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Concluding Remarks

(i) Elastic modulus of PAA gels increases with total comonomer concentration, at a fixed cross-linker weight fraction, as expected from scaling theories; moreover, successive additions of cross-linker above 5% do not improve the mechanical properties of the resulting gel; even more, they decrease, although this trend is not reflected on the ultimate properties (rupture elongation).

(ii) In the stress–strain isotherms, with either increasing C_T or C the upturn on the modulus becomes more pronounced, indicating a bimodal structure of the PAA gels. This non-Gaussian effect can be related to the previously reported heterogeneous structure of PAA gels.

(iii) The high values of the ratio M_c^{exp}/M_c^{th}, which is a measure of the cross-linking effectiveness and, therefore, of the network perfection, indicate a great degree of topological imperfections and inelastic structures. "Ideal" networks would be obtained only in the limits of high concentration and very low cross-linker percentage.

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Registry No. (Acrylamide)(*N,N'*-methylenebisacrylamide) (copolymer), 25034-58-6.

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Isotope Effect on the Melting Temperature of Nonpolar Polymers

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ABSTRACT: The isomorphous monoclinic (011) forms of "normal" (hydrogenated) and perdeuteriated hexatriacontanes (n-$C_{36}H_{74}$ and n-$C_{36}D_{74}$) have been examined by X-ray diffraction at room temperature. Substitution of deuterium for hydrogen results in slight reduction in the parameters $a_s = a \sin \beta$ and b of the orthorhombic subcell by 0.33 ± 0.02% and 0.19 ± 0.02%, respectively (within experimental error the c parameter appears to be unaffected). This reduction in cross-sectional area of the unit cell as seen in projection along the chain axis is primarily a consequence of C–D being slightly shorter than C–H bonds. Based upon the change in molecular volume, and an associated change in molecular polarizability, a relationship is proposed to account for the difference in melting temperatures of normal and perdeuteriated hexatriacontane. This relationship also predicts successfully corresponding differences in melting temperature occasioned by perdeuteriation of polyethylene and isotactic polystyrene but fails to do so in the case of isotactic polypropylene. We speculate that, in the latter case, isotope substitution influences rotational degrees of freedom of pendant methyl groups, leading to an isotope-dependent entropy of melting not experienced in the other species cited.

Introduction

In a series of recent publications[1-4] it has been shown that liquid mixtures of deuteriated and corresponding protonated polymers are characterized by a small but finite Flory–Huggins segment–segment interactions ($10^{-4} < \chi < 10^{-3}$) which under certain conditions may lead to phase separation. Such nonideal mixing has been attributed to the combined effects of zero-point motion ($h\nu/kT \sim 10$ for C–H vibrations at room temperature) and anharmonicity of interatomic potential energies, which together produce significant differences between C–H and C–D bonds in terms of bond length and polarizability. In this

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paper we present initial findings in a study of the influence of deuterium substitution upon crystalline nonpolar polymers (for present purposes we include monodisperse oligomers such as higher *n*-alkanes in the general term polymer).

There have been numerous reports over the past two decades describing the phase behavior of deuteriated and protonated crystalline polymers and their mixtures. To our knowledge, Stehling et al.[5] were the first to demonstrate that isotopic substitution can change the melting temperature of a polymer; perdeuteriated hexatriacontanes and polyethylenes were shown to be characterized by significantly lower melting temperatures than the corresponding "normal" (hydrogenated) species. Previously, Bank and Krimm[6] had concluded, from an infrared analysis, that mixtures of perdeuteriated and normal polyethylenes tended to segregate upon crystallization from the melt; this was subsequently verified by Schelten et al.[7] using the small-angle neutron scattering technique. These and other more recent results have firmly established that perdeuteriated and normal polyethylenes do not form ideal solid solutions. Such effects have been attributed to molecular weight differences,[6] chemical defects such as branching,[8] or polydispersity,[8] but explanation of the behavior or of associated differences in melting temperature have not so far been sought at a more fundamental level. In order to assess the impact of deuterium substitution on the crystalline state of polymers we have compared the lattice spacings of isomorphous crystals of perdeuteriated and normal hexatriacontanes by X-ray diffraction. Based upon arguments supported by our results, we conclude that the decrease in melting temperature with deuterium substitution in hexatriacontane derives primarily from the same isotope effect which has been shown elsewhere[4] to lead to phase separation in mixtures of liquid polymers. We further propose a relationship for the effect of isotope substitution upon melting temperature in nonpolar polymers which may have wide validity.

