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Impact Transition Temperatures and Polymer Densities

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ABSTRACT: The impact transition temperature T_I at which the behavior of a polymer changes from ductile to brittle under high-impact conditions is analyzed. T_I is related to the geometry of the notch or the main crack as expressed by the stress concentration factor K_t. At the same time, T_I depends on the chain relaxation capability (CRC) and thus on free volume v^f. A theory connecting K_t, T_I, and v^f is used in conjunction with the Guggenheim $\tilde{v}(T)$ formula, where $\tilde{v}(T)$ is the reduced volume and T the thermodynamic temperature. Calculations of K_t for low-density polyethylene (LDPE) produce values that agree with the measured ones within limits of the experimental accuracy. This would be, however, only one among various free-volume approaches used for prediction of macroscopic (thermophysical, mechanical, rheological, etc.) properties of polymer systems, with the reverse route very little explored. Therefore, moving from data to prediction in the opposite direction, specific volumes of LDPE are calculated from impact transition temperatures and stress concentration factors. The average difference between calculated and experimental $v(T)$ values is 0.921%.

Introduction and Scope

Performance of a polymeric material or component subjected to deformations can be characterized in a variety of ways. Foremost among them appears to be impact testing, which constitutes the most severe mechanical abuse. Reviewers of the field of impact behavior of polymers commonly point out the complexity of the subject.[1–4] As noted by Wolf,[5] this complexity pertains to most problems in polymer science and engineering. Even for a fixed fraction of each kind of monomeric units in a given sample, various ways of assembling the units produce chains of different length and stereoregularity, different cross-linking characteristics, and so on. Moreover, even when a detailed knowledge of molecular structure has somehow been achieved, interactions between chains have to be taken into account.

One way out of this complexity consists in concentrating on a very small number of parameters, chosen so that each parameter has a major role for properties to be studied. There is overwhelming evidence that free volume v^f plays such a role for a large number of properties. Numerous connections between v^f and viscoelasticity have been discussed by Ferry[6] and also by Aklonis and MacKnight.[7] The statistical–mechanical theory of the liquid state developed by Flory[8] and its various applications[9–11] and modifications[12] have proven conclusively the essential role of v^f in determining thermophysical properties of liquids with low molecular mass M, polymer melts, solutions, and amorphous polymers. The service behavior of polymers at temperatures below the glass transition region is influenced to a large extent by aging. Extensive work on aging by Struik and his school,[13,14] by Matsuoka,[15] and by others has clearly demonstrated the role of v^f in aging. Diffusion of liquid and vapor condensates into polymers is determined by an interplay of free volumes of polymer and of penetrant.[16–18]

The above list could be made still longer, but it suffices to prove our main assumption that mechanical, thermophysical, and rheological properties of polymeric systems are chiefly determined by free volume and chain conformations. Further, we note that a number of parameters not taken into account explicitly are *reflected* in v^f. Frequency of branching along the chain backbone and lengths of the branches are good examples of this. In fact, long before the present project Litt and Tobolsky[19] had shown that a connection exists between the impact strength and what they called a maximum fractional unoccupied volume.

In all applications of free volume known to us, those named above and otherwise, one goes from volume (v^f, specific volume v, or molecular volume) toward a macroscopic property of a different kind. If our basic premise stated above is correct, then the following corollary of it should also be true: volumetric properties of polymers, such as density v^{-1}, should be obtainable from properties of other kinds.

This situation has provided the motivation for the present work. We consider impact testing of notched specimens, all of the same size and shape, with the same energy provided to each specimen by the hammer in an impact event. We know that, for samples of the same material at the same temperature T and with the same radius of curvature at the end of the crack, ductile behavior will ensue for shallow cracks while brittle for deep cracks. Now, however, assume a *constant notch geometry* (=constant stress concentration factor K_t; for definition see the next section). Whether a crack will propagate in a brittle way or otherwise depends on K_t as well as on the resistance of the material against destructive processes. We call the latter the chain relaxation capability (CRC, discussed more in detail below). One way of manipulating CRC consists in varying the *temperature*. At low T values we have low v^f and low CRC, and fracture occurs. At high temperatures there is sufficient CRC to ensure ductile behavior. There is a transition point between the two regimes, that is, the impact transition temperature T_I. There is also another way to manipulate CRC: still keeping K_t constant but changing the *molecular structure*, for instance, by introducing more branching (or even by switching to an entirely different polymer). Thus, we enlarge v^f, provide more space for segmental motions, and enhance CRC. Moreover, we can improve CRC by increasing the *molecular mass*. In other words, for given geometries of the specimen and the notch, T_I depends on the situation at the molecular level. We have a sequence of connections: from purely geometric K_t via T_I and v^f to molecular structures and chain dynamics. We propose to find out whether that sequence can be used in both directions.

