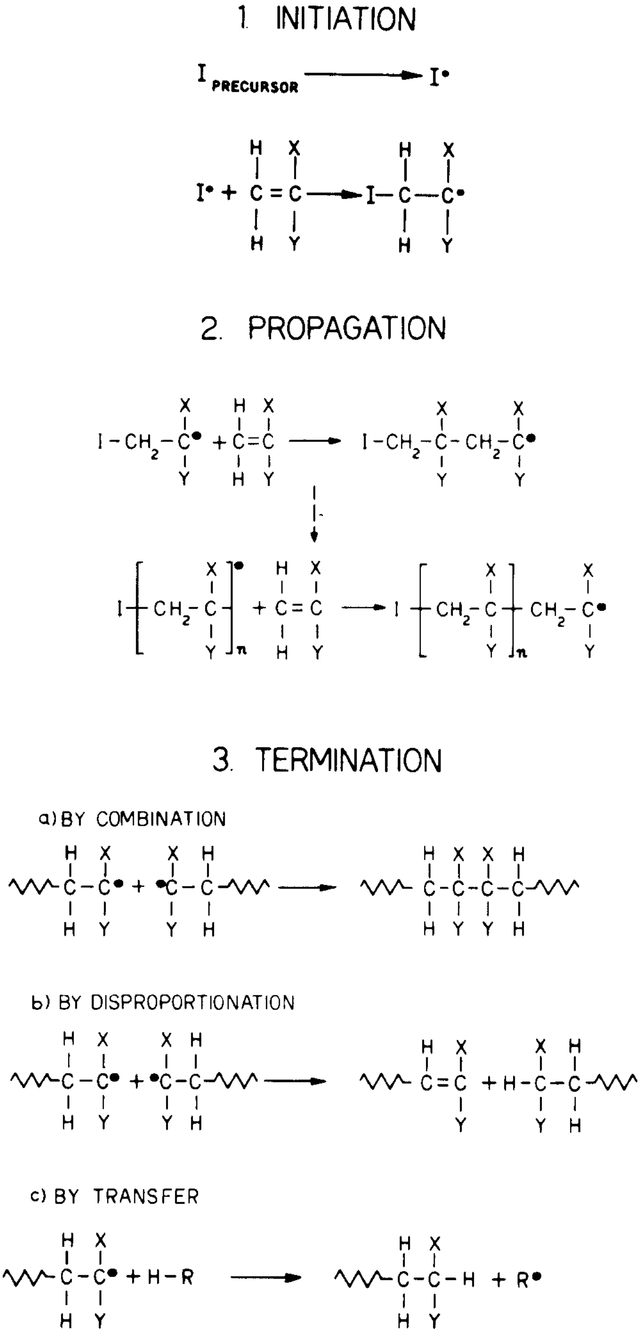

1. INITIATION
I PRECURSOR
I•
2. PROPAGATION
3. TERMINATION
a) BY COMBINATION
b) BY DISPROPORTIONATION
c) BY TRANSFER

FIGURE 4.

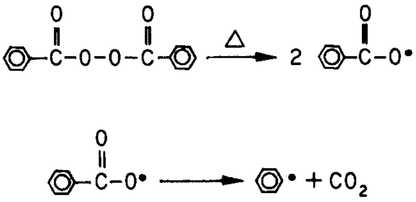


FIGURE 5.

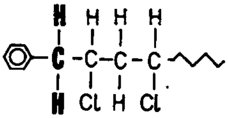


FIGURE 6.

Benzoyl Peroxide

The thermal dissociation of benzoyl peroxide can give rise to both benzoyloxy and phenyl radicals (Fig. 5); the proportion of phenyl radicals increasing with an increase in reaction temperature, or with a decrease in the concentration or reactivity of the monomer. The resultant polymer molecules therefore contain either ester or phenyl residues as endgroups. In the latter case the benzylic methylene is susceptible to a variety of hydrogen abstraction and oxidation reactions which may result in reduced stability of the polymer molecule. For example, poly(vinyl chloride) molecules with phenyl endgroups have been claimed to have lower thermal stability than benzoyloxy-terminated molecules (Fig. 6) [3].

Peresters

These initiators dissociate into alkoxy and acyloxy radicals or, in the case of peroxydicarbonates and peroxalates, into alkoxy radicals and carbon dioxide (Fig. 7). In the presence of unreactive monomers the alkoxy or acyloxy radicals may decompose to yield alkyl or aryl radicals which are alternative initiating species.

It has been established that the tert-butoxy radical, derived from decomposition of tert-butyl peroxalate, can abstract hydrogen from monomers as well as undergo double-bond addition (Fig. 8) [4-7]. If the radicals (2) or (3) propagate or are involved in chain termination reactions, the resultant polymer molecules will have unsaturated endgroups. The ability of the radical (3) to add to monomer has been confirmed [5], and propagation of similar radicals in vinyl ester

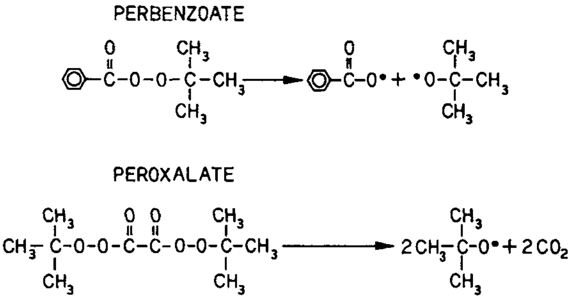


FIGURE 7.

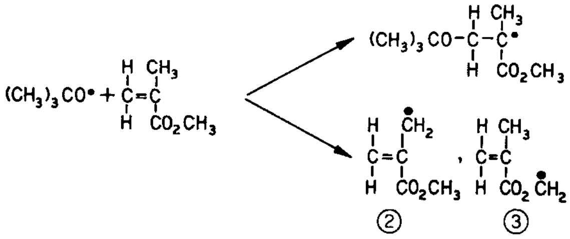


FIGURE 8.

systems is well known. In addition to a possible effect on polymer stability, the unsaturated residues can participate in further reactions, including those leading to chain branching (see later).

Other Peroxides

The use of other peroxides and hydroperoxides as initiators will result in the incorporation of alkoxy, peroxy, or hydroxy endgroups, depending on the initiator and reaction conditions (Fig. 9). The alkoxy radicals, unless trapped by reaction with monomer, may decompose to give alkyl radicals as the initiating species, for example, methyl radicals from the decomposition of tert-butyl hydroperoxide. The peroxide-derived radicals (Fig. 9) may also abstract hydrogen from monomers [8], polymers [9], or additives to form other radicals capable of initiating polymerization.

