

Structural defects in polymers—their identification and significance

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Abstract - It is well known that vinyl and acrylic polymers prepared by a free radical mechanism contain structural irregularities or defect groups. These defect groups can have a significant effect on the chemical properties of the polymer. Defect groups are, by definition, introduced into a polymer during the initiation and termination steps of the polymerization and also by "abnormal" propagation reactions. Their nature shows a marked dependence on the reaction conditions and, in particular, on such factors as the initiator and solvent employed and the degree of conversion.

INTRODUCTION

In the early days of polymer science there was tremendous argument regarding the chemical structure of polymers. Staudinger eventually overcame the proponents of the old micelle theory and established that "real" polymers, of the type now described as vinyl or acrylic polymers, are very large molecules which comprise monomer units linked together in a regular fashion by covalent bonds in a way that does not involve any rearrangement of the carbon skeleton of the monomer (ref. 1). Staudinger was still left with the problem of the unsatisfied valencies at the ends of the polymer chain. He solved this problem in a most ingenious manner by simply linking together the two ends so as to form a large cyclic macromolecule (Fig. 1). In this structure all monomer units are in the same chemical environment.

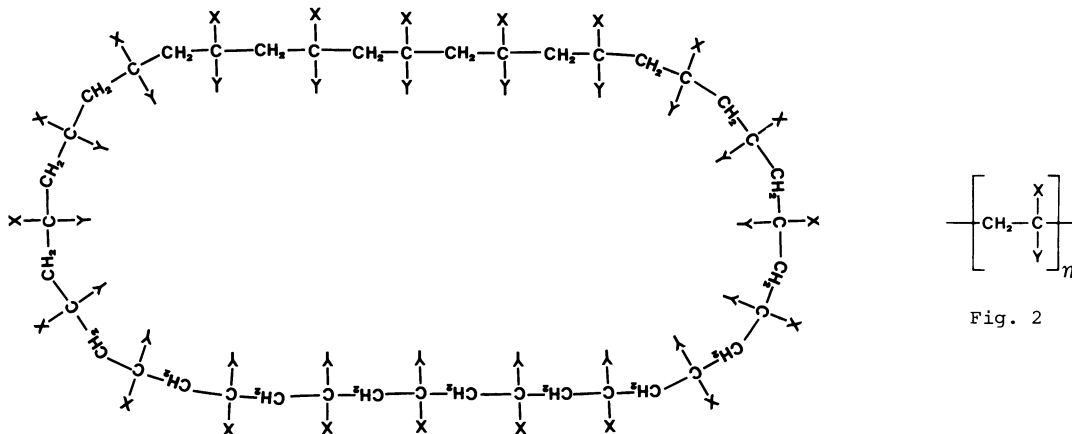


Fig. 1. Staudinger's cyclic polymer molecule

Subsequently, of course, it was realized that polymer molecules are essentially linear. However, because the end groups account for only a very small percentage of the total structure, the generalized formulae (Fig. 2) is usually used to describe a polymer chain and has proven to be adequate for many purposes (for example, as a basis for explaining certain physical properties). However, when chemical properties (UV stability, weather resistance, chemical resistance, etc.) of vinyl or acrylic polymers are considered, the properties observed in commercial polymers are often not those expected for a material with the structure shown in Fig. 2 (ref. 2). The unexpected properties are usually explained in terms of the existence of defect groups or structural imperfections in the polymer chains.

DEFECT GROUPS

These groups, although present in very small amounts, contribute significantly to the chemical properties. Two major pieces of evidence support the importance of defect groups in this context.

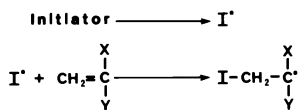
1. Polymers which have nominally the same chemical and physical compositions but which have been prepared by different processes can have quite different chemical properties. For example, poly(methyl methacrylate) prepared by an anionic mechanism is more thermally stable than poly(methyl methacrylate) made by a free-radical process (ref. 3).
2. Comparison of a low molecular weight model with a polymer of nominally the same chemical structure often reveals quite dramatic differences in properties. A classic example is poly(vinyl chloride) which has a substantially lower thermal stability than the model, 2,4,6-trichloroheptane (ref. 4).

