Thermal Degradation of Polystyrene. 3. A Reappraisal

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ABSTRACT: The data of Wall et al. on the rate of volatile formation and molecular weight changes that occur during pyrolysis of anionic and thermal (radical) polystyrenes at 300 to 350 °C are reexamined. Neither random nor chain end initiation of volatile formation occurs in the initial stages of decomposition of the former but both processes contribute to the early stages of volatilization of the latter. From this difference in behavior it is concluded that the undegraded thermal polymers contain a proportion of labile chain ends in addition to a small number of randomly distributed weak links within the chains. These structures are absent in the undegraded anionic polymers which are consequently more stable. During the main part of the degradation reaction chain end initiation is the dominant process leading to volatile evolution from both polymers; random initiation, if present at all, is insignificant by comparison. Labile chain ends can be generated by random chain scission and intermolecular transfer. The termination of active radical intermediates is first order throughout the reaction, except possibly in the early stages of decomposition of the thermal polymers when a proportion of second-order termination may occur. This reinterpretation reconciles previously conflicting accounts of the reaction mechanism.

In this paper we reexamine earlier publications on this subject[2-4] in the light of the last contribution by Wall and co-workers.[5] These authors measured the changes in molecular weights, molecular weight distributions, and initial rates of volatilization for a series of polystyrenes prepared by thermal (radical) and anionic methods. They claimed that their results were compatible with a slightly refined version of their previous interpretation of the reaction mechanism[6] but were incompatible, in certain important respects, with the accounts of other authors.[2,7-10] Thus, while the point that intramolecular transfer must feature in the mechanism[4] was taken, they claimed that their results were not in accord with a first-order termination reaction.[2,7] Furthermore, while end initiation was acknowledged as the process dominating volatile formation, random initiation was accorded a more important role by Wall et al.[5] than by other workers. We believe that if these authors had exploited their wealth of excellent experimental data more fully they would have modified their conclusions which could then have encompassed an even wider body of observations, settling in the process some of the controversy that has surrounded this subject. For example, their data, as we will show, throw some light on the controversy over the presence or otherwise of "weak links" in thermal polystyrenes. It is against this background that we reinvestigate the results in ref 5.

Theory

The kinetic equations of relevance were derived by Cameron.[2] They relate the rate of volatile production to the degree of polymerization $\overline{P}_n$ at any instant during degradation. The derivation of and the assumption underlying these equations are given in full in the original paper. In brief, it is assumed that volatile fragments are evolved by unzipping and intramolecular transfer from active radicals which may be produced by initiation at chain ends or within the chain interior. Termination of these radicals may be a first- or second-order process. The polymer chains are broken at random by homolytic scission and intermolecular transfer. For convenience the equations are quoted below in the form later employed in ref 5:

$$\frac{1}{1-C}\frac{\mathrm{d}C}{\mathrm{d}t} = k_2\left(\frac{k_{ie}}{k_{t2}}\cdot\frac{m}{\rho}\right)^{1/2}\left[\frac{k_{ir}}{k_{ie}} + \frac{1}{\overline{P}_n(t)}\right]^{1/2} \qquad (1)$$

and

$$\frac{1}{1-C}\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_2 k_{ir}}{k_{t1}} + \frac{k_2 k_{ie}}{k_{t1}}\cdot\frac{1}{\overline{P}_n(t)} \qquad (2)$$

The symbols in these equations have the following meanings: C is the fractional weight conversion of polymer to volatiles at time t; m is the monomer molecular weight; ρ is the density of molten polymer; $\overline{P}_n(t)$ is the number average degree of polymerization at time t; k_2 is the rate coefficient for depropagation, that is volatile evolution by intramolecular transfer and unzipping; k_{ie} is the rate coefficient for active radical formation at chain ends; k_{ir} is the rate coefficient for active radical formation by scission of interior bonds; k_{t2} is the rate coefficient for termination of radicals by a second-order process; and k_{t1} is the rate coefficient for termination of radicals by a first-order process.

When termination is second order eq 1 applies so that the square of the relative rate of conversion $[(\mathrm{d}C/\mathrm{d}t)/(1-C)]^2$ should be a linear function of $\overline{P}_n^{-1}$. Equation 2 applies to a first-order termination reaction which should yield a linear dependence of relative rate on $\overline{P}_n^{-1}$. Some of the controversial points discussed in this paper concern which of these equations is compatible with the experimental data.

