Kinetic Effects and Gas Chromatographic Peak Shapes Near Polymer Glass Transitions

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ABSTRACT: The general features of gas chromatographic peak shapes and peak retention volumes on polymeric stationary phases in the region of the glass transition may be predicted from the basic conservation equation of chromatography if adsorption onto the polymer surface is considered in addition to the slower bulk sorption process; the change from surface retention below T_g to solution above T_g is simply effected by increasing the rate at which bulk equilibrium is achieved. The theory predicts peak shapes which are in qualitative agreement with experiment, and provides some insight into observed phenomena such as the dependence of peak retention volumes on flow rate above T_g, the tailing observed on glassy polymers below T_g, and the peak shape changes that herald the beginning of the glass transition.

It is well known that kinetic factors may exert undesirable effects on GC retention data. The most important factor is the rate of establishment of bulk equilibrium between the polymer and the vapor probe, although contributions from other sources cannot be ignored. Kinetic effects may cause a dependence of peak retention times on carrier gas flow rate, and they are also one of the causes of peak asymmetry. The effects are most severe as the polymer melt cools toward the glass transition temperature. In a previous paper,[1] it was shown that the changes in retention behavior and peak shape on approaching the glass transition from higher temperatures may be predicted from basic chromatographic principles[2] if the diffusion rate of the probe through the polymer melt decreases sufficiently rapidly on cooling. In this paper, a simple modification of the previous theory to include surface adsorption effects will be shown to give peak shapes in qualitative agreement with experiment both above, through, and below the glass transition region.

Experimental Section

Peak shapes and peak retention volumes for *n*-tetradecane (Quantkits, PolyScience Corp.) were determined on a 0.25 in. o.d. copper column containing 32.5 g of 80–100 mesh glass beads coated with 0.333 g of polystyrene (Polysciences, Inc., mol wt 110000). The average polymer thickness, assuming even and complete coverage of the geometric surface of the beads, was estimated to be ~0.5 μm. The column was installed in a Hewlett-Packard 5711 gas chromatograph equipped with a flame ionization detector; the nitrogen carrier gas flow rate was 20 ml/min. Peak retention volumes were corrected conventionally for column dead volume and pressure drop.[2]

Equations for Peak Shapes

The basic mass balance equation of chromatography[1,2] is first rewritten with an added term taking explicit account of surface adsorption

$$\frac{\partial c}{\partial x} + a\frac{\partial c}{\partial V} + m\frac{\partial q}{\partial V} + s\frac{\partial \Gamma}{\partial V} = 0 \qquad (1)$$

where V is the volume of gas passed through the column (cm^3), x is the distance from the inlet end of the column (cm), q is the vapor concentration in the stationary phase (mol/g), c is the vapor concentration in the gas phase (mol/cm^3), m is the mass of stationary phase per unit length of column (g/m), and a is the volume of gas phase per unit length of column (cm^2). In the additional fourth term, s is the area of the interface between the stationary phase and the gas phase per unit column length (cm) and Γ is the Gibbs surface excess concentration[3] of vapor at this interface (mol/cm^2). As in the previous case,[1] it is assumed that the equilibrium between vapor concentration c and bulk concentration q is approached at a rate linearly dependent on the concentration difference from equilibrium

$$\mathrm{d}q/\mathrm{d}t = \dot{V}\mathrm{d}q/\mathrm{d}V = K(\beta c - q) \qquad (2)$$

where $\dot{V} = \mathrm{d}V/\mathrm{d}t$, the volume flow rate of carrier gas. The value of K depends on the rate of diffusion of the probe through the polymer, the polymer layer thickness, and possibly other column variables.[2] The variation in K with these factors and with temperature was considered previously.[1] In contrast to the bulk equilibration process, it is next assumed that the equilibrium between vapor and adsorbed layer is achieved rapidly, so that at all times

$$\Gamma = \beta_s c \qquad (3)$$

where β_s is an appropriate surface partition coefficient. The vapor is presumed to be injected as an infinitely sharp pulse at the start of the column so that the initial conditions remain

$$q(0,x) = 0 \text{ and } c(V,0) = \delta(V)$$

where δ is the Dirac δ function.