The Organizing Committee for this Symposium has suggested that speakers duly consider the industrial aspects of their subject. It is therefore proposed to analyze in some detail the preparation of a typical copolymer with a composition similar to those used commercially. The types of defect groups that might arise during each stage of the polymerization will be indicated and the manner in which these vary according to the particular reaction conditions employed will be discussed.

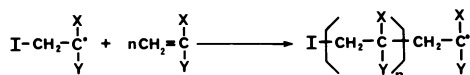
The formulation chosen comprises equal parts of methyl methacrylate and styrene in a solvent (50% v/v) and a free radical initiator. The temperature of polymerization has been fixed at 60°. For the purposes of this lecture, a defect group is defined as any group which is not an unrearranged monomer skeleton flanked on each side by another unrearranged monomer unit.

The generally accepted mechanism for a free-radical polymerization comprises three stages, namely, initiation, propagation, and termination and is shown in Fig. 3. Note that even if all the chemical reactions are clean (no unexpected competing side reactions) then defect groups will, by definition, still result from the initiation and termination steps. All polymers contain defect groups. In practice, side reactions occur at every stage of the polymerization, including propagation. These processes add to the types and number of defect groups that are present in the polymer.

Initiation:

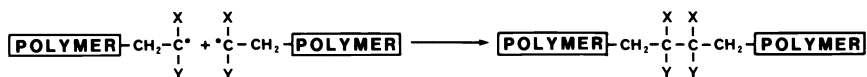


Propagation:



Termination:

COMBINATION



DISPROPORTIONATION

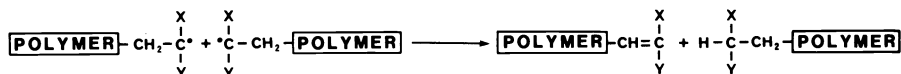


Fig. 3. "Text book" mechanism for free radical polymerization

In the past the study of defect groups has been made difficult by the lack of reliable techniques to identify and characterize the very small number of such groups present. The advances made in recent years owe much to the development of methods which have the high degree of sensitivity required.

INITIATION

The techniques employed in the study of initiation include NMR (Fig. 4) (refs. 5-7), chemical analysis (Fig. 5) (ref. 8) and radical trapping (Fig. 6) (refs. 9-14). It should be noted that, in general, no one technique can by itself provide all of the information necessary to fully characterize the initiation reaction and usually a combination of methods is required. For example, the NMR methods require that suitable model compounds

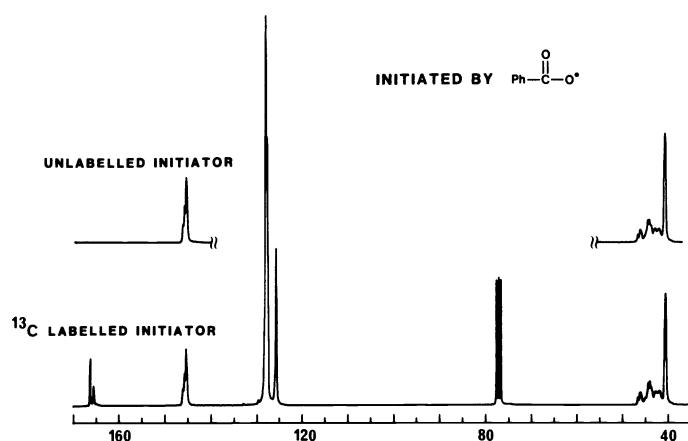
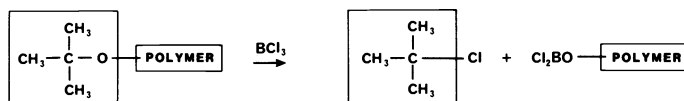


Fig. 4

Application of ^{13}C NMR to the detection of end groups in polystyrene. Upper spectrum is of polystyrene (M_n 45,000) prepared with unlabelled initiator. Lower spectrum is of polystyrene prepared under similar conditions but with benzoyl-carbonyl- ^{13}C peroxide as the initiator (ref. 5).