Experimental Section

Purified (zone-refined) hexatriacontane ($C_{36}H_{74}$) was kindly furnished by Dr. Harold Schonhorn. A differential scanning calorimetry (DSC) measurements obtained from approximately 6 mg of this paraffin at a heating rate of 1 K min^{-1} revealed three distinct thermal transitions, at 70.0, 73.2, and 75.7 °C, with a precision of 0.2 °C. Takamizawa et al.[9] report transition temperatures of 70.9, 74.0, and 75.9 °C for very high purity (>99.9%) $C_{36}H_{74}$ based on DSC measurements conducted at 5 °C min^{-1}, in good agreement with our values. The highest of these transition temperatures corresponds to the melting temperature while the lower two thermal transitions have been attributed to solid–solid phase transitions. Perdeuteriated hexatriacontane ($C_{36}D_{74}$) containing 99.4 atom % deuterium was obtained from MSD isotopes and used without further purification. DSC analysis of this material also carried out at a heating rate of 1 K min^{-1} yielded a melting temperature of 71.8 °C. There was also evidence of one, and possibly two, premelting transitions in the perdeuteriated paraffin, although the corresponding DSC peak(s) were considerably less pronounced than those found with the normal hydrocarbon. Within experimental error, the measured difference of 3.9 °C in melting temperatures between these isotopically different forms of hexatriacontane agrees with the 3.8 °C difference reported by both Stehling et al.[5] and English et al.[8]

Crystals of both normal and deuteriated paraffins were prepared by rapid cooling of 0.2% solutions in amyl acetate to room temperature, followed by filtering and drying of the precipitates. X-ray scattering powder patterns were first recorded on film by using a Guinier focusing camera of radius 57.3 mm which provided sufficient resolution to indicate small but systematic differences in lattice spacing, particularly of (h00) and (hk0) planes. Patterns for the two species were otherwise identical, both in terms of recorded lines and relative intensities. For more accurate measurement, crystals were packed in 2-mm thin-walled silica tubes and examined at high resolution by using a diffractometer on beamline X16C at the National Synchrotron Light Source at Brookhaven National Laboratory. A double-crystal Si(111) monochromator and Ge(111) analyzer were used at a wave vector ($2\pi/\lambda$) of 4.704 Å^{-1}. Diffraction from perdeuteriated and hydrogenated samples was compared at room temperature (±0.2 °C) by using a single instrumental setup, which had been calibrated with Si powder, thereby minimizing possible systematic error.

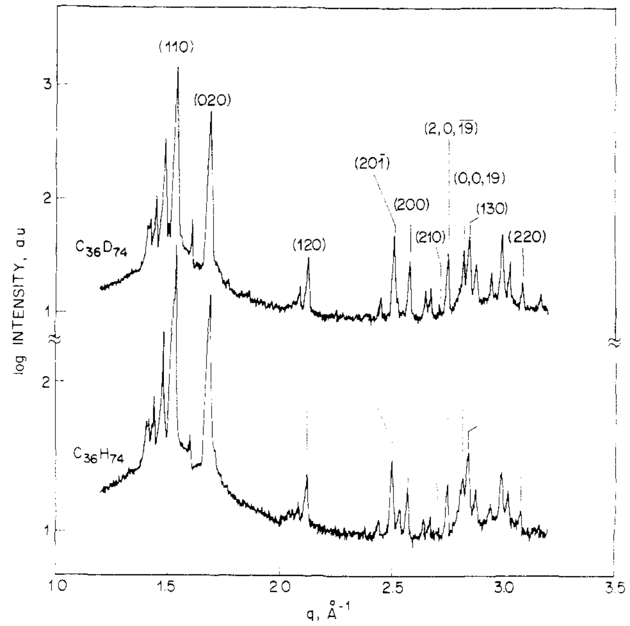

Figure 1. Comparison of the room-temperature X-ray scattering profiles for perdeuteriated (upper trace) and normal (lower trace) hexatriacontanes. The indicated reflections have been identified (Table I) on the basis of the monoclinic unit cell parameters and relative intensities reported by Shearer and Vand.[10]