Results and Discussion

(a) Thermal Polystyrenes. For thermal (i.e., free radical) polystyrenes the authors of ref 5 concluded that eq 1 applied. This conclusion was based on initial rate measurements, i.e., $(\mathrm{d}C/\mathrm{d}t)_{C\to 0}$, for a series of polymers of initial molecular weights ($\overline{M}_n$) in the range 90 000 to 900 000 (i.e., $\overline{P}_n(0)$ = 865 to 8650). No attempt was made, however, to check the validity of either eq 1 or 2 for any one of these polymers over a wide conversion range although the data for such a check are available in ref 5. Figure 1 tests eq 1 and 2 for the thermal polystyrene NBS 706, of initial $\overline{M}_n = 1.3 \times 10^5$. The points in these diagrams were computed using the $\overline{M}_n$ vs. C plot at 300 °C (Table 2 and Figure 3 of ref 5) with the rate vs. C plot at 353 °C (Figure 11 of ref 5). The temperature difference between these two sets of experiments in no way invalidates this procedure because it is well established that the variation of $\overline{M}_n$ with C is independent of the degradation temperature.[11] Clearly eq 2 is quite compatible with the data while eq 1 is not. Any attempt to fit the points in Figure 1a to a straight line results in a large negative ordinate intercept which is physically unreal. Figures 1a and 1b reproduce exactly the pattern of earlier, similar tests.[2] We must conclude that termination, certainly over the main part of the degradation reaction, is a first-order process. As was also observed previously the line in Figure 1b passes within experimental error through the origin. The significance of this is considered in more detail later. For the moment we return to the initial rate data; these

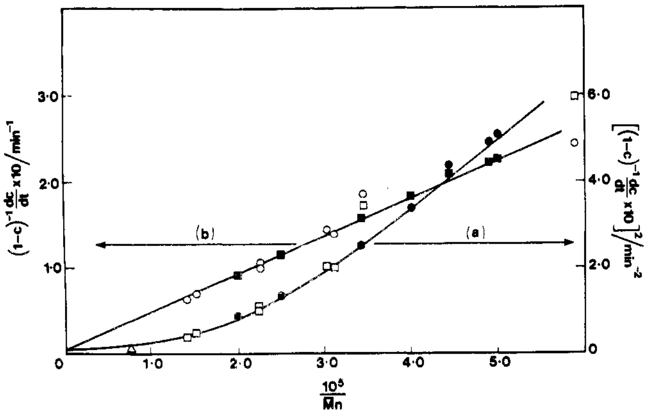


Figure 1. Dependence of relative rate of volatilization on reciprocal number-average molecular weight for NBS sample 706, initial $\overline{M}_n$ 130 000. Data points from dC/dt vs. C at 353 °C (Figure 11 of ref 5), and $\overline{M}_n$ vs. C at 300 °C (Table 2 of ref 5): (a) □, ●, according to eq 1; (b) ○, ■, according to eq 2; △, (dC/dt) × 10 for initial polymer, by extrapolation of initial rate data to T 353 °C (from Figure 9 of ref 5); ●, ■, by interpolation from the smoothed $\overline{M}_n$ vs. C curve.

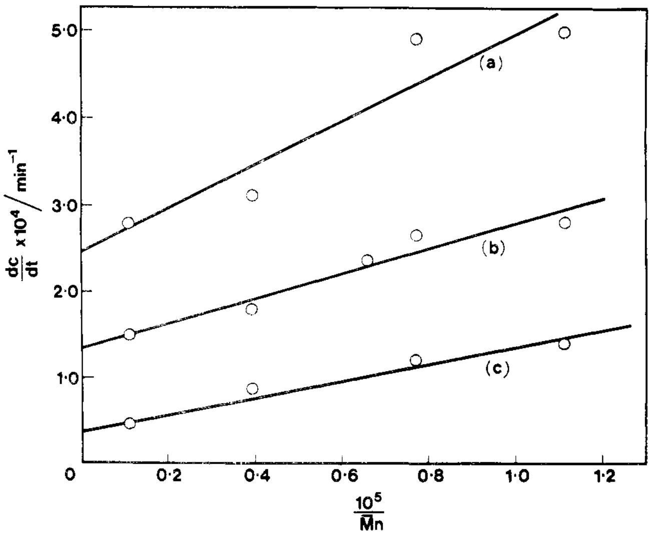


Figure 2. Variation of initial rate with reciprocal number average molecular weight according to eq 2. Data points from Figures 8 and 9 of ref 5: (a) 310 °C, (b) 300 °C, (c) 287 °C.