CHEMICAL ANALYSIS

CLEAVAGE

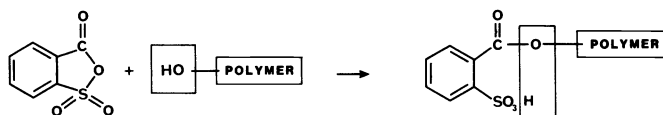


G.C. ANALYSIS

Fig. 5

Examples of end group determination by chemical analysis (ref. 8). Methods used for quantifying (a) t-butoxy end groups and (b) hydroxy end groups.

MODIFICATIONS



DYE-PARTITION ANALYSIS

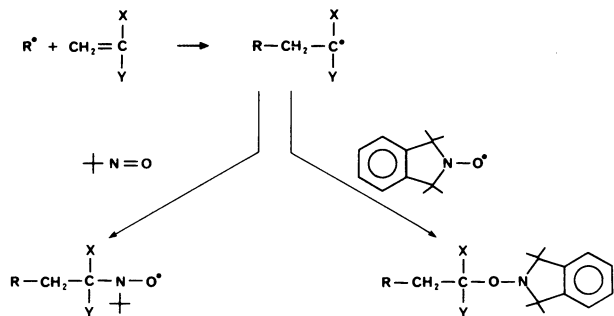


Fig. 6

Radical trapping techniques (a) use of 2-methyl-2-nitrosopropane to trap transient free radicals for examination by ESR (ref. 14) or (b) a nitroxide to afford stable alkoxyamines which can be isolated and characterized by conventional techniques (refs. 9-13).

ESR STUDIES

ISOLATION AND CHARACTERIZATION OF PRODUCTS

are available; chemical analysis requires foreknowledge of the types of groups which may be present; radical trapping only tells us the distribution of initiator-derived products at zero conversion.

Consider what these methods tell us about the model styrene/methyl methacrylate copolymer chosen for discussion when benzene is employed as the solvent and a source of t-butoxy radicals as the initiator. Radical trapping experiments have been conducted to establish the products formed when each of the components (styrene, methyl methacrylate, and benzene) react with t-butoxy radical. Methyl methacrylate reacts as shown in Fig. 7 (refs. 9-11). Note that only 60% of initiation proceeds by the "text book" tail addition pathway. As a consequence of this lack of selectivity, a significant fraction of polymer molecules will have unsaturated end groups. By way of contrast, the reaction with styrene is much cleaner and involves only tail addition (Fig. 8) (ref. 12). Benzene is relatively inert, however a small amount of abstraction occurs leading to phenyl radicals which in turn may initiate polymerization (refs. 11, 13).