The solution to eq 1 is simply that for the case where the surface term is neglected,[2] with a replaced by $a + \beta_s s$. At the column outlet, where $x = l$, the solution thus may be written

$$C(V) = c(V,l) = \frac{K}{V}\left[\frac{V_b}{V - V_m - V_s}\right]^{1/2} I_1\left\{\frac{2K}{\dot{V}}[V_b(V - V_m - V_s)]^{1/2}\right\}\exp\left\{\frac{-K}{\dot{V}}(V + V_b - V_m - V_s)\right\} + \exp\left\{\frac{-V_bK}{\dot{V}}\right\}\delta(V - V_m - V_s) \qquad (4)$$

where $V_b = ml\beta$, $V_m = al$, $V_s = sl\beta_s$, and I_1 is the first-order modified Bessel function. Thus $C(V)$ is the vapor phase concentration of the probe at the column outlet (per mole initially injected), expressed as a function of the volume V of carrier gas passed through the column, and so defines the chromatograph peak shape.

We consider the form of the chromatographic peak $C(V)$ for three situations: (A) for rapid equilibration in the bulk of the stationary phase, (B) for extremely slow approach to equilibrium in the stationary phase, and (C) for the intermediate case.

(A) Rapid Bulk Equilibration. When the kinetic parameter $K/\dot{V}$ is sufficiently large, then several approximations may be used to simplify eq 4.[2] The term containing the δ function may be neglected, and the Bessel function may be written as an exponential approximation, good to

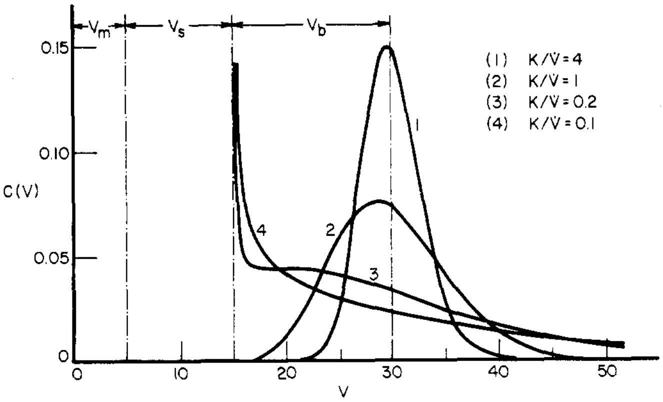

Figure 1. Calculated peak shapes showing change from bulk to surface retention as a function of the rate of bulk equilibration $K/\dot{V}$, with V_m, V_s, and V_b taken as 5, 10, and 15 volume units, respectively. (The curves are redrawn from Figure 1 of ref 1, where details of the calculation are given.)

within 1% when its argument is greater than 10.

$$C(V) \simeq \frac{K^{1/2}(V_b)^{1/4}}{(4\pi\dot{V})^{1/2}(V - V_m - V_s)^{3/4}} \times \exp\left\{\frac{-K}{\dot{V}}\left(\sqrt{V_b} - \sqrt{V - V_m - V_s}\right)^2\right\} \quad (5)$$

If the total width of the peak $C(V)$ is a small fraction of its retention, this further simplifies to give

$$C(V) \simeq \frac{K^{1/2}}{(4\pi\dot{V}V_b)^{1/2}} \exp\left\{\frac{-K(V_m + V_b + V_s - V)^2}{4\dot{V}V_b}\right\} \quad (6)$$

which is the equation for a Gaussian curve with peak maximum at $V^* = V_m + V_b + V_s$ and peak variance of $2\dot{V}V_b/K$ as illustrated in Figure 1, curve 1. (As $K/\dot{V}$ approaches infinity, eq 6 reduces to $C(V) = \delta(V - V_m - V_b - V_s)$, i.e., the Gaussian curve becomes a sharp pulse at the position of the peak maximum.) Thus the peak maximum occurs at a retention volume which may be regarded as the sum of the column gas phase volume together with independent contributions from the surface and bulk retention mechanisms. On the other hand, the peak spreading depends only on that fraction of the total retention volume attributable to bulk interactions. It should be noted that surface equilibrium is assumed to be instantaneous, and that other peak spreading mechanisms are ignored.