Definitions

Researchers work variously with the specific volume v, characteristic (often called hard-core or incompressible)

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volume v^*, free volume v^f, and/or reduced volume $\tilde{v}$. These quantities are related by

$$v = v^* + v^f \tag{1}$$

$$\tilde{v} = v/v^* \tag{2}$$

Ways of calculating these parameters are given by a number of authors. For instance, Flory[8,9] provides a procedure for computing $\tilde{v}$ from v and from the isobaric expansivity $\alpha = v^{-1}(\partial v/\partial T)_{P,\phi}$, where P is the pressure and ϕ defines a composition of the system. Two other scaling parameters, namely, T^* and P^*, can be similarly calculated[8,9] from v, α, and the isothermal compressibility $\kappa_T = -v^{-1}(\partial v/\partial P)_{T,\phi}$. Numerical values depend on the procedure, although calculations by Hartmann et al.[20] show that the scaling parameters for the Simha-Somcynsky equation[21] do not differ substantially from those for the Hartmann equation of state.[22-25]

The impact transition temperature T_I is that temperature at which the response of a material changes from brittle to ductile under high-impact conditions for a particular stress concentration factor K_t. As discussed in ref 26, the high-impact conditions are essential; otherwise, one might find only a temperature range rather than a single value.

The chain relaxation capability (CRC, in German die Kettenrelaxationsfähigkeit, KRF) is defined[27] as the amount of external energy dissipated by relaxation in a unit of time per unit weight of the polymer. All of the nondestructive processes belong here, such as transmission of energy across the chain producing intensified vibrations of the segments, transmission—mainly by entanglements but also by segment motions—of energy from the chain to its neighbors, conformational rearrangements executed by the chains, and elastic energy storage resulting from bond stretching and angle changes. Each of these processes is enhanced by an increase in molecular mass M. Thus, CRC goes symbatically with M; we note that the improvement of impact properties of polyethylenes with increased M is well-known from experiments. The constituents of relaxation are determined by external temperature and pressure, by molecular structure, and also by morphology. In particular, the role of tie molecules was analyzed by Lustiger and Markham[28] and by Lustiger.[29] Information on various types of local motions contributing to CRC can be obtained from NMR spectra, as in the study of O'Gara et al.[30] on polycarbonates. These authors discuss also an important connection between relaxation modes in solution and in the bulk. All CRC constituents except conformational changes are operative in both crystalline and amorphous regions. Since, moreover, tie molecules transfer mechanical energy between these two kinds of regions, we can work with overall specific volume for semicrystalline materials.

Necessarily, CRC and v^f are related. In molecular dynamics computer simulations of stress relaxation[31,32] frequency as well as amplitude of segment oscillations were found to depend strongly on v^f. When CRC is exceeded, destructive processes manifest themselves. A good example is provided by rapid crack propagation in plastic fuel pipes.[33]

Theory

Since T_I depends on the presence of cracks and/or artificial notches, we shall work with the stress concentration factor

$$K_t = 1 + 2(h/l)^{1/2} \tag{3}$$

where h is the depth of the notch or crack and l the radius of curvature at the tip of the notch. K_t represents the ratio of maximum stress at the end of the major axis of an elliptical hole to the average stress away from the flaw. Pascoe[34] in a very lucid review of fracture mechanics (FM) shows how FM concepts are applicable, with modifications when necessary, also far outside the linear-elastic bastion of birth of FM. The problem is discussed also by a number of other authors, notably by Kausch.[2,35] Elsewhere[36] a model of slow crack propagation is developed so that its parameters have connections to dynamics of chain segments. Thus, without further apology we shall use eq 3 to real notches, which only approximately are elliptical.

Since deeper notches make the temperature range of the ductile response smaller, the impact transition temperature goes symbatically with K_t. In an impact event we have competition between destructive processes—aided by the presence of the notch—and nondestructive ones. The latter prevail when we have the more unoccupied volume of Litt and Tobolsky,[19] or of our v^f, or in other words when CRC is high.