are now plotted in Figure 2 as required by eq 2. Surprisingly the points conform as well to eq 2 as to eq 1. Clearly the statement that these results "are incompatible with suggestions that termination is first order" [5] is unsupported by the facts.

The slope of the line in Figure 1b yields a value of 41.9 min^{-1} for k_2k_{ie}/k_{t1} at 353 °C. Unfortunately no initial rate data at this temperature were recorded and to obtain a comparable initial value of this parameter we are obliged to extrapolate. Thus, by plotting values of log $[k_2k_{ie}/k_{t1}]_0$ for the initial condition vs. $1/T$ and extrapolating the best fitting line to T = 626 K we obtain $[k_2k_{ie}/k_{t1}]_0$ = 1.1 min^{-1}. This figure is obviously subject to considerable error but as Figure 3 shows, the error is unlikely to be sufficiently large to encompass the value of k_2k_{ie}/k_{t1} (41.9 min^{-1}) for the main part of the degradation at 353 °C. If this is accepted, the conclusion follows that k_2k_{ie}/k_{t1} is considerably increased beyond the first increments of degradation, most probably because of an increase in k_{ie} (see later). An important consequence of this is that the partially degraded polymer is less stable than the original as reflected in the low position of the point in Figure 1b for the undegraded polymer (again from extrapolation of the initial rate data).

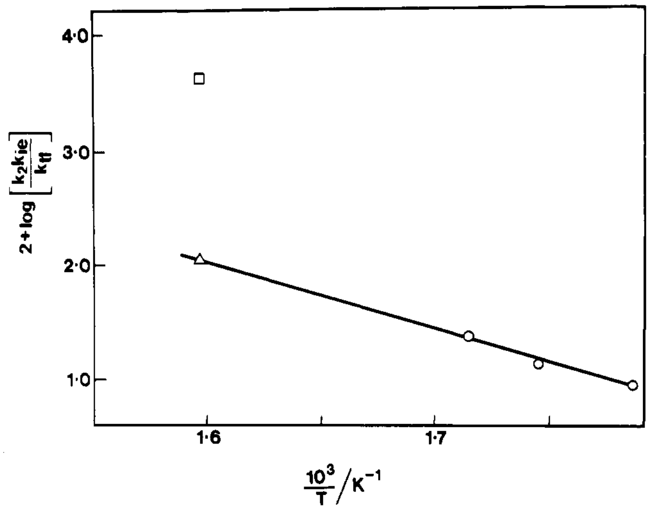
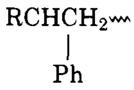


Figure 3. Arrhenius plot of $[k_2k_{ie}/k_{t1}]_0$ (from slopes of lines in Figure 2): (□) log $[k_2k_{ie}/k_{t1}]$ at 353 °C (from slope of Figure 1b); (△) log $[k_2k_{ie}/k_{t1}]_0$ at 353 °C (from extrapolation of initial rate data).