The peak maximum retention volume (measured at column temperature T) may readily be expressed in terms of the specific retention volume (per gram of stationary phase, measured at 273.2 K).

$$V_g = V_g{}^s + V_g{}^b \quad (7)$$

where

$$V_g{}^b = (273.2/T)\beta$$

and

$$V_g{}^s = \frac{s}{m}\frac{273.2}{T}\beta_s$$

The linear combination of surface and bulk retention volumes has been used to explain liquid surface effects in GC[4] and also in interpreting retention volumes close to polymer melting transitions.[5] The above derivation shows that under the usual chromatographic conditions, the combination of surface and bulk retention volumes follows in a simple manner from the inclusion of a term for surface adsorption in the basic chromatographic mass balance equation.

(B) Slow Bulk Equilibration. If the approach to bulk equilibrium is so slow as to be negligible, $K/\dot{V} \sim 0$, the first term in eq 4 becomes zero, and

$$C(V) = \delta(V - V_m - V_s) \quad (8)$$

Thus $C(V)$ is zero for all values of V other than $V = V_m + V_s$, at which value the probe vapor elutes as an infinitely sharp pulse. In practice, of course, the initial injection is not infinitely sharp, and neglected kinetic parameters such as gas phase diffusion will also cause the peak to show some degree of peak broadening. If such broadening is symmetrical, the result should be a sharp peak, with a peak maximum at

$$V^* = V_m + V_s \quad (9)$$

It must be noted that this result presupposes that the surface coverage is linearly related to the gas-phase concentration of vapor. This will be rigorously true only on homogeneous surfaces at very low coverages.

For finite but small values of $K/\dot{V}$, the sharp peak at $V = V_m + V_s$ is modified by the addition of a long tail at values of $V > V_m + V_s$. When the argument of the Bessel function in eq 4 is <0.2, $I_1(z) \simeq z/2$ to within 1% and so, for small values of $K/\dot{V}$, with V sufficiently close to $V_m + V_s$, it may be readily shown that

$$C(V) \simeq (K/\dot{V})^2 V_b \exp\left\{\frac{-K}{\dot{V}}(V + V_b - V_m - V_s)\right\} + \exp\{-V_b K/\dot{V}\}\delta(V - V_m - V_s) \quad (10)$$

indicating a sharp pulse at $V^* = V_m + V_s$, together with a tail which initially decays exponentially. As the value of $K/\dot{V}$ increases, the number of moles of probe in the sharp pulse decreases and the amount of vapor eluted in the tail increases. The peak shape, given by eq 4, takes on the appearance shown in curve 4, Figure 1. A formally similar result, modified to include a superimposed Gaussian spreading, has been used by Giddings to explain the kinetic origin of tailing in chromatography.[6]

(C) Intermediate Case. For sufficiently high values of $K/\dot{V}$, eq 4 simplifies to give eq 6, that for a Gaussian peak with maximum at $V^* = V_m + V_b + V_s$ (section A). As $K/\dot{V}$ decreases, the approximations no longer hold; eq 4 predicts a broadening of the peak, and a displacement of the peak maxima to shorter retention volumes, $V^* < V_m + V_b + V_s$, until eventually a sharp peak at $V^* = V_m + V_s$ with a long tail to $V > V_b$ is found, as discussed in section B. The present model thus predicts that decreasing the value of a single kinetic parameter results in peak retention volumes changing from values characteristic of bulk solution to values indicating surface adsorption only.