If the peroxide is used with a co-initiator, as in a redox system, the polymer may contain additional endgroups; for example, amino residues from peroxide-amine initiators. Hydroxy, hydrolyzable sulfate, and nonhydrolyzable sulfoxy endgroups arise from redox initiation by persulfate and reducing sulfoxy compounds (Fig. 10) [10].

$$(CH_3)_3CO\text{-}OC(CH_3)_3 \longrightarrow 2(CH_3)_3CO^{\bullet}$$

$$(CH_3)_3CO\text{-}OH \longrightarrow (CH_3)_3CO^{\bullet} + HO^{\bullet}$$

$$(CH_3)_3CO\text{-}OH + R^{\bullet} \longrightarrow (CH_3)_3CO\text{-}O^{\bullet} + RH$$

$$(CH_3)_3CO\text{-}OH + Ti^{3+} + H_3O^{+} \longrightarrow (CH_3)_3CO^{\bullet} + Ti^{4+} + 2H_2O$$

$$(CH_3)_3CO^{\bullet} \longrightarrow CH_3^{\bullet} + (CH_3)_2C{=}O$$

FIGURE 9.

$$S_2O_8^{=} + S_xO_Y^{=} \longrightarrow {}^{\bullet}OSO_3^{-} + {}^{\bullet}S_xO_Y^{-} + SO_4^{=}$$

$$S_2O_8^{=} \longrightarrow 2\,{}^{\bullet}OSO_3^{-}$$

$${}^{\bullet}OSO_3^{-} + H_2O \longrightarrow HO^{\bullet} + HSO_4^{-}$$

FIGURE 10.

Retention of ionizable initiation residues as endgroups has important consequences in emulsion and suspension polymerization systems as these groups assist in the stabilization and dispersion of the polymer particles. However, sulfate endgroups may undergo pH-dependent hydrolysis, resulting in the formation of hydroxy-terminated polymer molecules. For example, methyl methacrylate polymerized using persulfate initiator in neutral or alkaline media contains sulfate hemiester residues which comprise 80% of the endgroups, whereas these sulfates only comprise 30% of the endgroups of polymer prepared in acidic media [11]. Hydrolysis of sulfate endgroups results in an increase in the acidity of the polymerization medium, and this has been reported to interfere with the polymerization of vinyl esters in unbuffered media since the acetaldehyde formed by hydrolysis of the monomer is an efficient chain-transfer agent [12].

The retention of initiator-derived ionizable groups can also affect the macrostructure and performance of cross-linked ion-exchange resins. For example, triallylamine-based anion-exchange resins obtained using large amounts of persulfate-metabisulfite redox initiator show serious deterioration in their ion-exchange and regeneration capacities (Table 1) [13].

Azobisisobutyronitrile (AIBN)

AIBN decomposes on heating or on irradiation with UV light to yield the cyano-isopropyl radical (4) and other products shown in

TABLE 1. Properties of Triallylamine-Based Ion-Exchange Resins Prepared by Initiation with Varying Amounts of the Persulfate-Metabisulfite Redox System

Initiator concentration (mol%)	3.6	4.5	9.0
Resin sulfur content (%)	2.6	3.2	3.7
Ion-exchange capacity (meq/g)	5.9	5.0	4.2
Swelling ratio[a]	1.3	1.2	1.1
Titration $pH_{1/2}$	7.3	7.2	7.0
Titration ΔpH[b]	0.0	0.5	1.2

[a] Acid/base swelling ratio.
[b] Change in pH from 10 to 60% neutralization.

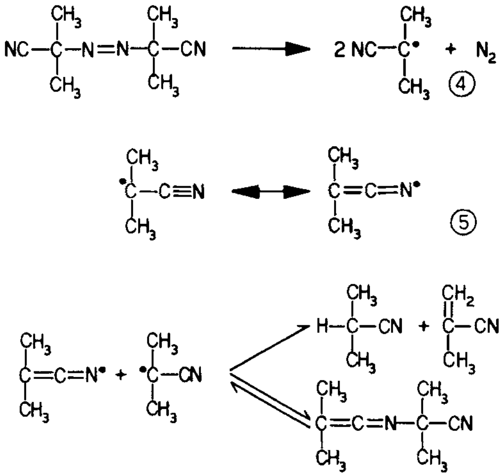


FIGURE 11.

Fig. 11. Apart from the expected cyano-isopropyl endgroups, the polymer may contain endgroups derived from reaction of the radical (4) via its mesomeric form (5). The latter endgroups are capable of further reaction, for example, forming amides in the presence of water. The keteniminyl endgroups are also thermally labile and could undergo radical dissociation during subsequent treatments of the

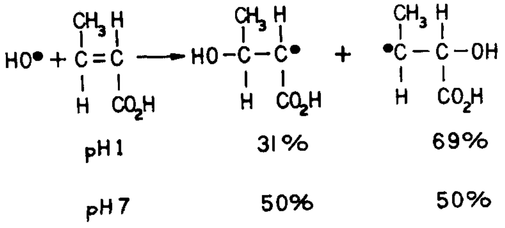


FIGURE 12.

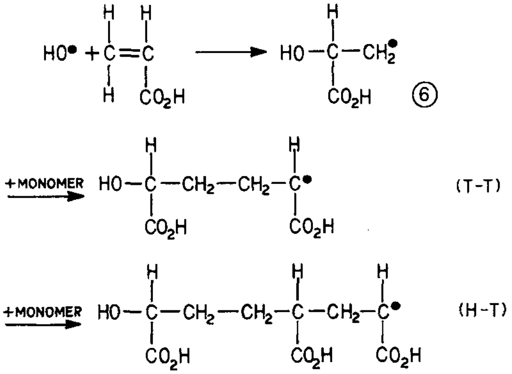


FIGURE 13.

polymer. Similar keteniminyl groups have been proposed as weak links in the degradation of poly(methacrylonitrile) [14]. However, it should be noted that AIBN-initiated polymers are usually more stable than those prepared with peroxide initiators. This has been attributed to the presence of a smaller number of abnormal groups resulting from abstraction reactions in the AIBN-initiated polymerizations [15].

It is often assumed that the only propagating radical is that formed by addition of the initiating radical to the "tail" of the monomer. Although in many cases the available evidence suggests that this is correct, there are examples where significant addition to the monomer "head" has been shown to occur. These include the reactions of benzoyloxy radicals with styrene [16] and those of hydroxy radicals with acrylic and crotonic acid. In the latter cases, the relative proportion of head and tail addition is dependent on the degree of ionization of the monomers (Fig. 12) [17].