From the ordinate intercept in Figure 1b we obtain a value of 6.0 × 10^{-3} min^{-1} for k_2k_{ir}/k_{t1} which is negligibly small compared with k_2k_{ie}/k_{t1}. Indeed, this figure is so small compared with the error in extrapolating that no reliance can be placed on it, but we are justified in saying that random initiation is insignificant in the main part of the degradation process. The same cannot be said for the initial rate results in Figure 2. The ordinate intercepts in these plots are clear evidence of a random initiation process. Extrapolating the values of log $[k_2k_{ir}/k_{t1}]_0$ to T = 626 K yields a value of 4.9 × 10^{-3} min^{-1} for $[k_2k_{ir}/k_{t1}]_0$ at 353 °C. The fair correspondence between this figure and that derived from Figure 1b is probably fortuitous because of the enormous error associated with the latter. Despite the errors in k_2k_{ir}/k_{t1}, $[k_2k_{ir}/k_{t1}]_0$ and $[k_2k_{ie}/k_{t1}]_0$ at 353 °C, it is fairly certain that the ratio k_{ir}/k_{ie} (1.4 × 10^{-4}) is substantially smaller than $(k_{ir}/k_{ie})_0$ (4.4 × 10^{-3}). As shown below this difference can be attributed to an increase in k_{ie} over $(k_{ie})_0$, but there are also grounds for believing that k_{ir} is less than $(k_{ir})_0$. As degradation proceeds the number of chain ends in the system increases, thus further increasing the swamping effect of end initiation. It is clear why random initiation can be identified with certainty only in the very early stages of the reaction.

The extensive literature on the mechanism of thermal initiation of polymerization of styrene[12-16] suggests that most of the chain ends have the structures A

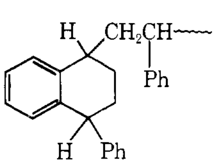


$$\mathrm{R}\underset{\displaystyle\mathrm{Ph}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\!\sim\!\sim$$

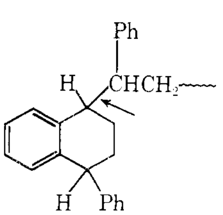
A

R = H, CH$_3$

with possibly a small proportion having structures B and C: Of these only C appears to be more vulnerable, at the bond

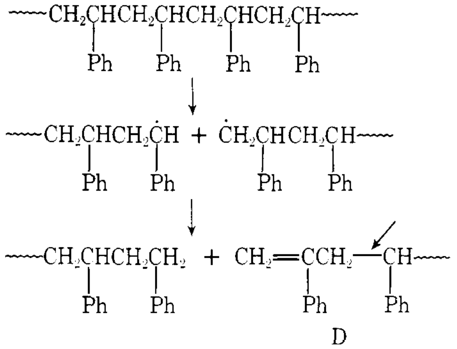


B



C

Scheme I



indicated, than an interior backbone bond. According to the widely accepted mechanism the new chain ends D produced by random scission are unsaturated and should break readily at the arrowed bond to yield a volatile allylic radical and an active radical chain end capable of depropagating. The structure D can also form on decomposition of radical E produced by transfer (Scheme II). Thus, the combined effects of random scission and intermolecular transfer can cause buildup in the population of unstable chain ends and lead to a faster end-initiated reaction, compared with the initial condition, and a decrease in the relative importance of random initiation.

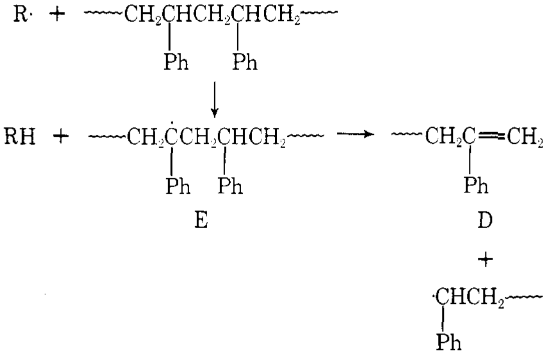
(b) Anionic Polystyrene. In the case of the anionic polystyrenes the initial rate of volatile evolution $(\mathrm{d}C/\mathrm{d}t)_0$ for all samples is zero at 300 °C (Figure 7 of ref 5). Therefore, neither chain-end nor random initiation can occur in the virgin polymer.

The kinetics of volatilization are analyzed in Figures 4 and 5 as before. The $\overline{M}_n$ vs. C data at 300 °C apply to NBS 705 of $\overline{M}_n = 1.709 \times 10^5$ (Table 2 in ref 5) and the rate data at 335 and 350 °C refer to a monodisperse polystyrene of $\overline{M}_n$ = 48 500 (Figure 6 in ref 5).[17] It has been pointed out that for fractions of $\overline{M}_n > 48\,000$ the $\mathrm{d}C/\mathrm{d}t$ vs. C curves are "nearly typical of all polystyrenes of higher molecular weight".[5]