An analysis of competition between these two types of processes has been performed by one of us and is described in detail in ref 26. We provide the key elements of that analysis in the following. First, the energy U_0 furnished to the specimen in an impact event can be represented at any time after the event by

$$U_0 = U_r + U_b + U_n \tag{4}$$

Here U_r represents the part of energy spent on relaxational processes. Constituents of CRC were listed above; particularly important seem to be conformational changes; Cook[37] has found in molecular dynamics simulations leading to stress vs strain diagrams that for carbonlike chains the plateau of the diagram corresponds to gauche-to-trans conversions. U_b is the part of energy spent on destructive processes, including breaking of chemical bonds and crack propagation; in stress relaxation simulations[32] crack propagation occurred in some of the runs. U_n is the part of the input energy which at a given time was not yet spent in either of the two categories of processes (denoted by U in ref 26). If one assumes that both ways of spending U_0 are first-order processes with respect to time t, one can write

$$dU_n/dt = -(c_b + c_r)U_n \tag{5}$$

where c_b and c_r are appropriate rate constants. Integration of eq 5 leads to $U_b(t)$ and $U_r(t)$ relations displayed in ref 26 but not used in the present calculations and also to the formula

$$U_b/U_r = c_b/c_r \tag{6}$$

A further element in the model is the Doolittle equation[38]

$$\ln \eta = \ln A' + Bv^*/v^f \tag{7}$$

where η is the viscosity while A' and B are constants. An extensive literature proves the validity of eq 7. As a measure of CRC that involves both η and v we take the shift factor

$$a_T = \frac{\eta T_{ref}\rho_{ref}}{\eta_{ref} T \rho} \tag{8}$$

where ρ is the mass density, that is, v^{-1}. The factor a_T is essential for the method of reduced variables; for succinct reviews see Venner[39] or Kubât and Rigdahl.[40]

Combination of eq 7 and 8 leads[26] to

$$\ln a_T = A + B/(\tilde{v} - 1) \tag{9}$$

where A is not equal to A' but related to it. a_T values calculated from eq 9 can be used to predict a variety of rheological and mechanical properties via the time–temperature equivalence principle. For the task at hand, we note that the shift factor decreases when the temperature increases. To avoid invoking too many parameters, we simply assume an inverse proportionality between a_T and the relaxation-rate parameter c_r, that is

$$c_r = c_r'/a_T \tag{10}$$

At the same time, the rate parameter for the destructive processes is necessarily proportional to the stress concentration factor, so that

$$c_b = c_b'K_t \tag{11}$$

where c_r' and c_b' are new proportionality factors; c_b' reflects specific test conditions and specimen dimensions. Now by combining eq 6, 10, and 11, using eq 9 at $T = T_I$, and introducing a symbol

$$F = c_r'U_b/c_b'U_r \exp(A) \tag{12}$$

we arrive at

$$K_t = F \exp(-B/(\tilde{v}_I - 1)) \tag{13}$$

where F is a parameter to be determined. While eq 13 does not contain the impact transition temperature explicitly, the reduced volume $\tilde{v}_I$ (or the respective free volume, see eq 1 and 2) is that at T_I.

Since T_I depends on the geometry of the notch—that is, K_t—on one hand, and on the chain relaxation capability—that is, v^f—on the other, we have a remarkably useful chain of relationships: from the purely geometric stress concentration factor via the impact transition temperature and chain dynamics to free volume. In turn, as noted in the introduction, v^f reflects and represents molecular structure and morphology. A difference between behavior of molecular segments in the presence and in the absence of external mechanical forces ought to be noted here. In the absence of a force, neutron-scattering studies of Fujara and Petry[41] over temperature ranges including the glass transition region show that the frequency of segment vibrations does not change with the temperature, but the amplitude does. Apparently, more v^f provided by a T increase allows larger amplitudes. On the other hand, results of molecular dynamics simulations adapted to polymer systems by Cook and Mercer[31,32] show that in the vicinity of a crack the frequency of segment vibrations varies considerably with v^f changes—in addition to changing with time in stress relaxation modeling.