Results

Powder patterns recorded for $C_{36}H_{74}$ and $C_{36}D_{74}$ in the Guinier camera were both closely consistent with the unit cell reported by Shearer and Vand[10] (a = 5.57, b = 7.42, c = 48.35 Å and β = 119.1°) for the monoclinic (011) form of n-$C_{36}H_{74}$. Crystals of this paraffin prepared in the same manner as used here were found by Khoury et al.[11] to be in the orthorhombic form. The difference may reflect the relative purity of the sample since, according to Takamizawa et al.[9] high purity hexatriacontane always crystallizes in the monoclinic form at room temperature.

High-resolution diffractometer traces are shown in Figure 1, the abscissa being $q = 4\pi\lambda^{-1}\sin(\theta/2) = 2\pi/d$, where θ is the scattering angle and d the corresponding lattice spacing. Our detailed analysis has been restricted to the reflections indexed which are mostly the prominent l = 0 lines; Table I indicates the measure of agreement in assignment and spacing with the monoclinic structure reported by Shearer and Vand. Other reflections have not been used either because of weak intensity or possible overlap or other ambiguity of assignment. Although the two traces in Figure 1 may appear indistinguishable, close examination shows that nearly all reflections from $C_{36}D_{74}$ occur at slightly larger values of q than their counterparts from $C_{36}H_{74}$. Two comparative examples are shown in Figures 2 and 3. In these expanded plots, background scattering has been subtracted and peak intensities adjusted to equality; asymmetry of profile is mostly due to instrumental effects,[12] which are essentially equivalent for both samples. It is evident that corresponding reflections are displaced along the q axis but can be brought into

Table I
X-ray Results for $C_{36}H_{74}$ and $C_{36}D_{74}$

	$10^2\Delta d/d$		$10^2\ \Delta d/d$	
hkl	SV[a]	present work[b]	measd[c]	calcd[d]
001	42.2	42 ± 1[e]		0
110	4.07	4.085	0.27 ± 0.02	0.288
020	3.71	3.720	0.19 ± 0.02	0.190
120	2.95	2.961	0.25 ± 0.03	0.242
200	2.43	2.443	0.33 ± 0.02	0.330
$20\bar{1}$	2.51	2.510	0.33 ± 0.02	0.338
210	2.31	2.320		
$2,0,\overline{19}$	2.29	2.286	0.13 ± 0.02	0.135
0,0,19	2.22	2.230		
130	2.20	2.211	0.24 ± 0.03	0.219
220	2.03	2.041	0.25 ± 0.04	0.288

[a] Calculated lattice spacings based on the monoclinic cell parameters reported by Shearer and Vand:[10] $a = 5.57$, $b = 7.42$, $c = 48.35$ Å, and $\beta = 119.1°$. [b] Lattice spacings measured for $C_{36}H_{74}$ by using the high-resolution X-ray diffractometer. [c] Percent change in lattice dimensions with deuterium substitution, determined by superimposing the corresponding $C_{36}H_{74}$ and $C_{36}D_{74}$ reflections, where $\Delta d = d_H - d_D$. [d] Based on the following change in unit cell parameters: $\Delta a_s/a_s = 1.0033$, $\Delta b/b = 1.0019$, $\Delta c = 0$, $\Delta\beta = 0$. [e] Estimated from several orders of the 001 spacing on the Guinier photograph.