As in the case of the thermal polymers eq 1 is incompatible with the data (Figure 4) but the points for $C > 0.10$ $(10^5/\overline{M}_n \simeq 2)$ fit well to eq 2 for first-order termination (Figure 5). The slope of the line for 350 °C in Figure 5 yields a value of 44.4 min^{-1} for k_2k_{ie}/k_{t1} in fair agreement with the value (41.9 min^{-1}) for the thermal polymer at 353 °C. Both lines in Figure 5 extrapolate within experimental error through the origin. Again random initiation, if present at all, has a negligible influence. Thus, although the degradation characteristics of the thermal and anionic polymers are quite different in the early stages of decomposition they become almost identical beyond ca. 10% conversion to volatiles.

The points in Figure 5 for $10^5/M_n$ less than ca. 2 (corresponding to $C \leqslant 0.1$) lie below the line. This is precisely as expected for a polymer which is initially more stable because there are no thermolabile chain ends. (The original chain ends of sample NBS 705 have the structures[6] $BuCH_2CHPh$ and CH_2CH_2Ph which are as stable as interior bonds.) Chain ends of structure D can, however, accumulate as a consequence of random scission and/or intermolecular transfer, and Figure 5 suggests that these ends account for a steady fraction of the total at $C = 0.1$.

Scheme II



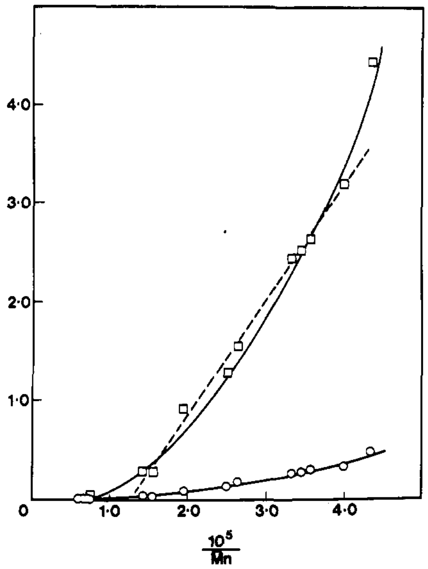


Figure 4. Dependence of the square of relative rate of volatilization on reciprocal number average molecular weight for anionic polystyrene. Data points from $\mathrm{d}C/\mathrm{d}t$ vs. C at 335 and 350 °C (Figure 6 of ref 5) for monodisperse polymer of initial $\overline{M}_n$ = 48 500 and from $\overline{M}_n$ vs. C at 300 °C (Table 2 of ref 5) for anionic polystyrene NBS 705 of initial $\overline{M}_n$ = 170 900: (○) 335 °C, (□) 350 °C.

It is important to appreciate the distinction between "random scission" and "random initiation". The former certainly occurs, otherwise the molecular weight of the anionic polymers could not decrease in the initial stages of the reaction, but this random scission does not initiate volatile formation directly. Therefore, if random scission produces radicals these must undergo deactivation in a cage, as in Scheme I, in preference to depropagation. Alternatively, random scission may involve some nonradical rearrangement process. The statement that "these polymers actually initiate at random in the limit of low conversion" [5] is misleading.

An important question, which was not considered by the authors of ref 5, is why the undegraded thermal polymers initiate at random while the anionic polymers do not. Clearly random initiation cannot occur at regular main-chain structures since these are common to both types of polymer. We are therefore driven to the conclusion that the thermal polymers contain within the backbone certain irregularities which are absent in the anionic polystyrenes. Breakdown of these randomly distributed irregularities in the early stages of degradation can account for the random component of volatile formation. This conclusion is in accord with findings from other comparative studies of radical and anionic polystyrenes.[3,18] These studies were concerned with low-temperature decomposition (<300 °C) where the only manifestation of reaction is a decrease in molecular weight, volatile evolution being negligible. Under these conditions radical polymers degraded more rapidly and it was concluded[3] that irregularities such as head-to-head links and unsaturation (incorporated during polymerization) contributed to the relative instability of these polymers. The decrease in molecular weight of the radical polymers was particularly precipitate in the very early stages of chain scission indicating the presence of highly thermolabile groups which were tentatively postulated as peroxides within the backbone. That this suggestion has now