As the propagation of the "tail" radicals (6) would most probably

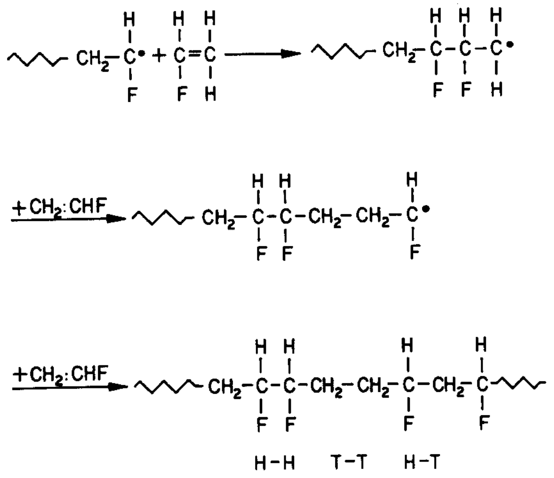


FIGURE 14.

proceed by a "normal" head-to-tail addition, the next monomer added in the chain would, by our definition, also constitute an abnormal group, as shown in Fig. 13.

Propagation

Most vinyl polymers are generally accepted as having a regular head-to-tail (H-T) arrangement of repeating units. This would imply that the only reaction occurring is that of the propagating radical adding to the "tail" of the monomer molecules, and that the propagating radical does not rearrange prior to reaction with monomer. However, few free radical reactions are as specific as this scheme requires. Even if the propagation reactions were 99.9% selective, there would still be the probability of one abnormal group per 1000 repeating units. In the case of poly(vinyl chloride), rearrangement of the propagating radical appears to occur approximately 6 times per 1000 monomer additions, as indicated by the concentration of pendant chloromethyl groups detected in the polymer [18]. As the conversion of monomer to polymer proceeds, the reaction conditions change significantly and the probability of abnormal reactions, such as grafting and reaction with "dead" polymer molecules, is increased.

Side reactions which may lead to abnormal groups in the polymer chain are also possible. The extent to which these reactions may occur depends on a number of factors including the structure of the monomer (i.e., the reactivities of the monomer and its derived propagating radical), the conditions of polymerization (such as concentration,

TABLE 2. Head-Head (H-H) Monomer Linkages in Some Important Polymers

Polymers	% H-H placements
Poly(vinyl fluoride)	26-32
Poly(vinylidene fluoride)	10-12
Poly(vinyl chloride)	$\sim 1^a$
Poly(vinyl acetate)	1-2
Poly(ethylene-co-vinyl acetate)	~ 13

[a] Before rearrangement to $-CH_2Cl$ branch.

temperature), and the nature of the polymerization medium. A selection of typical abnormal groups and their origins are described below.

Head-Head and Tail-Tail Placements

The normal process of termination of the propagating radical by combination results in a midchain head-to-head (H-H) linkage. Similar isolated linkages, together with tail-to-tail (T-T) linkages, can also occur during propagation if the propagating radical attacks a monomer "head." Theoretical studies [19] and the limited relevant experimental evidence indicate that a H-H placement of the propagating radical is more probably followed by a T-T placement, thus allowing restoration of the normal head-to-tail (H-T) addition sequence, as in the case of poly(vinyl fluoride) (Fig. 14) [20].

The presence of H-H linkages, other than those arising from termination reactions, has been established for a number of polymers, some of which are listed in Table 2. In general, the frequency of H-H monomer placements increases with increasing polymerization temperature. It is also dependent on the nature of the solvent used, and probably on the degree of ionization of ionizable monomers, but appears to be independent of the degree of polymerization of the polymer. In the case of poly(vinyl chloride), H-H linkages may contribute indirectly to the poor initial thermal stability of the polymer at moderate temperatures [21].

Rearrangement of the Propagating Radical

When polymerization involves the addition of a reactive propagating radical to an unreactive monomer, there is an increased opportunity for the radical intermediates to undergo rearrangement prior to addition. These rearrangements may take several forms; for

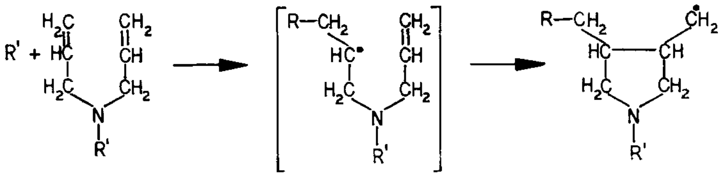


FIGURE 15.

example, 1,2-halogen shifts or 1,5-hydrogen shifts which can occur in the respective polymerizations of vinyl chloride (Fig. 26) and ethylene (Fig. 24) described later, or the cyclopolymerization of polyenes such as diallylamine (Fig. 15) [22].

Rearrangements of the carbon skeleton of the monomer are unusual in radical polymerization reactions, unlike cationic polymerizations where there are some classical examples of so-called "phantom polymers" in which rearrangement of the intermediate carbonium ions completely disguises the carbon skeleton of the monomer [23].

Inadvertant Graft Formation

Abstraction of an atom from a polymer molecule during a polymerization reaction results in the formation of a potential nonterminal propagating radical which can lead to the formation of grafts or long-chain branching. The extent of these reactions depends on a number of factors, but can be extensive in the case of the polymerization to high conversion of a relatively unreactive monomer such as a vinyl ester. Other sources of grafting or long-chain branching include the reactions of the propagating radicals with unsaturated centers, such as the abnormal endgroups described earlier as well as those formed by disproportionation or by attack of the propagating radical on the aryl substituents of vinyl-aromatic monomers. For many of the classical linear polymers, for example, polystyrene and poly(methyl methacrylate), analytical procedures have only recently achieved sufficient sensitivity and resolution to enable the quantitative assessment of such abnormal features on the properties of the polymers.

Inadvertant Copolymerization

The propagating radical may react with impurities, by-products, or components other than the monomers which may be present in the polymerization mixture. Usually these foreign reactive species act as chain terminators or as transfer agents, and are incorporated only as terminal units in the polymer chain. A variety of species may, however, be incorporated by copolymerization.

Oxygen is normally an effective inhibitor or chain terminator of radical polymerizations but can form peroxy-oligomers with methyl methacrylate, styrene, and other vinyl monomers under certain

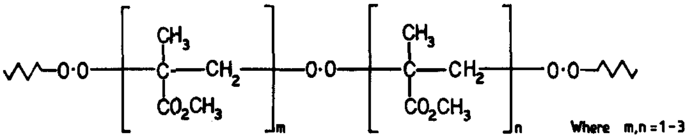


FIGURE 16.