The shapes of the curves predicted by eq 5 are the same as those given previously,[1] with the slight change of variable necessary to allow for surface adsorption. The complete progression is illustrated in Figure 1, from which it is evident that the calculated peaks in the transition region are extremely broad, spanning retention volumes from $V = V_m + V_s$ to $V \gg V_m + V_b + V_s$. A similar change of GC peak shape with decreasing rate of exchange between stationary and mobile phases recently has been calculated by Villermaux,[7] and an analogous shift in peak maxima is also predicted by the "lumped film" model of Funk and Haughton.[8] However, as far as is known, this phenomenon has been observed only for GC experiments on polymers at the glass transition.

Applications

In principle, the shape of a chromatographic peak may

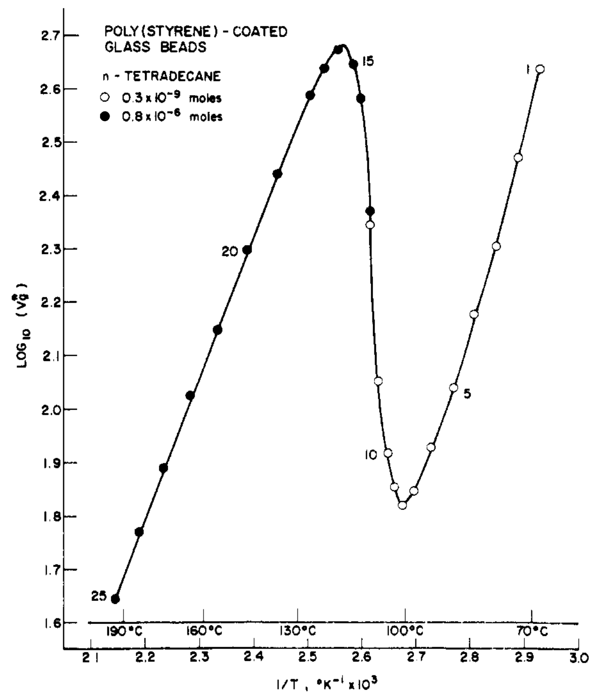

Figure 2. Retention diagram of *n*-tetradecane on polystyrene. V_g^* is the specific retention volume (ml/g) measured to the peak maximum.

be calculated if the equilibrium constants β and β_s, the column parameters a, m and l, and the kinetic parameter $K/\dot{V}$ are known. In practice, oversimplifications in the theory and the lack of suitable diffusion data with which to estimate $K/\dot{V}$ render meaningless any quantitative comparison of theory and experiment. Nevertheless, it seems useful to illustrate the experimental peak shapes observed on passing through the glass transition, and show that they are in qualitative agreement with eq 4.

The retention diagram for *n*-tetradecane on a polystyrene column is shown in Figure 2. The variation of the apparent specific retention volume, measured to the elution peak maximum, is shown as a function of reciprocal temperature. Following the interpretations of Guillet and coworkers,[9] the retention mode is surface adsorption between 70 and 100°C. A sharp deviation occurs at T_g, and retention volumes rise to a maximum before decreasing linearly again at higher temperatures where bulk sorption is occurring.

The peak shapes corresponding to some of the points in the retention diagram are shown in Figure 3. The changing peak shapes reflect the temperature dependence, not only of the kinetic parameter but also of the partition functions β and β_s. Peak 5 is typical of peak shapes found on glassy polymer surfaces, with a sharp front and a marked tail. On approaching the glass transition the tail becomes more pronounced, as predicted by the model for increasing rates of bulk sorption. On passing through the glass transition, the peaks become excessively broad, so broad indeed that it was convenient to increase the size of the vapor samples (at injection 13), otherwise for very small injections the peak disappeared into the baseline drift. The peak maxima for these broad peaks move in a short temperature interval to very much longer retention times, as predicted in the intermediate region, until at injection 17 the peak has the form of a skewed Gaussian. On increasing the temperature further, the peak becomes more symmetrical, until normal column performance is achieved about 50° above T_g (e.g., see injection 22). In the previous paper[1] it was shown that this temperature range is sufficient to alter the peak shapes predicted by eq 4 in the observed manner when account is taken of the temperature dependence of V_s and V_b as well as $K/\dot{V}$.