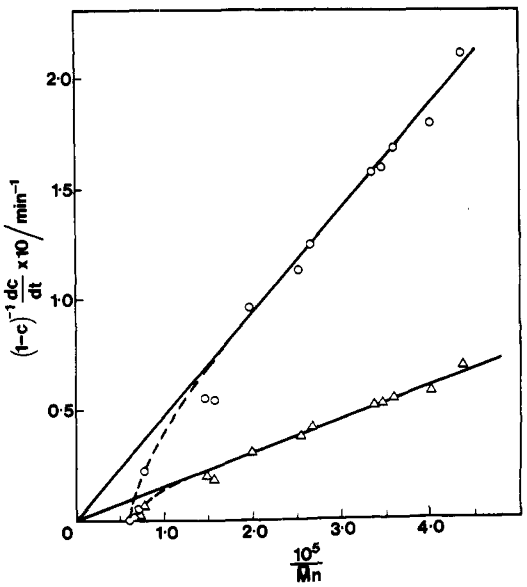


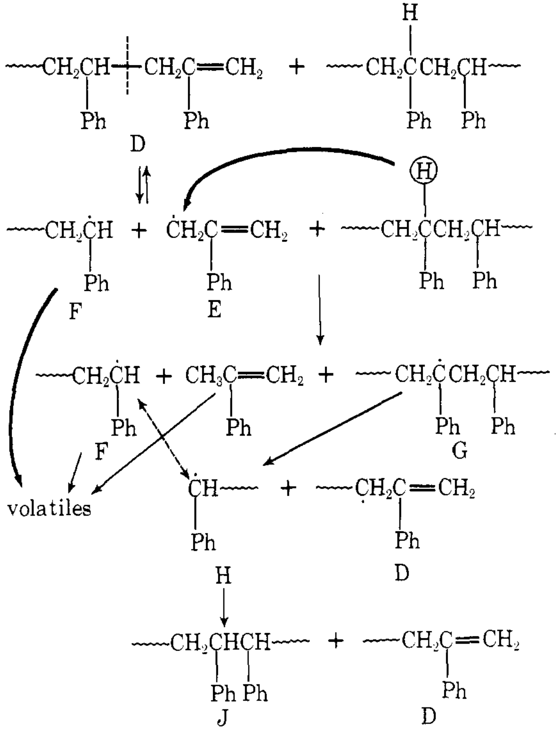
Figure 5. Data in Figure 4 plotted according to eq 2: (△) 335 °C, (○) 350 °C.

been disproved[19] is of no consequence for present purposes. What is important is that these earlier studies are consistent with the current analysis of the results in ref 5 and provide a reasonable explanation for the existence of a random initiation reaction in the initial stages of the degradation of thermal polystyrenes. These, as yet unidentified, "weak links" are absent from the anionic polymers which have a highly regular structure on account of the low temperature of polymerization, the nature of the propagating process, and the stringent purity requirements for the monomer and solvent.

From the analysis in Figure 1b it is not possible to say whether the abnormalities in thermal polymers survive at higher conversions and thus provide a very small component of random initiation. It would not be inconsistent with the data to suggest, however, that they have virtually disappeared beyond the first few increments of volatilization, hence the earlier comment that the decrease in k_{ir}/k_{ie} compared with $(k_{ir}/k_{ie})_0$ may be due to a drop in k_{ir} coupled with a rise in k_{ie}. Furthermore, with the possible exception of the termination step (discussed in the next section), it is difficult to envisage mechanisms which would regenerate randomly distributed weak spots during degradation, and indeed there are no compelling reasons for invoking such a complexity. Similar comments apply to the anionic polymers which do not initiate at random initially.

(c) Mechanism of Termination. It has been shown convincingly in this paper and elsewhere[2] that over the bulk of the reaction the termination step in the degradation process is first order. In formulating a mechanism in keeping with these kinetics we must take note of two other features of the reaction: (i) end initiation greatly predominates, and (ii) the heterogeneity index $\overline{M}_w/\overline{M}_n$ tends to 1.5 as degradation proceeds.[5] The second of these features precludes small radical vaporization as the termination step,[2] since this would lead to a most probable distribution with $\overline{M}_w/\overline{M}_n$ = 2.0, and requires that termination should involve a radical–radical coupling reaction. A mechanism which may satisfy these various requirements is shown in Scheme III.