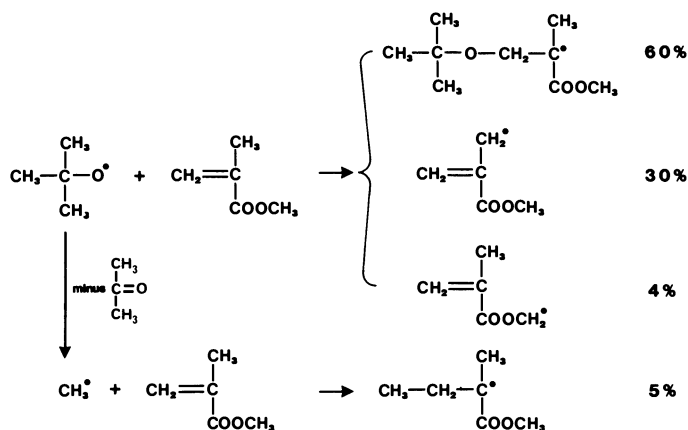


Fig. 7

Reactions of t-butoxy radicals with methyl methacrylate

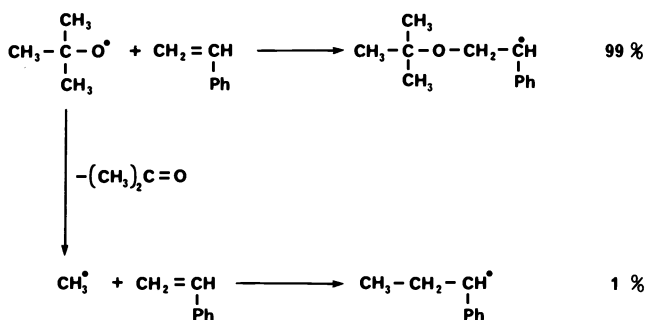


Fig. 8

Reactions of t-butoxy radicals with styrene

The relative rate constants of all the reactions which occur during the copolymerization of methyl methacrylate and styrene in various solvents have been established by means of competition experiments (ref. 13). The data from these trapping experiments, when taken in conjunction with literature values for the reactivity ratios, has enabled kinetic simulations to be carried out. The accuracy of the simulations is to some extent limited by the precision with which the literature kinetic data are able to predict the change in monomer feed composition with conversion, a problem which we are currently looking into. Nevertheless, the simulations do provide an estimate of how the distribution of the end groups of our copolymer might vary as a function of conversion and reaction conditions (Fig. 9) (ref. 13) and it should be remembered that in the industrial situation one is concerned with virtually quantitative conversion. For the example chosen where the reactions of the primary radical (t-butoxy radical) with monomer must compete with β -scission (giving methyl radicals) and reaction with solvent (affording solvent-derived radicals) the end group distribution at high conversion differs dramatically from that at zero conversion.

The results in Fig 9a relate to the use of benzene as the solvent (something which would not be tolerated today). However, it is convenient in theoretical studies since from a chemical point-of-view it is a relatively unreactive solvent and so does not markedly complicate the distribution of products formed in the initiation step. In industry, if it is desirable to use an aromatic solvent, the use of toluene might be contemplated as a replacement. Superficially such a substitution seems fairly innocent. However, the propensity of t-butoxy radicals for hydrogen abstraction and the very high reactivity of toluene in this regard (compared with benzene) (ref. 11, 13) leads to a substantial fraction of chains being initiated by benzyl radicals. This means that at high (90%) conversion, essentially all initiation is solvent mediated and approximately 50% of all chains in a high conversion polymer will have a benzyl end group (see Fig. 9b). Another solvent which finds widespread use in industry is butan-2-one (methyl ethyl ketone), see Fig. 9c (ref. 13) where again the simulation shows that a high proportion of end groups will be solvent-derived.

In addition to becoming directly involved in the initiation process, variation of the solvent has other more subtle influences. The β -scission of t-butoxy radical becomes of greater importance in more polar solvents (for example, the amount of methyl radical initiation doubles in switching from toluene to butan-2-one) (refs. 11, 13). The solvent also affects the extent to which t-butoxy radical undergoes addition vs. abstraction with methyl methacrylate (ref. 11) and the relative rates of addition of methyl and t-butoxy radicals to styrene vs. methyl methacrylate (ref. 13).

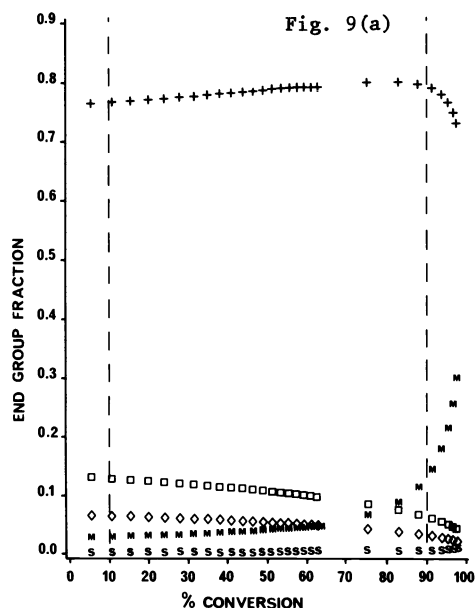


Fig. 9. Results of computer simulations showing the end group distribution as a function of conversion for methyl methacrylate - styrene copolymerization at 60°C with a source of t-butoxy radicals as the initiator and 50% (v/v) (a) benzene, (b) toluene, or (c) butan-2-one as solvent.