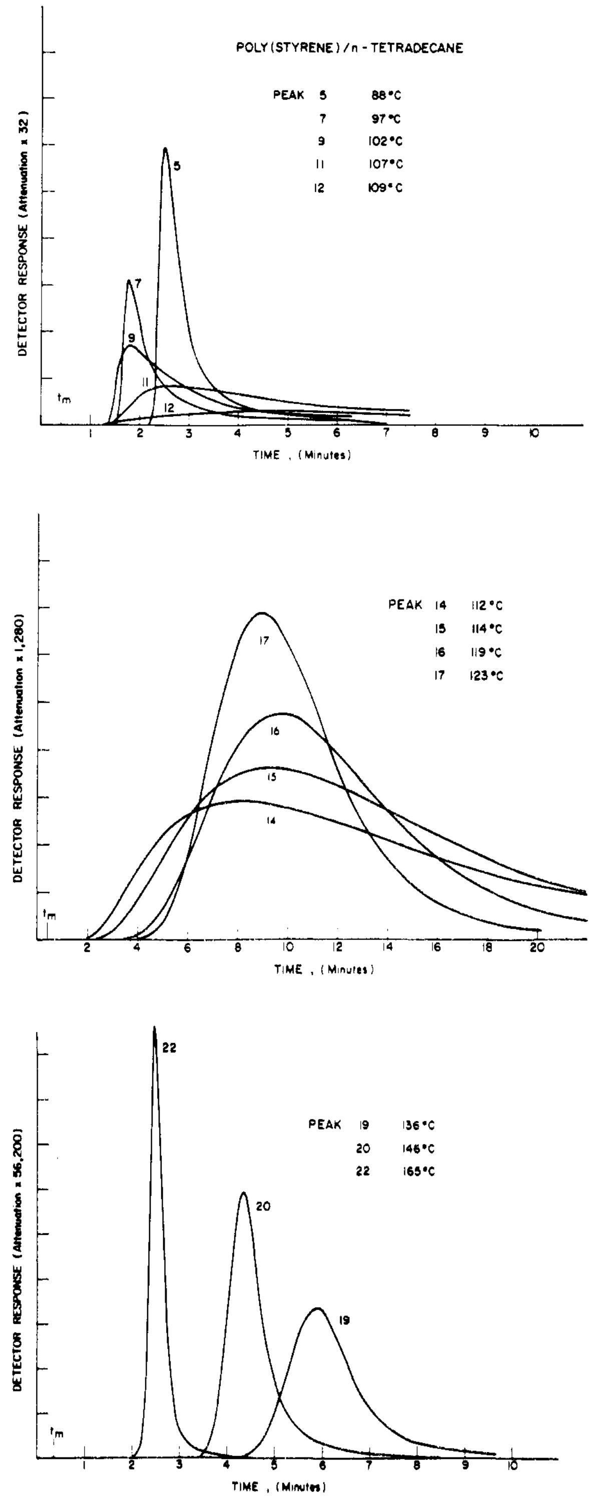

Figure 3. Experimental peak shapes for *n*-tetradecane on polystyrene at different temperatures. The numbers on the peaks correspond to those in Figure 2.

Despite the fair agreement between peak shape behavior predicted by eq 4 and that observed experimentally, it is evident that some discrepancy exists in the region where surface adsorption is first perturbed by bulk effects. This may be seen by comparing the shape of calculated (Figure 1) and experimental (Figure 3, curve 9) peaks in this region. The discrepancy appears related to the assumption, implied in eq 2 and 3, that the instantaneously established surface concentration is independent of the time dependent bulk concentration. Recently, a more complete gas chromatographic model incorporating nonequilibrium interaction with the stationary phase has been presented.[10] The model considers both partition and complex formation with the stationary phase, and is analogous to the situation at the glass transition, with bulk sorption playing the role of complex formation. The computed chromatographic peak shapes are in excellent agreement with those of Figure 3. Unfortunately, while the peak shapes may be evaluated numerically from assumed values of the rate and equilibrium parameters, the evaluation of these parameters from the peak shapes remain to be accomplished.