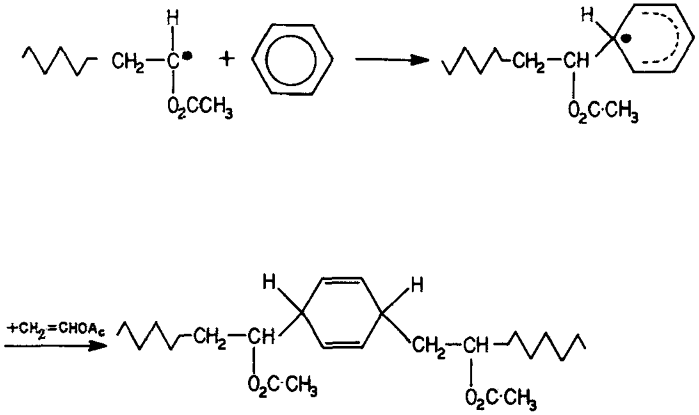


FIGURE 17.

conditions (e.g., Fig. 16) [24]. In most cases oxygen is combined as peroxidic endgroups, or is introduced via radical-induced oxidation into the backbone of preformed polymer molecules. These peroxy groups are usually unstable, and either decompose or undergo rearrangement during the polymerization process, or else remain in the product to act as initiators of subsequent autoxidation or degradation reactions.

Copolymerized methacrylonitrile as well as keteniminyl endgroups have been detected in AIBN-initiated polystyrene [25] and are likely to be present in other polymers obtained with this initiator (Fig. 11).

If the polymerization is conducted in an aromatic solvent, there is the possibility that solvent molecules may be incorporated in the polymer. Radicals derived from certain monomers, e.g., the vinyl esters, apparently can form dihydrobenzenoid adducts, and while these may rapidly dissociate, they may also be converted to stable polymer chain units by oxidation or radical-induced dehydrogenation. The extent of such reactions is small but significant. Poly(vinyl acetate) prepared in benzene is believed to contain approximately one nonterminal benzene per 1000 monomer units (Fig. 17) [26].

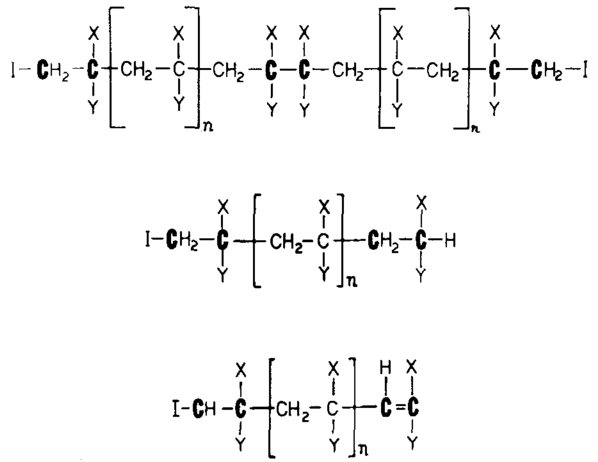


FIGURE 18.

Termination

The termination process of polymerization results in the formation of abnormal groups. The propagating radicals can terminate by combination, disproportionation, or chain transfer reactions, namely to solvent, to initiator, to polymer, to monomer, to a chain transfer additive, or to some species present as an impurity.

Combination

Normal combination of two polymer radicals results in the formation of a H-H linkage, but while such linkages are often claimed to have lower thermal stability than the corresponding polymeric H-T linkages, direct evidence for this is difficult to find, and thermal analyses of model copolymers are often inconclusive in this respect. For example, a stilbene-styrene copolymer, a model of a polystyrene with a high proportion of anomalous H-H placements, does not show significantly lower thermal stability than polystyrene itself [27]. Note, however (Fig. 18), that a polymer molecule terminated by combination has at least three sequences of abnormal groups, located at the ends and at the joining point.

Disproportionation

Disproportionation between two polymer radicals yields two polymer molecules, each with at least two sequences of abnormal groups located at either end of the molecules. In the case of poly(methyl methacrylate), polystyrene, or poly(vinyl chloride), there is direct

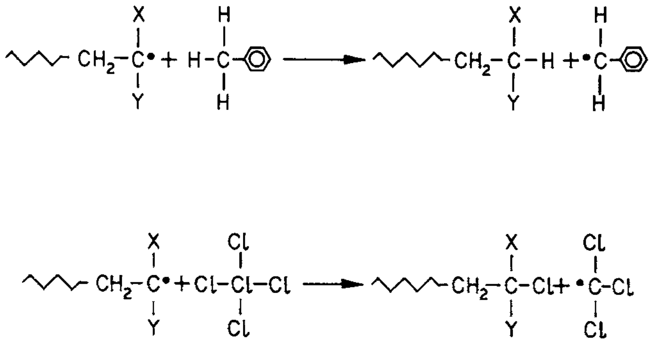


FIGURE 19.

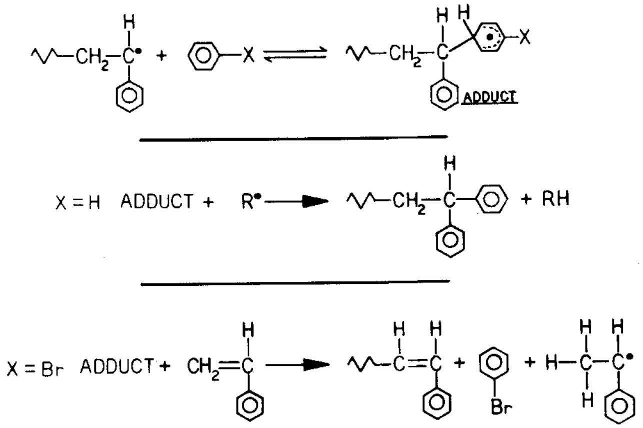


FIGURE 20.

evidence that the presence of unsaturated terminal groups lowers the thermal stability of the polymer [28].

Transfer to Solvent

This reaction usually involves the abstraction of hydrogen, for example, from an alkylaromatic solvent such as toluene, or of halogen from halogenated solvents such as carbon tetrachloride (Fig. 19).

In both these examples the solvent-derived radicals can initiate further chain polymerization. Apart from the effect on average degree of polymerization of the polymers, transfer to solvent can deliberately or accidentally result in the incorporation of reactive endgroups.

Polymerization chain-transfer to aromatic solvents lacking alkyl or haloalkyl substituents has been postulated to involve the formation of a labile σ-complex (Fig. 20) [26]; conversion to an aryl endgroup will require dehydrogenation or oxidation of this adduct.

Transfer to Monomer or Polymer

Chain transfer to monomer by hydrogen transfer from polymeric radical is unusual, although it has been postulated to occur in systems containing aromatic solvents, and may also occur in other systems in which cyclohexadienyl or similar radicals are intermediates. The solvent-mediated hydrogen transfer is believed to occur via the formation of a σ-complex, as shown in Fig. 20.