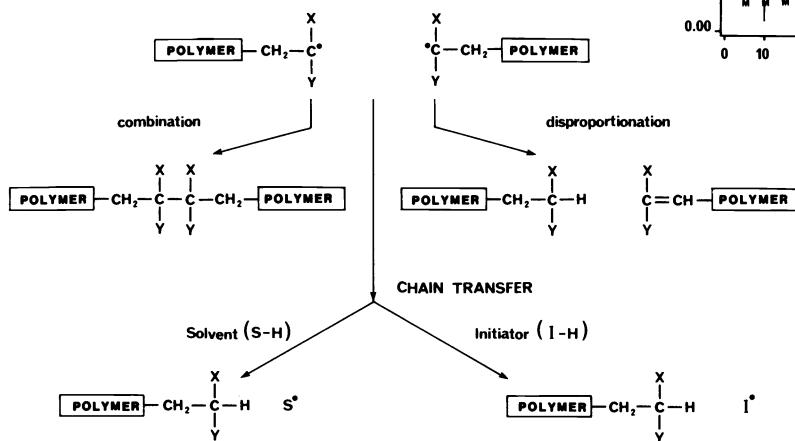
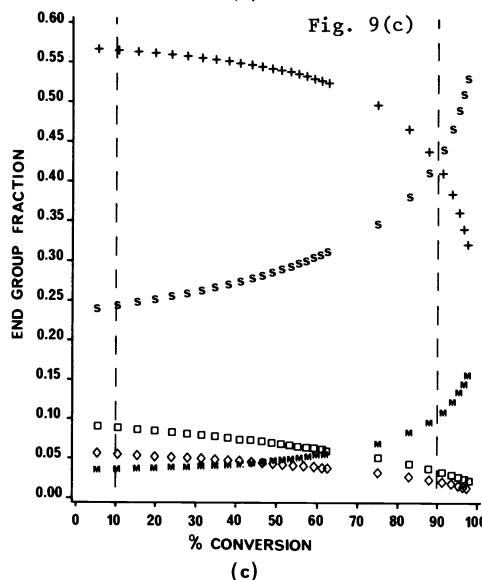
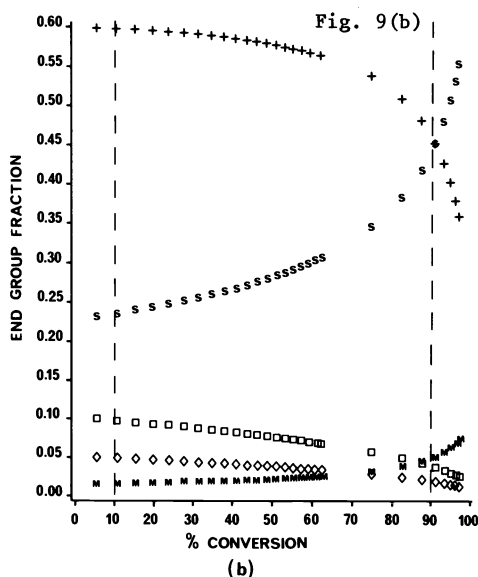


Fig. 10 Termination reactions in free radical polymerization

Thus, in a typical copolymerization, what might appear to be simple substitution of one solvent for another can lead to significantly different end group distribution. Moreover, the effect of such a switch becomes more pronounced as monomer is depleted at high conversions. It is worthwhile reflecting on the end groups present in polymers prepared using mixtures of solvents.