Several practical points emerge from this consideration of kinetic factors on peak shape. First, in the region above T_g, kinetic effects result in a displacement of the maximum of the peak given by eq 4 to values less than $V_m + V_s + V_b$. The displacement varies linearly with $\dot{V}/K$ for moderate displacements[1] so that the true equilibrium value of the retention volume may be found by extrapolating a linear plot of peak retention volume to $\dot{V} = 0$. However, in a recent paper where capillary columns were employed,[11] the intuitively reasonable statement was made that at sufficiently low flow rates, the peak retention volume should no longer be a linear function of flow rate; a more complex empirical equation was given relating retention volume and flow rate which fitted the experimental data more satisfactorily. Some consideration of this problem has been presented by Wicar et al.,[12] who concluded that the peak displacement is related to flow rate in a manner functionally identical with the peak spreading predicted by the Van Deempter equation.[2] The linear relationship between peak displacement and flow rate, which follows from eq 4, is based on the assumption that peak spreading is due only to the rate of equilibration between stationary and mobile phases, characterized by K. However, as the flow rate is decreased, the Van Deempter treatment shows that other peak spreading mechanisms, such as longitudinal diffusion in the carrier gas stream, become important, so that the linear relationship no longer holds. Thus, according to Wicar et al., the deviation of the peak maximum from the ideal position will also be similarly dependent on flow rate. Initially, a linear increase in peak retention volumes with decreasing flow rate at higher flow rates is predicted. As the flow rate decreases, the peak retention volumes deviate from the straight line, until at very low flow rates, the retention volumes may start to decrease with decreasing flow rates. (In other words, the deviation from equilibrium retention volume may pass through a minimum and then start to vary inversely with flow rate.) It seems reasonable therefore to determine equilibrium retention volumes for stationary phases above T_g by measuring retention data at flow rates where longitudinal diffusion is negligible, and extrapolating linearly to zero flow rate.

A second practical point relates to measurements of retention on glassy polymer surfaces. Peaks in this region often rise sharply to a maximum, and then drop off slowly giving a long tail (Figure 3, curve 5). Such behavior is sometimes due to partition isotherms which are not linear but which show Langmuir-like behavior.[13] It is shown in section B that a tailed peak may also result from surface adsorption together with slow bulk sorption. Tailing may thus be a kinetic rather than a thermodynamic effect. It should be noted that despite the peak asymmetry, the peak is close to its equilibrium value, and hence the maximum is relatively insensitive to changes in the flow rate. However, the existence of extremely long tails due to slow bulk sorption below T_g means that great care is necessary to ensure that retention volumes are measured on the pure polymer and not on the surface of a dilute solution of probe in the polymer (i.e., not on the tail of a previous injection). A simple but time-consuming way to eliminate this problem is to heat the column to well above T_g and then cool it to the working temperature before each injection.

Gas chromatography has been proposed as a method for determining the glass transition temperatures of polymers;[9,14] the transition temperature is taken empirically as that temperature at which the peak retention volume first starts to deviate from the linear surface adsorption region (Figure 2, points 7 and 8). The deviation from linearity is taken to correspond to the onset of bulk penetration and hence of polymer segment mobility. However, both theory (Section B) and experiment (Figure 3, curves 5, 7, and 9) suggest that the onset of bulk permeation is first indicated by an enhancement of the tail prior to any peak displacement. In general, the cooperative nature of the onset of segmental motion will ensure that bulk permeation will increase very rapidly with temperature, so that the onset of tailing, the deviation of peak maxima from the linear surface retention portion of the retention diagram, and the minimum in the retention curve will occur over a small range of temperatures; the dependence of all of these phenomena on flow rate and GC column parameters will in this case be small. The detection of T_g by GC may be less unequivocal if the probe vapor diffuses readily through the glassy polymer either because of its small size or because it is such a good solvent for the polymer that it induces relaxation in the glass. (In this latter case the real values of T_g might also be shifted to lower temperatures by a plasticization effect.) Similarly, difficulties may be experienced if the diffusion of the probe in the bulk polymer increases only slowly with temperature above T_g. Thus the ideal probe should have a zero or negligible rate of diffusion in the glassy polymer, and the diffusion rate should increase to a high value just above T_g. Otherwise flow rate, polymer film thickness, and other column parameters may influence both the GC peak shape and the shape of the retention diagram in the glass transition region.