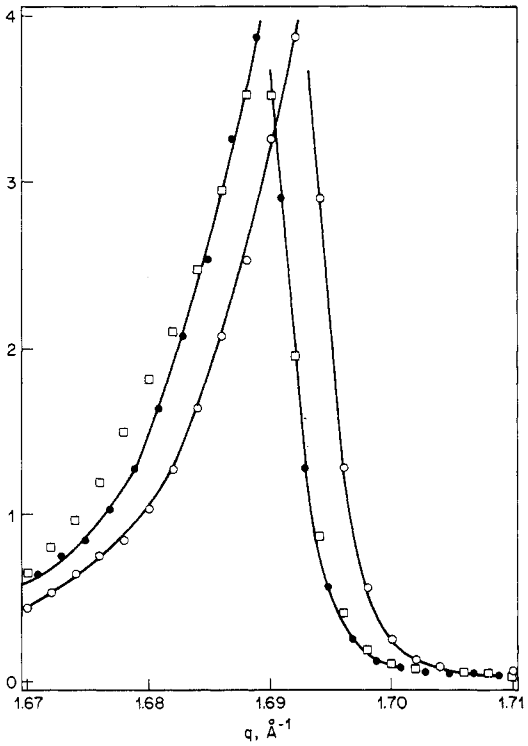

Figure 2. High-resolution X-ray trace of the 020 reflections from $C_{36}H_{74}$ (square symbols) and $C_{36}D_{74}$ (open circle symbols), where the background scattering has been subtracted and peak intensities adjusted to comparable levels. Solid curves have been sketched through the data points as a guide to the eye. Filled circles represent the $C_{36}D_{74}$ data superimposed on the $C_{36}H_{74}$ data by displacement (multiplication of q) along the axis. From this fitting procedure the change in 020 lattice spacing with deuterium substitution is determined to be $\Delta d/d = 0.0019 \pm 0.0002$.

coincidence by a translation (adjustment of q by a constant factor) from which a relative difference in spacing $\Delta d/d$ can be measured with fair accuracy. We were unable to adopt this approach with 210 and $0,0,\overline{19}$ reflections, however, because of dissimilarity in line shapes arising in the first case from weak intensity and in the latter from the presence of a stronger reflection nearby. Our results are listed in Table I. We conclude that parameters $a_s = a \sin \beta$ and b of the orthorhombic subcell of the monoclinic n-$C_{36}H_{74}$ are larger than those of the corresponding n-$C_{36}D_{74}$ by factors 1.0033 ± 0.0002 and 1.0019 ± 0.0002, respectively. We have been unable to measure directly the effect of deuterium substitution on the c parameter of the unit cell which might, in any event, be expected to be of a smaller order of magnitude. As indicated in the table, however, the measured change in the $2,0,\overline{19}$ spacing can be accounted for within experimental error assuming no change in either c or the monoclinic angle β. As we shall see presently, our results are reasonably consistent with expectation on the basis of a difference between C–H and C–D bond lengths of 0.005 Å as estimated by other methods.

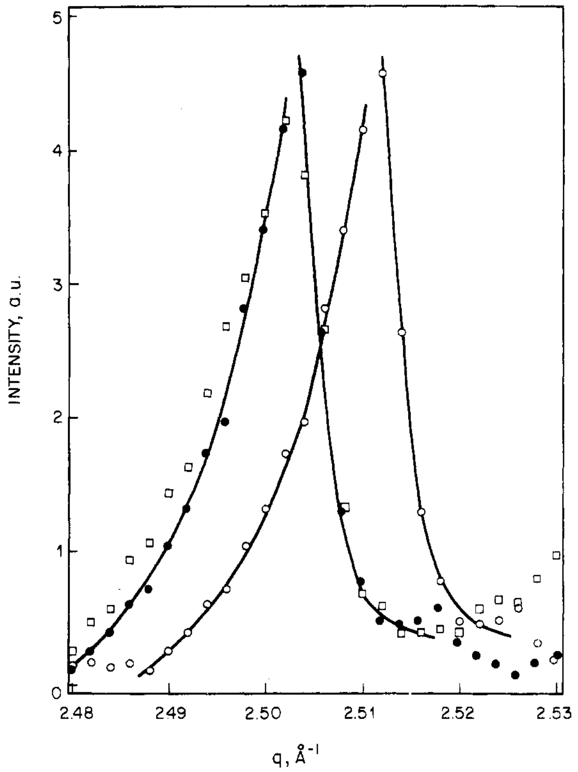

Figure 3. High-resolution X-ray trace of the 200 reflection from $C_{36}H_{74}$ (square symbols) and $C_{36}D_{74}$ (open circle symbols). The $C_{36}D_{74}$ scattering peak has been superimposed on the $C_{36}H_{74}$ reflection as specified in Figure 2, yielding $\Delta d/d = 0.0033 \pm 0.0002$ for the 200 lattice spacing.