Chain transfer to monomer usually involves hydrogen (or halogen) abstraction by the polymer radicals, for example, from the α-methyl of methacrylates or the acetate group of vinyl acetate (Fig. 21). These reactions are analogous to the hydrogen abstraction by initiator radicals, and can result in the incorporation of similar abnormal endgroups into subsequently polymerized molecules.

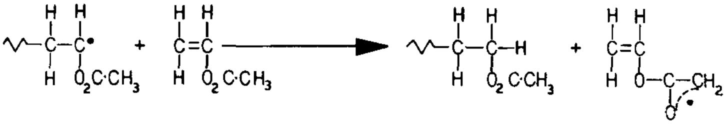


FIGURE 21.

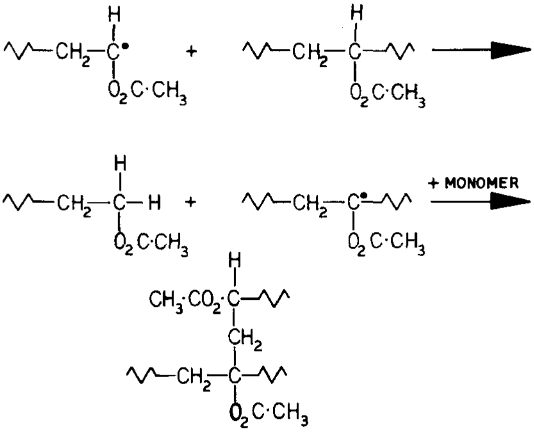
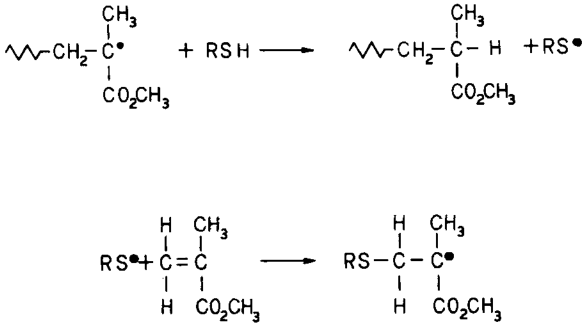


FIGURE 22.



$$\sim\!\!\sim CH_2-\overset{CH_3}{\underset{CO_2CH_3}{C^\bullet}} + RSH \longrightarrow \sim\!\!\sim CH_2-\overset{CH_3}{\underset{CO_2CH_3}{C}}-H + RS^\bullet$$

$$RS^\bullet + \overset{H}{\underset{H}{C}}=\overset{CH_3}{\underset{CO_2CH_3}{C}} \longrightarrow RS-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CO_2CH_3}{C^\bullet}}$$

FIGURE 23.

Chain transfer to polymer can also involve the abstraction of hydrogen or halogen from polymer molecules (Fig. 22) and, as stated earlier, can result in the formation of long-chain branching or grafting.

Transfer to Additives or Impurities

Transfer agents are usually sources of hydrogen or other atoms which can be abstracted by polymer radicals. The radical derived from the transfer agent then initiates further polymerization (Fig. 23). As well as being used for the control of molecular weight, transfer agents can decrease the average residual unsaturation of the polymer, often resulting in increased thermal stability of the product.

Termination by chain transfer can also result in the incorporation of undesirable endgroups. For example, the carbonyl fragments derived from aldehyde impurities or ketonic solvents can promote the UV light-induced degradation of the polymers.

ABNORMAL GROUPS IN SOME COMMERCIALLY IMPORTANT POLYMERS

Having described some of the abnormal groups that can be introduced into polymers prepared by radical-initiated processes, it is appropriate to review the reports of the presence of these groups in some well-known commercial vinyl polymers. A quantitative assessment of the abnormal groups in commercial polymers has not always been possible, partly because of the lack of published data, but also from uncertainties as to the nature of the initiators and chain-transfer agents used in the manufacture of the various grades of the polymers.

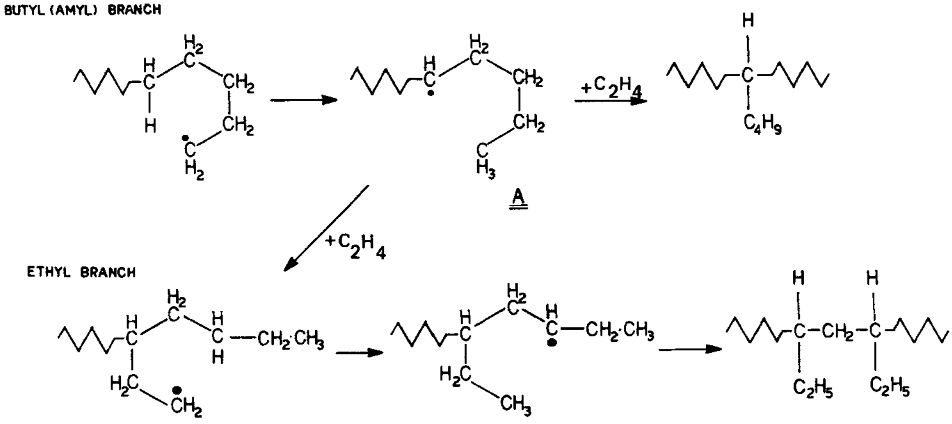


FIGURE 24.

Polyethylene

The formation of chain-branching in low-density polyethylene via "back-biting" of the propagating radical has been known for some time, and is one of the classic examples of formation of abnormal groups during polymerization (Fig. 24). Basically, it is an example of intramolecular chain-transfer by hydrogen abstraction, and typically can result in the formation of approximately 10 n-butyl, and 4 n-amyl chain branches per 1000 monomer units via the respective 1,5- and 1,6-hydrogen shifts. Ethyl chain branches, typically 2 per 1000 monomer units, may also be present and these are formed via a sequence of 1,5-hydrogen shifts [29]. In addition, there are usually at least 1-2 long-chain branches per 1000 monomer units, resulting from intermolecular chain-transfer or hydrogen-abstraction from sites remote from the chain ends [30]. The presence of relatively high proportions of chain branching not only affects the physical and mechanical properties, but also the chemical properties of the polymer. The tertiary hydrogen atom at the branching points are susceptible to abstraction and can be initiating centers for oxidation and degradation of the polymer during subsequent fabrication and service. Hydrogen abstraction at branching points and the subsequent β-scission of the nonterminal polymeric radicals has been proposed as the source of vinylidene groups present in polyethylene (Fig. 25) [31].

Poly(vinyl Chloride)

Several workers have suggested that poly(vinyl chloride) (PVC) contains approximately one anomalous H-H monomer placement per

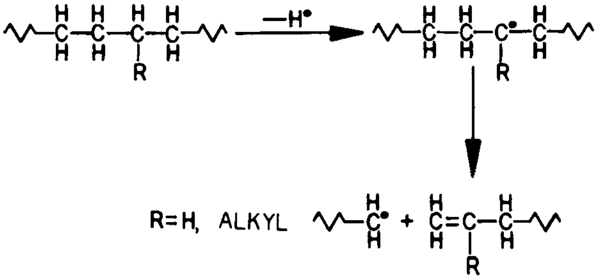


FIGURE 25.