To convert eq 13 into an explicit relation between K_t and T_I, one has to assume a specific form of $\tilde{v}(T)$ relationship. A number of possibilities exist here, including a very simple one suggested by Williams, Landel, and Ferry (WLF):[6]

$$\tilde{v}^{-1} = a_0 - a_1T \tag{14}$$

The use of eq 14 or of any other $\tilde{v}(T)$ formula for the evaluation of $\tilde{v}_I$ in eq 13 results in an explicit $T_I = T_I(K_t)$ equation.

Calculations and Results

Experimental T_I data corresponding to a set of stress concentration factors K_t were determined for low-density polyethylene (LDPE) by Zewi et al.[42] They used Alathon 20, LDPE of E. I. du Pont de Nemours Co., with the number-average molecular mass $M_n = 2.5 \times 10^4$ and the melt index of 2. The room-temperature density of the material after annealing the samples at 378 K for 1.5 h was $\rho = 0.920$ g cm^{-3}. Test bars 76 × 10 × 7 mm were molded on a Dake hydraulic press with heated platens. The Charpy machine was a Wiedemann-Baldwin impact tester instrumented with a Dynatup system of Effects Technology Inc. A load vs time curve was displayed on a Textronics screen and recorded. The specimens were notched just prior to testing by using a single-edged razor blade mounted in a special fixture. Afterward, the test specimens were saved, the notch depths checked, and the fracture surfaces inspected. For each notch depth, that is, for each K_t value, multiple series of tests were conducted, each series corresponding to a single temperature. The temperature at which 50% of samples exhibited brittle fracture while others responded in a ductile manner was recorded as T_I. Thus, each experimentally determined pair of K_t and T_I values represents the outcome of such multiple series of tests. The ductile/brittle ratio of numbers of samples at temperatures above and below T_I is such that a fairly sharp transition is found. Details of specimen preparation and testing are described in ref 42. The range of impact transition temperatures found extends from 293 to 179 K. The glass transition temperature T_g of PE provided by Wunderlich[43] is 237 K. We assume continuity in the glass transition region—as Flory taught us decades ago, as discussed in ref 27, and as demonstrated by neutron-scattering results of Fujara and Petry.[41]

Previously[26] we have applied eq 13 to the LDPE data in ref 42 by using two $\tilde{v}(T)$ formulas: the present eq 14 of WLF and a series expansion of the form

$$\tilde{v} = \sum_{i=0}^{3} c_i\tilde{T}^i$$

where c_i's are constants and $T = T/T^*$, with $T^* = 7956$ K.[44] It was found that the WLF equation produced good results for the top part of the $T_I(K_t)$ curve, while at lower temperatures the WLF prediction was fundamentally inappropriate. This was expected in view of the T_g value quoted above and a statement by Ferry[6] that the WLF formula is not applicable below T_g. By contrast, the series expansion provided quite a satisfactory agreement between calculation and experiment when eq 13 was solved for two $T_I(K_t)$ pairs to evaluate F and B.

In those earlier calculations, values of specific volume v of PE were not involved, since eq 13 requires only the knowledge of $\tilde{v}$. Now, having decided to use eq 13 to predict $v(T)$, we proceeded differently. Checking our eventual prediction was possible, since reliable experimental v values for LDPE are reported by Zoller.[45] He used samples annealed at 373 K for 1 h before testing; the density of 296 K after annealing was $\rho = 0.917$ g cm^{-3}, $\bar{M}_n = 2.0 \times 10^4$.

In view of eq 13, the path toward v leads via $\tilde{v}$. Thus, we were confronted again with a choice of $\tilde{v}(T)$ formulas. The WLF equation was eliminated before; the series expansion mentioned above, while producing good results, contains four parameters in addition to the scaling temperature T^*. We turned to a $v(T)$ equation proposed by Guggenheim[46] for liquid argon and extended to other materials by Lu and his colleagues.[47,48] The equation contains only two parameters, plus P_{cr}, T_{cr}, and V_{cr} at the liquid–vapor critical point, and gives good results for inorganic and organic compounds including oligomeric alkanes[49] and also for multicomponent systems.[48] Further, it is also usable with good results with the equation of state parameters for the normal boiling point replacing[50] those for the critical point. Since both these characteristic points are meaningless for polymers, we now take a further step in the generalization of the Guggenheim equation:

$$\frac{1}{\tilde{v}} = \tilde{\rho} = \frac{\rho}{\rho_{ref}} = 1 + \rho'\left(1 - \frac{T}{T_{ref}}\right) + \rho''\left(1 - \frac{T}{T_{ref}}\right)^{1/3} \tag{15}$$

The index ref pertains to reference parameters. Thus, the original Guggenheim formula is a special case of eq 15. For dealing with polymer systems, we take $T_{\mathrm{ref}} = T^*$. In the present work we have used the same value of T^* as before and already quoted above.