The incorporation of solvent residues with UV chromophores into the polymer (as occurs when toluene or butan-2-one are employed as solvent) might well be expected to have an effect on stability, resistance to weathering, etc. The dependence of polymer properties on end and other defect groups is an area we are currently studying further. The influence of end groups on thermal stability will be briefly considered later in this lecture.

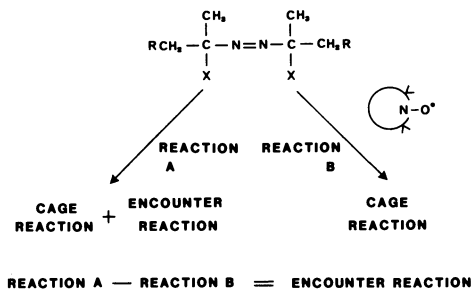


Fig. 11

Method for examining the termination step of free radical polymerization by using azo compounds as a source model polymer radical.

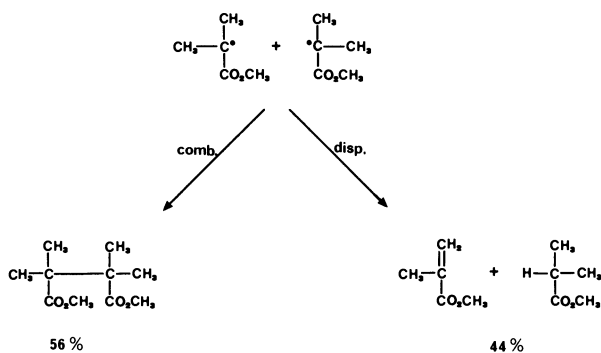


Fig. 12

Methyl methacrylate model system.

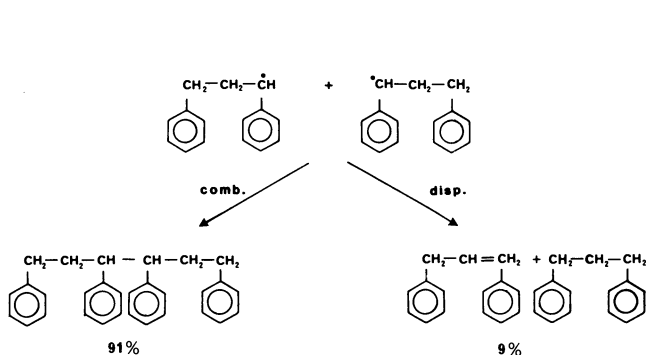


Fig. 13

Styrene model system.

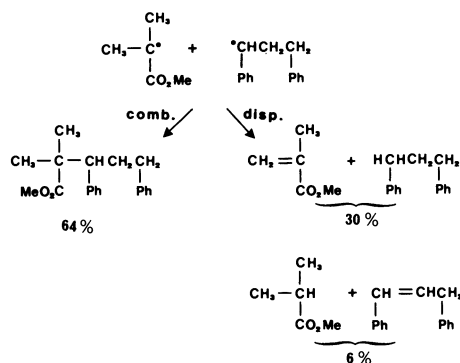


Fig. 14

Methyl methacrylate-styrene model system.

Numbers given in Figs. 12-14 represent the percentage of radicals consumed in the combination vs. disproportionation processes (at 80°C in benzene). They are based on the yields of products (based on precursor azo-compound) formed from the cage reaction of the two radicals shown (see Fig. 10).

Time does not permit a similar analysis of the copolymerization with other initiators, solvents, etc. The types and relative importance of the various reactions involved in the initiation step are very much dependent on the nature of the initiating radical (refs. 10-13) and care in selection of the initiator may provide one way of controlling defect groups. Clearly, much more attention has to be paid to substituting one component (solvent, initiator) of the polymerization reaction mixture for another than has hitherto been the case.