Discussion

The carbon–hydrogen bond length in an organic molecule is proportional to the C–H interatomic spacing averaged over all vibrations. For the temperatures we are presently considering (~400 K) this bond length is essentially completely determined by ground-state (zero-point) vibrations. Substituting the more massive deuterium isotope for hydrogen leads to a slight decrease in bond length[13] as a consequence of the combined effects of the reduction in zero-point energy and the anharmonicity of the interatomic potential. For similar reasons single-crystal ^{22}Ne exhibits a smaller lattice constant than single-crystal ^{20}Ne, as elegantly shown by Batchelder et al.[14] However, in the case of monoatomic crystals governed by dispersion interactions, such as neon, the more massive isotope exhibits the *higher* melting temperature, in contrast with the behavior of the hexatriacontanes and other polymers.[5,15]

In the condensed state, the reduction in C–H bond length with deuterium substitution, $l_{C-H}-l_{C-D} \cong 0.005$ Å, is most obviously manifested as a decrease in molar volume in liquid hydrocarbons as shown by Bartell and Roskos.[16]

Table II
Isotope Effects on Simple Organic Liquids

	benzene	toluene	isoprene	cyclohexane
H/C	1	1.14	1.6	2
V_H, cm^3 mol^{-1}	88.867[a]	106.284[a]	100.14[b]	108.102[a]
V_D	88.626[a]	105.983[a]	99.92	107.737[a]
n_H	1.50110[c]	1.4961[d]	1.4219[b]	1.42630[c]
n_D	1.49911[c]	1.4942[e]	1.4189[b]	1.42181[c]
$\alpha_{C-H}\alpha_{C-D}$	1.0164	1.0146	1.0170	1.0181

[a] Reference 16. [b] Reference 33. [c] Reference 34. [d] Reference 35. [e] Reference 36. [f] Based on a reported[33] 97.5 atom % deuterium.

Four representative examples of this behavior, taken from the literature, are given in Table II. In separate publications[3,17] one of us has reported similar results for nonpolar organic polymer liquids. This volume isotope effect is certainly expected also to be apparent in nonpolar organic molecules in the solid state, although we are unaware of measurements other than those presently discussed which demonstrate this behavior. Our X-ray scattering results for the lattice parameters of normal and perdeuteriated crystalline hexatriacontanes confirm the expected analogy with the volume isotope effect exhibited by nonpolar organic liquids. We estimate a ratio of intramolecular cross-sectional areas perpendicular to the $C_{36}H_{74}$ and $C_{36}D_{74}$ chain axes of $A_H = 1.0039A_D$, in comparison with the ratio of measured areas, $(a_sb)_H = 1.0052(a_sb)_D$; these calculations are based on $l_{C-H}-l_{C-D} = 0.005$,[16] $l_{C-H} = 1.073$,[18] $a_{CCC} = 112°$,[10] $a_{HCH} = 104°$,[18] and $r_H = 1.2$ Å where l,a, and r_H refer to bond lengths, bond angles, and the atomic radius of hydrogen, respectively. Thus, the isotope-induced change in the crystalline dimensions of hexatriacontane appears to derive in large part from the change in C–H bond length, analogous to what occurs in the liquid state.

If the only consequence of replacing deuterium for hydrogen in nonpolar organic liquids were a reduction in molar volume, we would expect a corresponding *increase* in refractive index. Actually the opposite is true, as indicated in Table II, because reducing the C–H bond length concurrently decreases the bond polarizability, which results in a diminished molecular polarizability. Although this polarizability isotope effect has been recognized and studied for many years,[19,20] the only direct measurements of its magnitude that we are aware of have been conducted in the gas phase.[20] We estimate the ratio of C–H and C–D bond polarizabilities $\alpha_{C-H}/\alpha_{C-D}$ for condensed-state organic molecules by making use of the Lorentz–Lorenz relationship

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}N_A\frac{\alpha}{V} \tag{1}$$

for which the molecular polarizability is approximated from the individual bond polarizabilities,

$$\alpha = \tfrac{1}{3}\sum_{\text{bonds}}(\alpha_{\parallel} + 2\alpha_{\perp}) \tag{2}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ refer to the parallel and perpendicular components of the bond polarizabilities listed by Hirschfelder, Curtiss, and Bird.[21] The average of the four values calculated in this way, and listed in Table II, is $\alpha_{C-H} = 1.0165\alpha_{C-D}$, which is in good agreement with the measurement reported by Bell[20] for gas-phase methane, $\alpha_{C-H} = 1.01445\alpha_{C-D}$. As discussed below, we believe that the combined molar volume and polarizability isotope effects are primarily responsible for the melting temperature isotope effect in hexatriacontane and various other nonpolar organic polymers.