In the first series of calculations we have checked the validity of our eq 15 against the experimental v data for LDPE of Zoller.[45] An overdetermined system of eq 15 was solved by calling ZXSSQ, a least-squares Marquardt-type FORTRAN subroutine from IMSL, Houston, TX. While ZXSSQ solves systems of nonlinear relations, and eq 15 is linear in the unknowns, for consistency we used the same subroutine in all computations.

Values of $\rho' = 14.653$ and $\rho'' = -14.249$ were found, nearly fulfilling an additional simplifying relation:

$$\rho'' = -\rho' \tag{16}$$

Clearly, the use of eq 16 would turn eq 15 into a one-parameter relation. Then, substituting the values of ρ' and ρ'' so found into eq 15 for all experimental Zoller temperatures, we have found the root-mean-square deviation $\sigma = 0.0117$ and the average deviation $\bar{D} = 0.771\%$, where

$$\bar{D} = \frac{100\%}{n}\sum_{i-1}^{n}\frac{|F_i^{\mathrm{exptl}} - F_i^{\mathrm{calcd}}|}{F_i^{\mathrm{exptl}}}$$

n is the number of points in the data set and here $F_i = v(T_i)$. Thus, we conclude that eq 15 provides the capability of predicting $v(T)$ values for LDPE with two adjustable parameters or possibly even one if eq 16 is assumed. The final conversion from $\tilde{v}$ to v was accomplished by taking $v^* = 1.123$ cm^3 g^{-1} given in ref 44. By adjusting v^* to one of the experimental points of Zoller, smaller values of σ and $\bar{D}$ would be obtained (see below).

In the second series of calculations, we have substituted eq 15, with the known ρ' and ρ'' values, into eq 13. While for every notch as we know there is a corresponding impact transition temperature, that is, $T_{\mathrm{I}} = T_{\mathrm{I}}(K_{\mathrm{t}})$, we have used eq 13 as written, and computed K_{t} values for the experimental set of T_{I} data. The extent of agreement between calculated and experimental K_{t} values is represented by $\sigma = 2.240$ and $\bar{D} = 13.6\%$. While this is somewhat outside of the range of the experimental accuracy, the reasons for the differences are clear. The v^* value taken from the literature does not pertain either to samples used by Zoller in his volumetric studies or to those used by Zewi et al. in their mechanical testing. Also, the LDPE samples studied in ref 42 and 45, while similar (see above ρ and $\bar{M}_{\mathrm{n}}$ values), are not quite identical, contrary to the assumption made in our calculations.

We now proceeded toward the main task. From eq 13 and 15 we have

$$K_{\mathrm{t}} = F \exp\left[-\frac{B}{[1 + \rho'(1 - T_{\mathrm{I}}/T^*) + \rho''(1 - T_{\mathrm{I}}/T^*)^{1/3}]^{-1} - 1}\right] \tag{17}$$

Using the same T^* value for LDPE as before and the experimental K_{t} and T_{I} pairs, we have solved an overdetermined system of eq 17 with the ZXSSQ subroutine. The results were $F = 0.089$, $B = 0.466$, $\rho' = 14.358$, and $\rho'' = -13.914$. We see that this time also eq 16 is approximately obeyed. The agreement between the ρ' and ρ'' here and in the first series of calculations is worth noting.

Substitution of the parameters so evaluated into eq 17 for experimental T_{I} values has produced the results reported in Table I. The root-mean-square deviation between the calculated and experimental K_{t} values is $\sigma = 1.863$ and $\bar{D} = 8.037\%$. This is clearly within the limits of the experimental accuracy; the accuracy can be judged in particular at 285 and 288 K, where there are two experimental K_{t} values for each temperature.