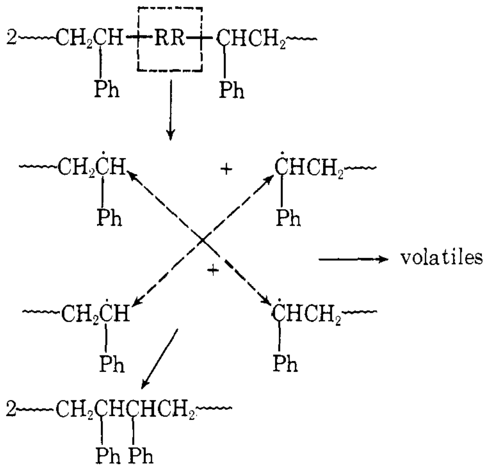
Scheme III



In Scheme III decomposition of a chain end D leads to radicals E and F confined within a "cage", the walls of which comprise segments of neighboring chains. The radical E may recombine with F or can abstract a hydrogen atom from the cage wall leading to daughter radicals G and H. If F and H couple within the cage then this leads both to the required heterogeneity index in the degraded polymer and to the observed first-order dependence of the rate of volatilization on the concentration of chain ends. The head-to-head structure J thus formed could act as a site for subsequent random initiation. A mechanism of this type was considered by Wall and co-workers[20] but was later rejected in favor of conventional biradical termination.[5] The main weakness in this mechanism is the assumption that the coupling of F and H may be treated kinetically as a cage combination. This aspect of the reaction might be clarified by further investigation.

The one outstanding point which has not been resolved in the foregoing discussion is why the initial rate measurements for the thermal polymer are compatible with either a first- or a second-order termination process. It is tempting to suggest that the latter is a feature that follows from random initiation at labile structures R–R and the former from end initiation. Until more information is available on the structure and decomposition of the labile groups in radical polystyrenes Scheme IV must be viewed as highly speculative.

Scheme IV



Summary and Conclusions

We believe that the foregoing reexamination of the data in ref 5 explains and reconciles a much wider body of observations than before. In particular, it reemphasizes the first-order kinetics of the termination reaction and places in a truer perspective the relative contributions of end and random initiation of volatile formation. But possibly the most interesting feature of this work is the difference it reveals between thermal (radical) and anionic polystyrenes. This provides strong circumstantial evidence for the existence of labile structures within the backbone of the former. When considered alongside evidence from earlier comparative studies of such polymers, we believe that the case for weak links in radical polystyrenes is satisfactorily proven.

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References and Notes

(1) (a) University of Aberdeen; (b) Robert Gordon's Institute of Technology.

(2) G. G. Cameron, *Makromol. Chem.*, **100**, 255 (1967).

(3) (a) G. G. Cameron and G. P. Kerr, *Eur. Polym. J.*, **4**, 709 (1968); (b) *ibid.*, **6**, 423, (1970).

(4) G. G. Cameron and I. T. McWalter, *Eur. Polym. J.*, **6**, 1601 (1970).

(5) L. A. Wall, S. Straus, R. E. Florin, and L. J. Fetters, *J. Res. Natl. Bur. Stand., Sect. A*, **77**, 157 (1973).

(6) L. A. Wall, S. Straus, J. H. Flynn, D. McIntyre, and R. Simha, *J. Phys. Chem.*, **70**, 53 (1966).

(7) D. H. Richards and L. A. Salter, *Polymer*, **8**, 153 (1967).

(8) M. Gordon, *Trans. Faraday Soc.*, **54**, 1345 (1958).

(9) R. H. Boyd, *J. Chem. Phys.*, **31**, 321 (1959).

(10) R. H. Boyd, *J. Polym. Sci., Part A-1*, **5**, 1373 (1967).

(11) N. Grassie and W. W. Kerr, *Trans. Faraday Soc.*, **53**, 234 (1956); **55**, 1050 (1959).

(12) F. R. Mayo, *J. Am. Chem. Soc.*, **90**, 1289 (1968).

(13) K. Buchholz and K. Kirchner, *Makromol. Chem.*, **177**, 935 (1976).