The melting of solids has been a subject of great interest and intense study for many years, and while there are numerous theories of melting, applicable to various classes of crystalline matter,[22] no single universal concept has emerged. Nevertheless within many groups of structurally related materials there exist correlations between melting temperatures.[22] Of these, the heavier noble gas elements are probably the most familiar. Here, the melting temperatures can be closely related by using the principle of corresponding states,[21] $T_m \sim \epsilon/k$, where ϵ is the Lennard-Jones energy parameter and k is the Boltzmann constant. The success of the corresponding states principle in the case of the melting of noble gases, and other compounds, can be traced in part to a constant entropy of fusion, and a single-crystal structure,[22] e.g., fcc in the noble gases. In general, the entropy of fusion represents the sum of positional (p), orientational (o), conformational (c), and other degrees of freedom gained upon melting,[22]

$$S_f = S_p + S_o + S_c + \ldots \tag{3}$$

For the noble gases there exists only positional entropy of fusion, which does not vary significantly between these elements. We believe that the corresponding states principle may also be applicable to nonpolar polymer isotopes. For such polymers S_f is almost completely determined by the conformational entropy S_C,[23] which should not change significantly with substitution of deuterium for hydrogen; this presumes that the carbon–carbon bond lengths and angles remain unchanged. As we have shown, the crystals of normal and deuteriated hexatriacontane are isomorphous with molecules in identical conformations. Thus, although the corresponding states principle has generally found application in systems characterized by strictly positional melting, we suggest that for nonpolar polymer isotopes $S_{f,H} \cong S_{f,D}$ owing to strictly conformational melting, and

$$T_{m,H}/T_{m,D} \cong \epsilon_H/\epsilon_D \tag{4}$$

Previously,[4] we have demonstrated that the polymer isotope effect in liquids can be accounted for based on the difference in bond polarizabilities and molar volumes using the London dispersion formula to describe the intersegmental forces,[21] $\phi_{DISP} \sim I\alpha^2/r^6$ where I is the segment ionization potential. Combining this with the attractive part of the Lennard-Jones potential, $\phi_{LJ} = 4\epsilon(\sigma/r)^6$, and noting that for hydrocarbons larger than ethane $I_H = I_D$ within 0.1%[18] yield

$$\frac{T_{m,H}}{T_{m,D}} \cong \left[\frac{\alpha_H}{\alpha_D}\frac{V_D}{V_H}\right]^2 \tag{5}$$

where $V \sim \sigma^3$ represents the segment core volume. Alternatively, the dispersion energy between polymer segments can be approximated by using the modified Slater–Kirkwood theory,[24] $\phi_{SK} \sim (N\alpha^3)^{\gamma}/r^6$, where N is the number of electrons in the molecular valence shell. Although the original theory prescribes $\gamma = {}^1/_2$,[25] Brandt[26] has shown empirically that for a wide range of spherically symmetric molecules $\gamma = 0.62$. Combining this with the attractive Lennard-Jones term and noting that $N_H = N_D$ lead to a result very similar to eq 5, the exponent for the polarizability ratio now being reduced to 1.86. Brandt also demonstrated that the estimated core parameters for the repeat unit of polyethylene fall on the same modified Slater–Kirkwood plot (log $N\alpha^3$ versus log $4\epsilon\sigma^6$) as the 14 simple molecules from which the exponent γ was determined, in support of our crude treatment of the dispersion energies for hexatriacontane. Based on the polarizability ratio obtained from Table II, $\alpha_{C-H}/\alpha_{C-D} = 1.0165 \pm 0.0015$, and assuming that the c unit cell parameter, parallel to the chain axis, is not affected by isotope substitution so