Table I
Experimental and Calculated Stress Concentration Factor, K_{I}, Values for LDPE Corresponding to Impact Transition Temperatures, T_{I}

	stress concn factor K_{I}			stress concn factor K_{I}	
T_{I}, K	exptl	from eq 17	T_{I}, K	exptl	from eq 17
179	1.1	1.1	288	16.0	20.2
269	8.5	7.6	289	22.2	21.6
273	9.4	9.1	290	24.5	23.0
285	12.6	16.8	291	27.0	24.7
285	11.9	16.8	293	29.0	28.4
288	19.4	20.2			

Table II
Experimental and Calculated Specific Volumes of LDPE

		calcd	
T, K	exptl[45] $v/(\mathrm{cm^3\ g^{-1}})$	$\tilde{v}/(\mathrm{cm\ g^{-1}})$	$v/(\mathrm{cm^3\ g^{-1}})$
293.15	1.0881	0.9192	1.0881
296.15	1.0905	0.9223	1.0917
302.15	1.0962	0.9285	1.0991
310.05	1.1042	0.9360	1.1080
322.35	1.1144	0.9500	1.1245
331.25	1.1219	0.9597	1.1360
340.15	1.1315	0.9697	1.1478
351.15	1.1464	0.9823	1.1627
361.85	1.1622	0.9949	1.1777
372.75	1.1807	1.0081	1.1933
380.15	1.1990	1.0172	1.2040
390.95	1.2471	1.0308	1.2202

Finally, we have used the ρ' and ρ'' parameters obtained from the impact transition data to calculate specific volumes v of LDPE. Values of $\tilde{v}$ were obtained from eq 15. Then from the experimental v value for the lowest temperature, 293.15 K, and calculated $\tilde{v}$ for the same temperature we have obtained $v^* = 1.1837$ cm^3 g^{-1}. Conceivably, choosing a point in the middle of the experimental range could produce a better overall agreement, but we preferred a more severe test. With this v^* value we have converted calculated reduced volumes into specific ones. The results are listed in Table II.

The agreement between the experimental data of Zoller and our specific volumes obtained from the impact transition information corresponds to $\sigma = 0.0136$ and $\bar{D} = 0.0921\%$. We recall that the samples used in the two kinds of experiments are not identical; the temperature ranges covered are not the same either. Further, eq 15 represents an approximation, independent of the theory of the impact transition[26] culminating in eq 13. Thus, the extent of the agreement is truly gratifying.

Discussion

The decisive role of free volume for many properties of polymeric materials was noted in the beginning. We now find that our approach à rebours produces useful results: specific volumes of LDPE were successfully calculated from data on stress concentration factors and the corresponding impact transition temperatures. The theory of impact behavior of polymers exposed in ref 26 has thus found a new application. Underlying that theory is the concept of competition between what we now call CRC and the destructive processes; we infer such an approach will be useful also for dealing with other mechanical properties.

Equation 17 contains two parameters, ρ' and ρ'', characterizing the volume (and thus also v^{f}) in the system, plus two more parameters, F and B, providing connections to mechanical and rheological properties. We already know that it is possible to eliminate ρ'' via an approximation, eq 16. There is a temptation to eliminate the Doolittle constant B, particularly since many researchers apparently got away with setting $B = 1$. On the other hand, Fillers and Tschoegl,[51] who studied the time–temperature–pressure superposition of stress relaxation under superposed hydrostatic pressure, found B varying from 0.175 (for a copolymer of vinylidene fluoride and hexafluoropropylene) to 0.608 [for poly(vinyl chloride)]. They have used an equivalent of our eq 9 with a full P–V–T equation of state. This contradiction can be explained on the basis of eq 9: the shift factor is determined mainly by the $B/\tilde{v}$ ratio, rather than by B itself. Thus, the choice of a specific $\tilde{v}(T)$ or $\tilde{v}(T,P)$ relation and also the choice of v^* affect the value of the Doolittle constant.

Free volume v^f can be considered as consisting of at least two components and/or of holes of different sizes.[16,52–59] For instance, following this route Litt[58] obtained a $\tilde{v}(t)$ equation with a $T^{3/2}$ term that gives very good results for polyethylene at lower temperatures.[60] We have found, however, that—for the connection to impact properties—dealing with the free volume as a whole is sufficient. The fact that this connection is usable in both directions is significant not as a new method of density prediction but because it strengthens the belief in the validity and usefulness of the approach. Other macroscopic mechanical properties should similarly contain information on volumetric properties and connections to behavior at the molecular level. Depending on the property, one might have to take into account separately different constituents of free volume, the attached and detached (independent) holes in particular.