TERMINATION

The four principal types of reactions involved in the termination of free radical polymerization are summarized in Fig. 10. Pairs of radicals may react to afford combination or disproportionation products. In addition, some chains may terminate by interaction with solvent or initiator in the process known as chain transfer. Techniques used to study termination include various forms of polymer analysis (for example, end group determination (refs. 5-8, 15) and analysis of the molecular weight distribution (ref. 16) and model studies (Fig. 11) (refs. 17, 18)). With the aid of these techniques, the relative importance of combination and disproportionation can be assessed both in model systems and in polymers. Our results for methyl methacrylate and styrene model systems are shown in Figs. 12 and 13 respectively (ref. 19). In copolymerization, cross-termination (reaction of the unlike radicals) also occurs and in model systems we have been able to quantify the relative importance of cross and homotermination and establish the types of structural groups formed. These are shown in Fig. 14. The model studies show that the rate constant for cross-termination is approximately three times greater than that for the faster of the two homotermination reactions (ref. 18). It has yet to be determined whether this is true in the copolymerization of methyl methacrylate and styrene. However, we have established by means of a kinetic simulation that, because styryl radicals maintain a significantly higher steady state concentration than methacrylyl radicals during the copolymerization, the main termination reactions should be styryl-styryl homotermination and cross-termination (ref. 18).

Currently, we are conducting NMR studies employing carbon-13 labelled initiators to establish the relative importance of chain transfer to initiator and primary radical termination (Fig. 15). Chain transfer shows a marked dependence on conversion and with benzoyl peroxide as the initiator at high conversions, a substantial proportion of chains may be terminated in this way (refs. 5, 6). This has important consequences for the molecular weight distribution and hence on properties.

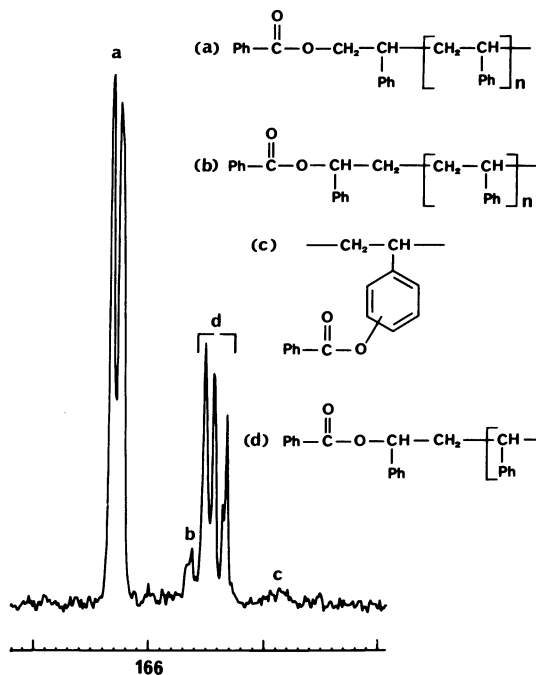


Fig. 15

Carbonyl region of ^{13}C NMR spectrum of polystyrene prepared with benzoyl-carbonyl- ^{13}C peroxide (ref. 5).

THERMAL STABILITY OF GROUPS

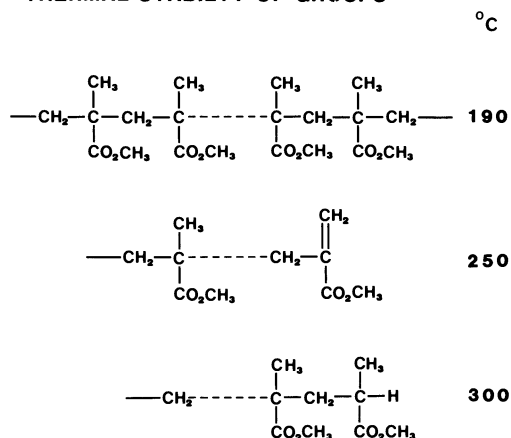


Fig. 17

Relative thermal stability of termination derived functionality in poly(methyl methacrylate). Temperatures given are those for the onset of degradation as determined by differential scanning calorimetry and thermal gravimetric analysis with a heating rate of 20°min^{-1} (see ref. 23).