(14) H. F. Kauffmann, O. F. Olaj, and J. W. Breitenbach, *Makromol. Chem.*, **177**, 939 (1976).

(15) O. F. Olaj, *Monatsh. Chem.*, **102**, 648 (1971).

(16) O. F. Olaj, H. F. Kauffmann, and J. W. Breitenbach, *J. Polym. Sci., Polym. Lett. Ed.*, **15**, 229 (1977).

(17) By comparison with Figure 11 of ref 5 and with data on the same polymers published in ref 6 it can be established that the ordinate scale on Figure 6 of ref 5 should read $(dC/dt) \times 10\ \text{min}^{-1}$.

(18) A Nakajima, F. Hamada, and T. Shimizu, *Makromol. Chem.*, **90**, 229 (1966).

(19) I. T. McWalter, Ph.D. Thesis, University of Aberdeen, 1977.

(20) L. A. Wall, S. Straus, and L. J. Fetters, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **10** (2), 1472 (1969).

Methyl Group Tunneling and Viscoelastic Relaxation in Poly(methyl methacrylate)[1]

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ABSTRACT: This paper describes a dynamic mechanical investigation of the backbone methyl relaxation in poly(methyl methacrylate) (PMMA); the normal and fully deuterated polymers were studied by high precision torsional pendulum, vibrating reed, and ultrasonic techniques in the temperature region of ca. −200 to +50 °C. Two very small relaxations were observed in the backbone methyl region of free-radically prepared PMMA and interpreted as due to motions of backbone methyls corresponding to syndiotactic and heterotactic main chain configurations. Evidence of quantum mechanical tunneling was present for the syndiotactic methyl relaxation, which showed not only pronounced curvature in the log ν vs. $1/T$ plot at low frequencies but also a large isotope effect, with the linearity in the log ν vs. $1/T$ plot for fully deuterated PMMA continuing to a much lower frequency than that for the nondeuterated polymer. Both of these effects have been predicted from theoretical considerations and have now been verified experimentally. This is the first observation of an isotope effect in the field of polymer mechanical properties. When the present data for the backbone methyl relaxations together with literature data for the glass transition, ester side group, and "water" dispersions in PMMA were extrapolated to high temperatures, the relaxations all appeared to converge in a frequency/temperature region near log $\nu \sim 9$ and $T \sim 200$ °C.

I. Introduction

A. Development of the Quantum Mechanical Tunneling Hypothesis for Methyl Group Motions in Solids. Methyl group motions in methyl-containing solids have long been investigated by various experimental techniques, especially proton NMR methods such as spin–lattice relaxation, line width, and second moment studies.[2] As the temperature is lowered, minima in the spin–lattice relaxation time and increases in line width and second moment occur, corresponding to freezing-in of methyl motion. In each type of experiment, a frequency ν may be associated with the motion[3] and correlated with the temperature. In this way frequency–temperature relationships can be established for particular methyl group motions.

The temperature dependence of group motions such as barrier hopping of various side chains including methyl groups has, in the past, frequently been expressed by an Arrhenius equation, which may be written as:[4]

$$\nu = \nu_0 e^{-E/RT} \qquad (1)$$

where T is the absolute temperature and E is the energy barrier restricting the motion of the group. Here, ν_0 is the frequency corresponding to infinite temperature, for which a value of 10^{13} Hz has been suggested.[5] This equation predicts a straight line relationship between log ν and $1/T$ with the slope proportional to the barrier height E.

Low-temperature NMR tests on methyl-containing solids have not, however, shown an Arrhenius type of behavior. This can be seen, for example, from the frequency–temperature relation calculated by Das[6] from line width measurements for methyl chloroform (CH_3–CCl_3) conducted by Powles and Gutowsky[7] as early as 1953. It is clear that the log ν vs. $1/T$ graph is curvilinear over the region studied. Such deviations from Arrhenius behavior have been correlated with rotational quantum mechanical (QM) tunneling of methyl groups in these materials at low temperatures.

Rotational QM tunneling of methyl groups has been treated from a theoretical point of view by Das[6] in 1957 and Stejskal and Gutowsky[8] in 1958 and more recently by Apaydin and Clough,[9] Davidson and Miyagawa,[10] Bloom,[11] Allen,[12] Huller

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