Table III
Nonpolar Polymer Melting Temperature Isotope Effect

polymer	T_m, K	$T_{m,H} - T_{m,D}$ exptl	α_H/α_D	V_H/V_D	$T_{m,H} - T_{m,D}$ calcd
hexatriacontane					
$C_{36}H_{74}$	348.6,[a,b] 348.9[c]	3.8; 4.0	1.01100	1.0052	4.0
$C_{36}D_{74}$	344.8,[a,b] 344.9[c]				
polyethylene					
$[CH_2]_n$	407.4,[a] 408.4[b]	4.9; 4.8	1.01100	1.0052	4.7
$[CD_2]_n$	402.5,[a] 403.6[b]				
i-polystyrene					
$[C_8H_8]_n$	488.2[d]	5.5	1.00627	1.0013	4.8
$[C_8D_8]_n$	482.7[d]				
i-polypropylene					
$[C_3H_6]_n$	440.2[e]	0	1.01100	1.0014	8.7
$[C_3D_6]_n$	440.2				

[a] Reference 8. [b] Reference 5. [c] This work. [d] Reference 15. [e] Reference 28.

that $V_H/V_D = 1.0052 \pm 0.0006$ (Table I), we calculate a difference in melting temperatures for $C_{36}H_{74}$ and $C_{36}D_{74}$ of 4.0 ± 1.0 using eq 5 and 3.5 ± 0.9 using the modified Slater–Kirkwood form, respectively. These values agree with the measurements of 4.0 ± 0.2 and 3.8 ± 0.2 °C (Table III), supporting our suggestion regarding the application of corresponding states to the polymer melting isotope effect.

We are aware of three additional pairs of polymer isotopes for which the melting temperatures have been published: perdeuteriated and normal polyethylenes,[5,8] isotactic polystyrenes,[15] and isotactic polypropylenes.[27,28] These are listed in Table III. The most extensive study of the polymer melting isotope effect has been conducted on polyethylene by Stehling et al.,[5] who examined the melting temperatures for both solution grown and rapidly melt cyrstallized isotopic specimens. They report that $T_{m,H} - T_{m,D} = 4.8$, in agreement with the melt-quenched value of 4.9 °C published recently by English et al.[8] Based on the chemical and structural similarity between polyethylene and hexatriacontane, we have used the value of V_H/V_D measured for hexatriacontane in calculating a melting temperature difference of 4.7 °C for polyethylene based on eq 5. For isotactic polystyrenes and polypropylenes there are no measurements of V_H/V_D. We have estimated the change in cross-sectional areas perpendicular to the chain axes with deuterium substitution on the basis of the previously quoted change in C–H bond length, using standard values for the carbon–carbon bond lengths and angles.[18] These estimates are given in Table III along with the calculated ratio of polarizabilities (again, see eq 1). With these parameters we have calculated the difference in melting temperatures listed in Table III using eq 5. The calculated difference lies within the expected uncertainty for isotactic polystyrenes but well outside the anticipated uncertainty in the case of isotactic polypropylenes. We now consider possible reasons for the latter discrepancy.

Our conjecture regarding the applicability of the corresponding states principle is based on the assumption that the entropy of fusion is dominated by an isotope-independent conformational entropy and that the crystal structure remains unaffected by isotope substitution. On the basis of our X-ray powder patterns of perdeuteriated and protonated isotactic polypropylenes, the latter condition appears to be fulfilled, in agreement with the neutron scattering results of Stamm et al.[25] However, the former assumption may not be satisfied for isotactic polypropylenes.

In general, the condition $S_{f,H} = S_{f,D}$ is not valid for simple organic liquids, owing to changes in the rotational degrees of freedom with isotope substitution, in both the crystalline and liquid state, near the melting temperature.[29] Even in the case of methane, the rotational degrees of freedom appear to be influenced by deuterium substitution.[30] Comparison of the entropies and heats of fusion for CH_4 and CD_4[30] reveals that the relative change in S_f with perdeuteriation is nearly as great as that for H_f. In contrast, for the noble gas elements S_f remains essentially constant while H_f increases with increasing mass.[31] Therefore, we do not expect eq 5 to be applicable to low molecular weight nonpolar organic molecules. This point can be illustrated by using the data for benzene given in Table II. Equation 5 predicts $T_{m,H} - T_{m,D} = 1.9$ °C, when actually the difference is −1.3 °C.[31] It should be noted that our arguments concerning the volume and polarizability isotope effect cannot accommodate any negative difference.