Summary and Conclusions

The general features of gas chromatographic peak shapes and retention volumes on polymeric phases in the region of the glass transition are given by eq 4 and illustrated in Figure 1. It is assumed that the vapor phase concentrations of the probe are linearly related to the bulk and surface concentrations, and that slow equilibration in the bulk of the polymer is the only peak spreading mechanism. As the rate at which bulk equilibrium is achieved becomes slower (i.e., $K/\dot{V}$ decreases), the peak shape goes from a pulse at $V = V_m + V_b + V_s$ to a Gaussian curve with a peak maximum at the same retention volume. Further decreasing $K/\dot{V}$ causes the peak to become skewed, with a maximum at $V < V_m + V_b + V_s$, until an extremely broad skewed peak, starting at $V = V_m + V_s$ and tailing to $V \gg V_m + V_b + V_s$, is formed. The mass of probe vapor in the peak builds up at $V = V_m + V_s$ giving a pulse at this retention volume together with a long tail; the tail eventually disappears as $K/\dot{V} \rightarrow 0$. The predicted peak shapes are in qualitative agreement with experiment, but quantitative determination of kinetic parameters and diffusion rates from peak shapes in the glass transition region is not yet possible. Further progress may result from recent and more complete treatments of nonequilibrium peak shape.[10] Nevertheless, despite its shortcomings eq 4 does provide a simple and unified picture of GC behavior near T_g, and is of use in interpreting the effects of kinetic factors on GC peak shapes.

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References and Notes

(1) D. G. Gray and J. E. Guillet, *Macromolecules*, **7**, 244 (1974).
(2) See, for example, A. B. Littlewood, "Gas Chromatography", 2nd ed, Academic Press, New York, N.Y., 1970, Chapters 2 and 6.
(3) See, for example, A. W. Adamson, "Physical Chemistry of Surfaces", 2nd ed, Wiley-Interscience, New York, N.Y., 1967, p 78.
(4) D. E. Martire, "Progress in Gas Chromatography", J. H. Purnell, Ed., Wiley-Interscience, New York, N.Y., 1968, p 93.
(5) G. J. Courval and D. G. Gray, *Macromolecules*, **8**, 326 (1975).
(6) J. C. Giddings, *Anal. Chem.*, **35**, 1999 (1963).
(7) J. Villermaux, *J. Chromatogr.*, **83**, 205 (1973).
(8) J. E. Funk and G. Haughton, *J. Chromatogr.*, **6**, 193 (1961).
(9) O. Smidsrod and J. E. Guillet, *Macromolecules*, **2**, 272 (1969); A. Lavoie and J. E. Guillet, *ibid.*, **2**, 443 (1969).
(10) K. P. Li, D. L. Duewer, and R. S. Juvet, Jr., *Anal. Chem.*, **46**, 1209 (1974).
(11) R. N. Lichtenthaler, D. D. Liu, and J. M. Prausnitz, *Macromolecules*, **7**, 565 (1974).
(12) S. Wicar, J. Novak, and N. Ruseva-Rakshieva, *Anal. Chem.*, **43**, 1945 (1971).
(13) P. R. Tremaine and D. G. Gray, *J. Chem. Soc., Faraday Trans. 1*, **71**, 2170 (1975).
(14) J.-M. Braun, A. Lavoie, and J. E. Guillet, *Macromolecules*, **8**, 311 (1975).