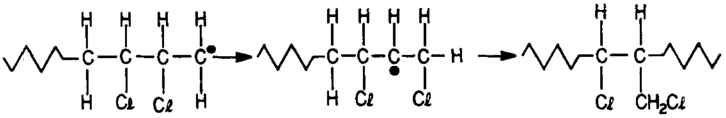


FIGURE 26.

100 monomer units, and it has been suggested that such H-H linkages could act as centers for the initiation of thermal dehydrochlorination. This has been disputed on theoretical grounds and is not convincingly supported by the results of thermal analyses of model compounds [32]. In addition, detailed NMR and IR spectroscopic studies have indicated the presence of few, if any, of the expected associated T-T linkages in the conventional radical-initiated polymer. However, PVC does contain a similar proportion of chloromethyl branches which are believed to be formed by a facile 1,2-chlorine shift in the anomalous H-H adduct radical (Fig. 26) [18, 33]. It has been proposed that these chloromethyl branches may provide some of the initiation points for the thermal dehydrochlorination [34].

A molecule of commercial PVC (MW = 32,000) could contain the following numbers of abnormal groups: chloromethyl branches, 6; long-chain branches, 1; terminal $-CH=CHCl$ groups arising from β-chain scission or chain-transfer to monomer, 1; nonterminal unsaturated groups resulting from chlorine abstraction or dehydrochlorination during polymerization, ~1. The actual amount of unsaturation in a nascent PVC molecule is difficult to determine as significant dehydrochlorination can occur during sample preparation or during many of the chemical assaying methods used for obtaining the published data.

Evidence suggests that, in the absence of initiator residues, other impurities or peroxidized material, the most likely of the potential initiating centers for the thermal dehydrochlorination of practical samples of PVC are unsaturated groups, particularly nonterminal

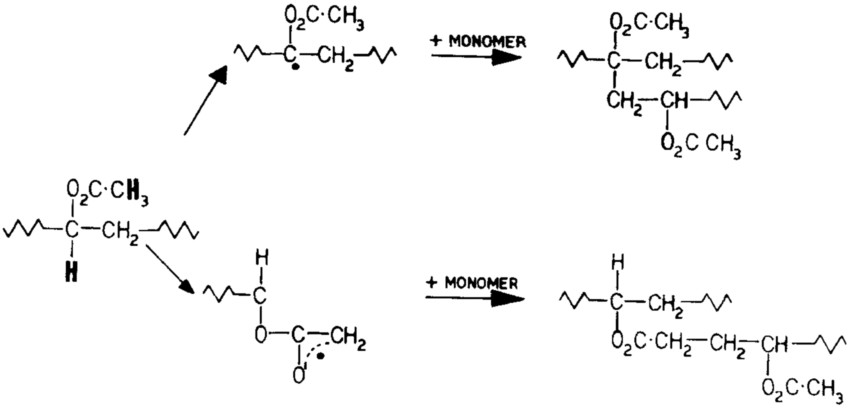


FIGURE 27.

groups [35]. PVC prepared using AIBN as the initiator has greater thermal stability than PVC samples prepared using peroxide initiators. This has been ascribed to the greater tendency of peroxide-derived radicals to generate unsaturated centers in the polymer molecules [32].

Poly(vinyl Acetate)

Poly(vinyl acetate) (PVAc) and its hydrolyzed derivative, poly(vinyl alcohol) (PVA), may contain up to 1% of anomalous H-H monomer placements, or roughly 3-10 such placements per molecule of commercial emulsion-polymerized material. However, the extensive long-chain branching which results from chain transfer to polymer is of greater significance. The transfer occurs by abstraction of either a tertiary backbone hydrogen or from one of the acetate hydrogens (Fig. 27). The latter mode of transfer results in the formation of hydrolysable long-chain branches, and these may account for 75% or more of the total long-chain branches [36]. The transfer to polymer may also involve a "backbiting" 1,6-hydrogen shift to an acetate group, as well as the remote or intermolecular transfer reactions. The 1,6-hydrogen shifts also result in the formation of hydrolysable chain branches.

It has been estimated that the activation energies for addition of the polymer radical to monomer and for chain-transfer to polymer are approximately equal, thus rationalizing the extensive chain branching which occurs in PVAc, particularly in solvent-free systems taken to high conversion. In vinyl acetate polymerizations taken to 80-90% conversion of monomer, approximately 30% of the polymer is contained in long-chain branches [37]. Copolymers of vinyl acetate with vinyl

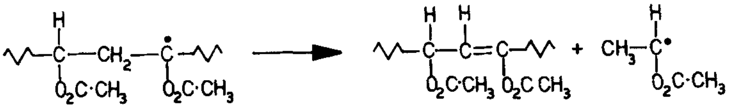


FIGURE 28.

chloride may contain even more extensive chain branching than either of the homopolymers. Copolymers of vinyl acetate with ethylene have also been reported to contain increased amounts of chain branching, for example, 60 branches per 1000 monomer units for a copolymer consisting of 8% vinyl acetate; this proportion decreasing with increasing vinyl acetate content [38].

Transfer reactions involving the tertiary backbone hydrogens not only may result in formation of nonhydrolyzable long-chain branches, but also in the formation of nonterminal unsaturation following subsequent transfers to monomer (Fig. 28). It has been suggested that the termination of the polymer chains may involve some hydrogen transfer to monomer, as well as the more usual modes of termination. Alternatively, the polymer radical may abstract hydrogen from the acetate moiety of the monomer to yield another initiating species. Either of these reactions would result in terminal unsaturation of the polymer molecules.

Other abnormal groups present in PVAc prepared in aqueous media include carbonyl, carboxy, and hydroxy groups, resulting from chain-transfer and hydrolysis reactions. Polymerization of vinyl acetate in the presence of aromatic solvents may also result in extensive transfer to solvent, with the incorporation of solvent as both terminal and nonterminal units; these transfer processes have been described earlier.

The thermal degradation of PVAc at low temperatures involves largely a stepwise autocatalytic elimination of acetic acid; the reaction producing a series of short ($n < 5$) polyene sequences. The degradation appears to initiate at numerous points along a polymer molecule, probably at branching points. Whereas the thermal degradation of PVC occurs by both homolytic and heterolytic mechanisms, that of PVAc is thought to be largely heterolytic, i.e., it is not sensitive to radical initiation.