Although isotactic polypropylene does not have any significant *molecular* rotational degrees of freedom, each repeat unit does contain a rotating methyl group. Perdeuteriation may influence methyl group rotation in the melt and/or in the crystal, analogous to what occurs in methane,[30] thereby contributing a nonconstant term to the entropy of fusion. In this regard it would be interesting to examine the melting behavior of normal and deuteriated isotactic polypropylenes containing deuteriated and protonated methyl groups, respectively.

In future work we intend to examine further the validity of eq 5 by measuring the variations in lattice parameters and melting temperatures of additional isotopic nonpolar polymer pairs. While the simple empirical relationship we have proposed undoubtably neglects many fundamental and important features, we believe the qualitative assessment of this phenomena to be correct and anticipate that a more complete understanding of the polymer melting isotope effect will lead to insight into isotope effects in crystalline matter in general.

Summary

We have presented X-ray diffraction data for perdeuteriated and normal hexatriacontanes ($C_{36}H_{74}$ and $C_{36}D_{74}$) in isomorphous monoclinic forms showing contractions of $0.33 \pm 0.02\%$ and $0.19 \pm 0.02\%$ in the $a_s (= a \sin\beta)$ and b unit cell parameters, respectively, upon deuterium substitution. The change in cross-sectional area perpendicular to the chain axis derives primarily from the C–D bond length being smaller than the C–H bond length. A relationship is proposed for predicting the change in melting temperature with deuterium substitution in nonpolar polymers based on this reduction in C–H bond length and the associated decrease in bond polarizability. This simple relationship accounts successfully for reported differences in melting temperatures for perdeuteriated and normal hexatriacontanes, polyethylenes, and isotactic polystyrenes but fails in the case of isotactic poly-

propylenes. We suggest that the latter may reflect an isotope dependence on the rotational degrees of freedom available to the pendant methyl groups.

In conclusion, deuterium substitution influences lattice spacings in hexatriacontane, and presumably other nonpolar polymers, in a predictable way. We believe that the underlying changes in molecular volume and polarizability, which have been previously shown to lead to nonideal mixing in binary liquid isotopic polymers mixtures,[1-4] are also primarily responsible for the melting temperature isotope effect in these systems.

Registry No. $C_{36}H_{74}$, 630-06-8; $C_{36}D_{74}$, 16416-34-5; $[CH_2]_n$, 9002-88-4; $[CD_2]_n$, 25549-98-8; $[C_8H_8]_n$, 25086-18-4; $[C_8D_8]_n$, 108765-83-9; $[C_3H_6]_n$, 25085-53-4; $[C_3D_6]_n$, 108073-51-4.

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The Effect of Molecular Size on the Absorption Spectra of Macromolecules

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ABSTRACT: The applications of the theory of scattering of electromagnetic radiation to the estimation of the absorption coefficients of macromolecules yield values for the absorption coefficients that are considerably different from those obtained from the direct application of Beer–Lambert law. The differences in absorption coefficients can be explained in terms of the size and the optical properties of the macromolecules. This paper reports on the effects of the molecular size on the absorption spectra of macromolecules using as a basis the theory of electromagnetic radiation. As a result from this investigation, the conditions for the strict correspondence between Mie theory and Beer–Lambert law have been derived. A sensitivity analysis is conducted to define the limits of application of Beer–Lambert law and the conditions required to extract size information from transmission measurements in the region of intrinsic chromophore absorption. As case studies, the UV/vis spectra of well-characterized polystyrene standards have been investigated.

Introduction

The primary purpose of this paper is to examine in detail the effect of the molecular size on the absorption spectra of macromolecules in solution. This is achieved theoretically, through the use of the theory of electromagnetic radiation, and experimentally, through careful analysis of commercially available narrow molecular weight distribution polystyrene standards. The motivation for this study stems from the discrepancy found in literature reported values of the absorption coefficients of macromolecules and on the implications of such differences for the estimation of polymer compositions and polymer concentrations. The results from the investigation are particularly relevant to the characterization of macromolecules using spectroscopy techniques.

Absorption spectroscopy techniques are routinely used to investigate reaction kinetics and to determine the concentration and composition of macromolecules in chromatographic effluents. In these cases the spectra are recorded at frequencies where at least some of the chromophores present absorb strongly. According to Bouger and later to Lambert,[1] the decrease in intensity of incident light of any given wavelength on passage through an absorbing medium can be described as a first-order process proportional to the thickness (l) of the absorbing material[1,2]

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