Autoxidation of Polyolefins. Absolute Rate Constants and Effect of Morphology

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ABSTRACT: Benzoyl peroxide (BP) has been used to initiate autoxidation of polyolefins from 71 to 105°. The measurements were made for 0.6 to 2% conversion. The initiation efficiency was found to be much lower (by as much as tenfold) for semicrystalline polymer than amorphous polyolefins. The former increases rapidly, approaching the efficiency in the amorphous systems, as the temperature approaches the melting point of the polymer. The difference was attributed to the presence of "encumbered" segments and molecules at the phase boundaries. The "encumbered" radicals probably combine with much higher probability than the radicals of the "free" amorphous molecules. The rate constant ratios $k_pk_t^{-1/2}$ for polypropylene from 130 to 45°, as well as those for model compounds 2,4-dimethylpentane and 2,4,6-trimethylheptane, lie on the same Arrhenius plot. The rate constant of propagation for polypropylene is $k_p = 1.61 \times 10^7 \exp(-12080/RT)(M\ \text{sec})^{-1}$; it is $k_t = 1.11 \times 10^{13} \exp(-11600/RT)(M\ \text{sec})^{-1}$ for the termination process. The values of k_p and k_t for the model compounds appear to fall within experimental errors of these equations. Compared to polypropylene, poly(1-butene) has higher values of k_p and k_t and higher activation energy for propagation. The values of $k_pk_t^{-1/2}$ are nearly the same for poly(4-methyl-1-pentene) as polypropylene. The present work showed that the rate constants reported earlier by us for self-initiated autoxidation of polypropylene are valid.

Over the years there have been many studies on the autoxidation of polyolefins often with contradictory results. This is certainly due to the complexity of the processes and the number of variables involved. Dulog et al.[1] reported the first study of autoxidation of polyethylene (PE), polypropylene (PP), and poly(1-butene) (PB) in trichlorobenzene. For isotactic samples of polypropylene (c-PP) and poly(1-butene) (c-PB) the reaction is autocatalytic and the rate of reaction is proportional to the amount of oxygen absorbed. In contrast, the rate of autoxidation of atactic samples of polypropylene (a-PP) and poly(1-butene) (a-PB) and of PE increases linearly with time and is proportional to the square root of the amount of oxygen absorbed. They attributed the kinetic differences to the isotactic polymers having conformations favoring intramolecular propagation but not for the atactic or syndiotactic polymers. The overall activation energies are about 7–8 kcal mol^{-1} greater for the amorphous polymers than the corresponding crystalline polyolefins. That the chain conformations of isotactic and atactic polyolefins in solution at temperatures between 120 and 176° should be different is both unexpected and surprising. In a more recent study by van Sickle,[2] the autoxidations of both amorphous and crystalline polypropylene in benzene solution from 100 to 130° were found to be very similar. The reaction rate is proportional to [initiator]$^{0.58}$[polypropylene]$^{0.73}$ and is independent of reaction time. Up to half of the oxygen consumed was found to be hydroperoxides. On the other hand, the rate of autoxidation of a-PP in solution was found by Bawn and Chandhri[3] to depend upon [polypropylene]$^{1.7}$[O$_2$]^1 both in uncatalyzed systems[3a] and in reactions catalyzed by manganese salts.[3b] The dependence on oxygen pressure in the range of 450 to 750 Torr for autoxidation in solution is unusual. Fractional kinetic order for autoxidation of polypropylene was also observed by Niki et al.[4] who found the rate to be proportional to [polypropylene]$^{0.44}$[initiator]$^{0.68}$. These authors concluded that even though intramolecular propagation is favored, its chain length is short.

The autoxidation of model hydrocarbons appears to be uncomplicated; the kinetics are simply first order in the substrate concentration and half-order in the initiator concentration. Intramolecular propagation, k_p, is favored over the intermolecular propagation, k_p'. The ratio of $k_p/k_p' \approx 66\ M$ for both 2,4-dimethylpentane[5,6] and 2,4,6-trimethylheptane[7,8] with the dihydroperoxide and the trihydroperoxide, respectively, as the major products.

One faces a number of technical difficulties in studying autoxidation of bulk polymers. The sample thickness is important; oxidation occurs less rapidly and is less extensive in the interior of thick samples.[9,10] For semicrystalline