Polystyrene

Radical-initiated polystyrene has been shown to consist predominantly of molecules having the ideal structure expected from the reaction sequences shown in Fig. 4. Termination of the molecular chains occurs by both combination and disproportionation, and by chain transfer if suitable additive species are present. In addition there is a small but significant proportion of chain branching resulting from chain transfer to polymer [39]. While normal attack of the initiating radical occurs at the β-carbon ("tail") of the monomer, reactive initiating radicals, such as hydroxy, show detectable amounts of addition via the aromatic ring. Although the importance of these adducts in the initiation process is uncertain, the substituted phenyl groups are potential reactive sites for chain transfer or subsequent degradation processes. Recent studies have shown that the use of benzoyl peroxide as an initiator can result in the formation of phenyl- and benzoyloxy-styrene which could be incorporated into the polystyrene molecules [16].

Thermal degradation of polystyrene at moderate temperatures ($<300°C$) proceeds by a process of consecutive α-hydrogen abstraction and β-chain scission reactions occurring at random points along the polymer molecules, with low yields of monomer production in the initial stages of the process [40]. At higher temperatures (>330-350°C) chain scission occurs more frequently near the ends of the chains, with the formation of styrene, styrene oligomers, and other radical-derived products. Thermal analyses of various radical-initiated (atactic) polystyrenes indicates that a small proportion of "weak" linkages are broken at temperatures near 280-300°C, resulting in a rapid initial drop in the average molecular weight of the polymer, while the bulk of the degradation occurs at 330°C or above. These "weak" links have been variously ascribed to the presence of initiator residues, terminal and nonterminal unsaturation, H-H linkages resulting from chain termination by polymer-polymer combination, chain branches, semibenzenoid chain units, or hydro-aromatic terminal groups. A recent reevaluation of the degradative thermal analyses of polystyrene has shown that some form of weak link does exist in the polymer, although their nature remains speculative. The weak links are not an artifact of the thermal analytical technique [41].

Semibenzenoid weak links are claimed to arise from reaction of the propagating radical via one of its mesomeric forms [42], as shown in Fig. 29. While the presence of these groups has not been established in polystyrene, midchain semibenzenoid groups have been detected in copolymers containing 1,1-diphenylethylene and result from termination by combination of two polymer chains [43]. Cumyl radicals, which are models for the propagating radicals of α-methylstyrene, dimerize at near-ambient temperatures with the formation of about 20-30% of thermally-labile products, identified as the o- and p-semibenzenoid isomers of dicumyl (Fig. 30) [44]. The formation of similar unstable species has been detected during the dimerization of benzylic radicals [45, 46]. Although the semibenzenoid radicals are unlikely to be involved in the propagation reactions, they could participate in the termination of polymer chains. The resultant non-aromatic structural units would then be susceptible to oxidation.

Some workers have suggested that the weak links in polystyrene are not derived from abnormal groups of the types described above, but rather are oxygenated species resulting from reaction of the

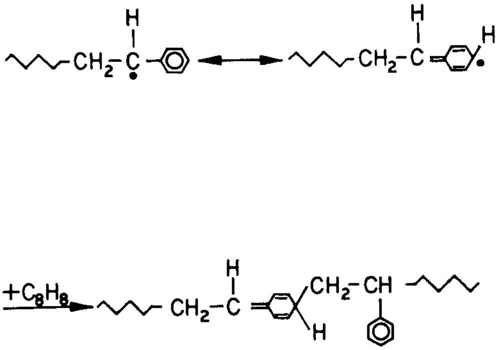


FIGURE 29.

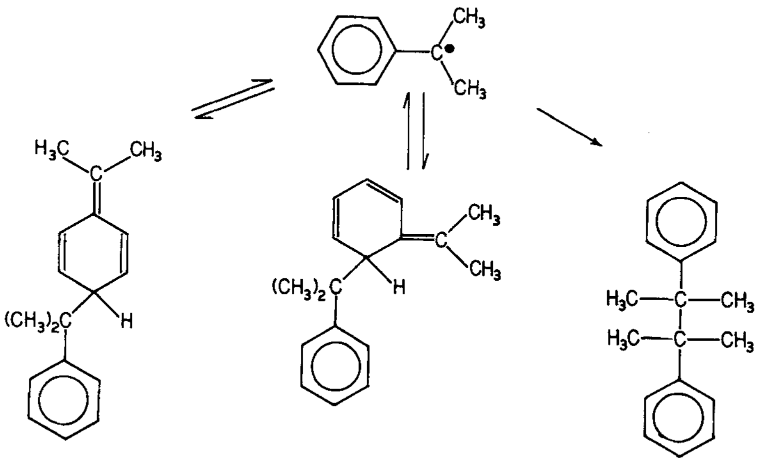


FIGURE 30.

polystyryl radicals with trace amounts of residual atmospheric oxygen or initiator-derived peroxides, the proportion of "weak links" being dependent on the particular experimental techniques. The ease of incorporation of adventitious oxygen is demonstrated by the 15,000-fold greater rate of addition, at 50°C, of the polystyryl radical to oxygen compared to its rate of addition to monomer [47]. Even radical-initiated polystyrenes prepared in conventional thoroughly outgassed systems appear to contain carbonyl groups [48] formed, presumably, by decomposition of α-peroxy species [49]. Apart from possible effects on the thermal stability of polystyrenes, the ketonic products would have a considerable promoting influence on the UV

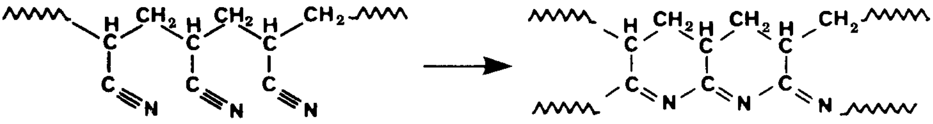


FIGURE 31.

light-induced degradation of the polymers in service [49, 50]. There also appears to be a correlation between the susceptibilities of the polymers toward "premature" thermal degradation and toward autoxidation reactions, indicating the presence of species which are both thermally labile and readily oxidized [51].

Polyacrylates and Polymethacrylates

Both polyacrylates and polymethacrylates consist essentially of polymer molecules having the ideal structures expected from the reaction scheme shown in Fig. 4. Both contain a small proportion of chain branches resulting from chain-transfer to polymer, although until recently poly(methyl methacrylate) was believed to be essentially unbranched. Abstraction leading to chain transfer may occur from the alkoxy groups, from the α-methyl groups, and from the tertiary backbone hydrogens. Hydrogen abstraction from monomer has been demonstrated in our recent studies of the reactions of tert-butoxy radicals with alkyl methacrylates [5]. This suggests that tert-butoxy-initiated and probably other radical-initiated polymer molecules could contain unsaturated endgroups of the type shown in Fig. 8. These unsaturated endgroups could also serve as branching points in subsequent copolymerization with monomer.