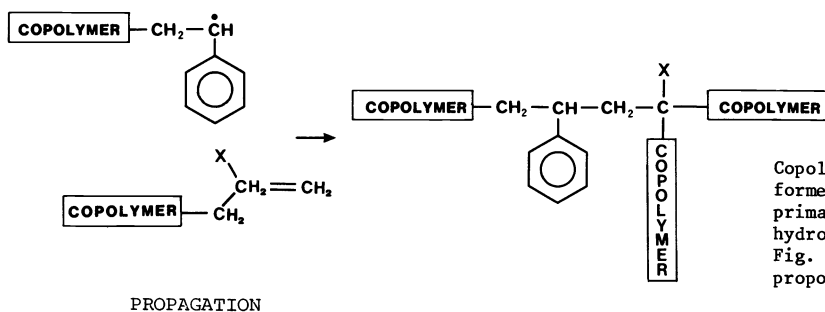


Fig. 16

Copolymerization of macromonomers formed during initiation (by primary radical abstracting hydrogen from monomer - see Fig. 7) or termination (by disproportionation - see Fig. 10)

The study of propagation is more difficult since one is forced to use techniques which rely on polymer analysis. The most widely studied systems are ethylene and vinyl chloride polymerizations and copolymerizations where such techniques as NMR, GPC coupled with light scattering or viscometry, and chemical analysis are used to detect branching and other defect groups. These topics are discussed elsewhere in this Symposium and are covered in recent reviews (refs. 20, 21).

One process which needs to be considered, and which is often overlooked, is the further reaction of the unsaturated end groups which originate in the initiation or termination processes. Polymer molecules with unsaturated ends can be effective macromonomers and, particularly at high conversion when the monomer is depleted, can become incorporated into the polymer or copolymer, see Fig. 16 (ref. 22). This can have a number of important consequences.

1. Measurements of end groups as a means of ascertaining the mode of termination or initiation or as a way of estimating molecular weight are likely to be in serious error.
2. The degree of branching is likely to increase significantly with conversion. This should be reflected in 'properties vs. conversion' studies.

EFFECT OF END GROUPS ON STABILITY

Our understanding of the significance of each of the many defect groups in polymerization is still at an early stage. One polymer where we have unequivocal evidence that one defect group per polymer chain can have a profound influence on thermal stability is poly(methyl methacrylate).

The normal termination reaction leads to the formation of three types of end group. A saturated and an unsaturated end group are produced if termination occurs via disproportionation while a head-to-head linkage will be formed if termination is by combination. In poly(methyl methacrylate) the relative stability of these three functional groups has been evaluated using oligomeric models and the results are summarized in Fig. 17 (ref. 23). These results explain why anionic poly(methyl methacrylate) is more stable than that produced by a free radical process (ref. 3). The anionic polymer contains no head-to-head linkages or unsaturated end groups. These results suggest that control of the termination so as to avoid reactions between polymer radicals (for example, by adding a chain transfer agent) could prove to be an effective means of producing a more stable polymer by a free radical process. Of course, care must also be taken as regards any other (initiator and transfer agent-derived) end groups that may be created.

CONCLUSIONS

The results discussed above illustrate the variety of defect groups that may be incorporated into polymers during their manufacture and demonstrate that the particular groups present in a given polymer sample are very much dependent on the polymerization conditions (i.e., solvent, initiator, temperature, etc.). In this light, the need for caution, both in the initial selection of reaction conditions and when changing formulations in laboratory studies and in industry, cannot be overemphasized.

The results also indicate the directions in which future studies in this area should lead. In particular there must be more laboratory studies aimed at establishing what occurs at high conversions in order that we may better relate to the industrial situation. In addition much work remains to be done so that the correlation between reaction conditions, defect groups, polymer properties can be fully understood.

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