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Photon Harvesting Vinylphenanthrene–Methacrylic Acid Polymers: Singlet-State Migration and Trapping

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ABSTRACT: Random and alternating copolymers of 9-vinylphenanthrene and methacrylic acid have been prepared. These polymers have been doped with low mole fractions of anthryl energy traps. The photophysics of these polymers with and without these traps have been studied as a function of phenanthryl content in tetrahydrofuran (THF) and water. The fluorescence properties of the alternating polymers indicate an absence of excimer-forming sites in THF but not in water. Significant singlet energy migration has been implicated by fluorescence quenching methods. The quantum efficiency of anthracene sensitization has been found to be ca. 0.4 for the alternating polymer in THF and water. There is a very strong dependence of the photophysical properties of the random copolymers on pH, which is reflected in the energy-transfer efficiency.

Introduction

As part of our continuing interest in electronic energy-transfer (EET) phenomena in vinyl aromatic polymers we have recently published several papers dealing with alternating naphthalenic polymers.[1-4] These studies served to illustrate some of the advantages of alternating polymer structures with respect to singlet-energy migration, primarily because naphthalene excimer formation is repressed. Also these polymers were water soluble under conditions that the corresponding random polymers were not. However we still do not have a clear model for the conformation of these polymers in the solution phase and the effect this structure has on the polymer photophysics.

The present paper deals with alternating and random copolymers containing 9-vinylphenanthrene and methacrylic acid (a-MPh and r-MPh, respectively). The corresponding methyl methacrylate copolymers have been prepared for studies in organic solvents. The phenanthrene chromophore shares many properties with naphthalene: (1) a relatively long singlet lifetime (57.5 and 59 ns for phenanthrene and 2-methylnaphthalene, respectively[5]), (2) a moderate Förster R_0 for self-transfer[6] (R_0^{Ph} = 0.88 nm, R_0^{2MNaph} = 1.2 nm), and (3) a fairly large Förster radius for transfer to anthracene[6] ($R_0^{\mathrm{Ph\text{-}A}}$ = 2.2 nm, $R_0^{\mathrm{2MNaph\text{-}A}}$ = 2.5 nm). However phenanthrene has a much decreased tendency to form singlet excimers. We find that even in aqueous solutions there is no classical excimer fluorescence although there are some broadening and a spectral feature that can be assigned to a "weakly bound excimer". More importantly in view of our general motivation, both the homopolymer PVPh and r-MPh with reasonably high phenanthrene loadings exhibit an apparent energy migration constant (Λ_S) that compares favorably with a-MPh. This is a completely different finding than for the corresponding naphthalene polymers, in which Λ_S was much larger for the alternating polymer. We ascribe this difference to the almost complete lack of self-trapping for phenanthrene polymers, although there does seem to be significant self-quenching. However the value of Λ_S estimated from quenching studies seems to be a function of the fundamental quenching rate. In the present case the quencher CCl_4 yields $\Lambda_S > 0$ for these polymers while for O_2 $\Lambda_S \cong 0$ is estimated. This will be discussed in more detail elsewhere.[7]

The phenanthrene–methacrylic acid copolymers may have anthracene moieties covalently attached by direct esterification (see the Experimental Section). Anthracene acts as a long-range trap for the phenanthrene singlet (R_0 = 2.2 nm[6]). We find the quantum efficiency for anthracene sensitization (χ) to be reasonably high for a-MPh (ca. 0.4) in organic and aqueous solution. These χ values in THF are similar to alternating naphthalene polymers.[3] On the other hand, the χ values in aqueous solutions are ca. 2× smaller than obtained for alternating naphthalene polymers.[4] Part of this difference may be attributed to self-quenching in phenanthryl polymers even in the absence of obvious excimer formation. Also the general photophysical properties of phenanthrene are more dependent on the environment than naphthalene. Thus elimination of excimer formation is not itself sufficient to ensure efficient photon–harvesting polymers.

Experimental Section

Materials. 9-Vinylphenanthrene (VPhen) and 9-anthrylmethyl methacryrate (AMMA) were synthesized according to the literature.[8,9] Methacrylic acid (MA) (Aldrich) and trimethylsilyl methacrylate (TMSiMA) (Petrarch Systems) were purified by distillation under reduced pressure. 9-Anthracenemethanol (Aldrich) was recrystallized from ethanol. Ethylaluminum sesquichloride ($Et_2AlCl{\cdot}EtAlCl_2$, Aldrich) was used as received. Carbon tetrachloride (spectrophotometric grade, MCB) was

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