Thermal degradation of the polyacrylates, like that of polystyrene, proceeds by a process of random α-hydrogen abstraction followed by β-scission, principally of the alkoxycarbonyl groups. The degradation is probably initiated by peroxidic species formed during the polymerization or in subsequent autoxidation [51]. In contrast, and as mentioned earlier, the thermal degradation of the lower primary and secondary alkyl methacrylate polymers proceeds by a chain-depolymerization process initiated largely at the endgroups of the molecules, particularly at unsaturated endgroups. However, poly(methyl methacrylate) containing small percentages of acrylonitrile or maleic anhydride as comonomer shows lower thermal stability than the homopolymer, suggesting that depolymerization may also be initiated at abnormal nonterminal groups. Although copolymerized acrylonitrile can interrupt the monomer-producing radical degradation, it also introduces weak links into the polymer chain which then become susceptible to nonradical chain-scission reactions [52].

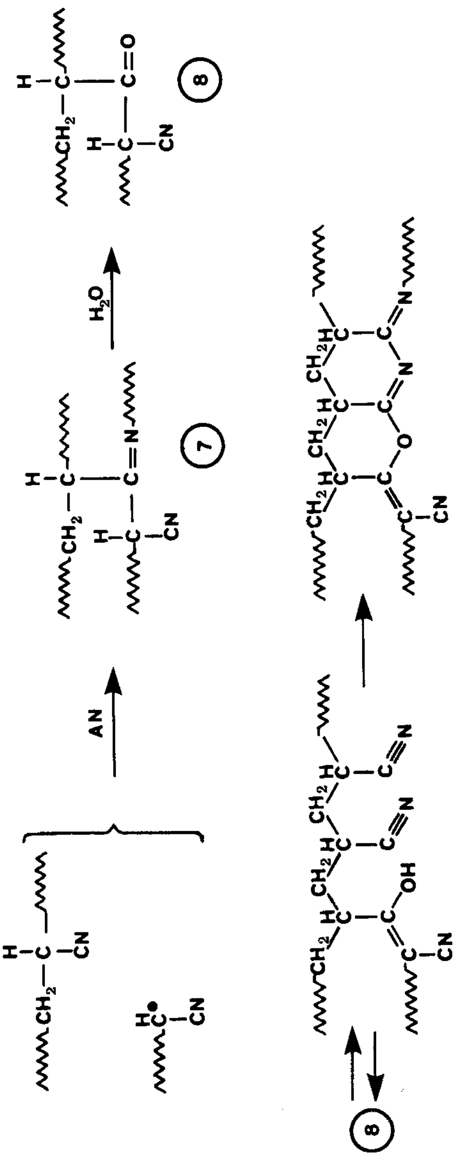
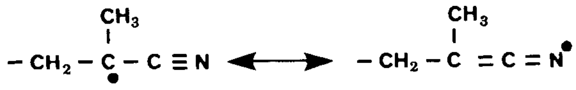


FIGURE 32.



$$-CH_2-\overset{CH_3}{\underset{\bullet}{C}}-C\equiv N \longleftrightarrow -CH_2-\overset{CH_3}{C}=C=N^{\bullet}$$

FIGURE 33.

Poly(acrylonitrile) and Poly(methacrylonitrile)

Pure poly(acrylonitrile) (PAN) and poly(methacrylonitrile) (PMAN) are colorless polymers that darken readily on heating, especially in the presence of oxygen at temperatures in excess of 150°C, or on treatment with base. The ready discoloration is disadvantageous for the production of PAN textile fibres. The colored species are believed to consist of sequences of polyazomethine linkages derived from the pendant nitrile groups of the polymers, forming ladder polymeric structures of the type shown in Fig. 31 [53]. The polymerized nitrile groups may be partially converted to nitrones in the presence of oxygen.

PAN and PMAN prepared by radical polymerization, as well as anionic isotactic PAN, are more susceptible to nitrile polymerization than polymers prepared using other methods. The activating species are believed to be abnormal groups, formed during the radical or anionic polymerization, which can act as nucleophiles. Chain transfer to polymer nitrile groups can result in the formation of enamine-linked chain branches (7). On hydrolysis during the usual suspension or emulsion polymerization processes, these can yield ketonitrile groups (8). These groups, typically present in the ratio of 1 per 2000 monomers, can act as initiators for the heterolytic polymerization of the pendant nitriles (Fig. 32). Nitrile polymerization can also be initiated by a variety of other mechanisms which are reviewed elsewhere [54]. Related abnormal units may also be generated during the polymerization of methacrylonitrile, but while these cannot form nucleophilic enolic isomers like those derived from PAN, PMAN is nevertheless very sensitive to nitrile polymerization, particularly during polymerization of the monomer.

Copolymerization of small amounts of acrylic acid or similar nucleophilic monomers can also promote, and allow control of, the exothermic nitrile polymerization, for example, in the initial stages of conversion of PAN fibers to graphite fiber precursors.

PMAN is thought to contain a proportion of monomer units incorporated via the keteniminyl form of the propagating radical (Fig. 33) [14]. The presence of these thermally-labile linkages in PMAN can be detected by IR spectroscopy. These groups are destroyed without color development on heating the polymer at 80°C, and their destruction is accompanied by only a small reduction in the average molecular weight of the polymer. It would appear, therefore, that these species are largely involved in chain termination.

CONCLUSION

This review has outlined the mechanisms by which some abnormal structural groups may be introduced into vinyl polymers during their manufacture. The most important of these abnormal groups are initiator fragments, chain-branching points, terminal and nonterminal unsaturation, and adventitious peroxy groups or their carbonyl rearrangement products. When particular structural anomalies can be correlated with the chemical and physical properties of the polymer or its fabricated products, it should be possible to overcome deleterious effects by suitable modification of the polymer or polymerization system. Often, as in the example of polystyrene, the defects appear to be associated with some unresolved abnormal groups present in such small proportions that they cannot be identified by conventional chemical or physical methods, and are disclosed only in thermal analytical or similar studies.

It should be noted that polymer "weak links" which are apparent in studies of thermal degradation at 250-300°C may not be relevant to the "weak links" that limit the long-term service life of plastics articles at near-ambient temperatures or on outdoor exposure. Failure under these conditions is largely the result of oxidative degradation promoted by the presence of activating groups such as unsaturation or chain branching which themselves do not directly weaken the polymer chain, but provide initiation points for peroxidation by atmospheric oxygen. It is probable that these peroxy groups are the true "weak links" in practical polymer samples; their radical decomposition products initiating the polymer chain degradation processes which result in the weakening, discoloration, and embrittlement of plastics products.

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