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Deuterated Polymers: Chemical and Physical Properties and Future Prospects

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In this report the benefits derived from new materials based on fully deuterated polymers are assessed; the chemical and physical properties of deuterated polymers are reviewed exhaustively. The new properties of the deuterated polymers, according to the scientific literature, are identified and used to stimulate the production of new devices, technologies, products, and materials for special applications.

The literature search conducted

a. identifies each area of science in which deuterated polymers have been used,

b. identifies the purpose and results of such work, and

c. abstracts pertinent data on chemical and physical properties from the studies reviewed.

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Numerous tables compare the measured properties of a variety of polymers studied, and their deuterated and partially deuterated similarities are presented. Polymer properties related to optical fibers, pyrolytic and oxidative stability, structure, and neutron stopping power are discussed.

The goals of this review are to highlight the reported differences in properties between deuterated and undeuterated polymers. In some cases, the potential benefits of these differences will be clear; and indeed, some related work has been carried out with specific applications in mind. Generally, it is expected that the data will serve to suggest further development, or to provoke imaginative responses to existing materials needs.

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EXECUTIVE SUMMARY

The deuterium kinetic isotope effect is a well founded concept in experimental and theoretical chemistry [1]. Deuterium labeling of molecules is used routinely in chemistry to aid in understanding various reaction processes such as kinetics, reaction mechanisms, rearrangements and structures of ions and molecules, and for the interpretation of spectra from the chemical spectroscopies used to probe the reaction chemistry.

The deuteration of molecules can change the chemical and physical properties of the molecules significantly. These new properties of the molecules can be used advantageously to produce new materials. For example, researchers at the Navy laboratories (Naval Air Development Center and NRL) have shown that the oxidative stability of lubricant base stocks is increased remarkably (5-to-10 fold) upon full deuteration [2]. Exploratory Development Programs are underway in these laboratories to demonstrate the payoff of using such deuterated materials in selected oil-lubricated mechanical systems. In an effort to decrease the potential cost and to improve the quality of deuterated materials, researchers at NRL have also been investigating techniques of biotechnology to manufacture deuterated materials. For example, algae grown in heavy water (D_2O) will be fully deuterated. The deuterated fatty acid-containing lipids, which are 30 to 70% dry weight of the algae, can be extracted from the algae, and the deuterated fatty acid moieties can be used to synthesize deuterated lubricant molecules. Other organisms could be used to produce different biochemicals, which can be used to produce deuterated materials other than lubricants economically.

The purpose of this report is to suggest and stimulate other practical applications of the deuterium isotope effect and of deuterated materials. Specifically, we chose to review and summarize the open literature on deuterated polymers in which there is a wealth of data, although limited to only a few chemical systems and materials applications.

Generally, over 10 properties of deuterated polymers are reviewed, summarized, and discussed in this report. Some of them, such as the discussion on optical transmission, are very applied. Optical transmission characteristics of deuterated polymers can be exploited in optical fiber telecommunications; and in fact, there are several patents in this area. But, there has been no apparent applied interest of deuterated polymers, other than in telecommunications. However, with emerging technologies, the increased resistance to degradation (oxidative and thermal) of deuterated polymers suggests that deuterated polymers may be useful in some space applications. Also, the tremendous increase in the neutron stopping-power (~700 times) of deuterated polymers (relative to undeuterated) should be of considerable interest to the nuclear power community.

The primary goal of this report is to present and discuss the numerous published experimental observations on the properties of deuterated polymers in one report which may be used as a reference to those involved in materials science. It is our intention to stimulate interest, research—both fundamental and applied, as well as to stimulate futuristic foresight of those in the research and development community.

DEUTERATED POLYMERS: CHEMICAL AND PHYSICAL PROPERTIES AND FUTURE PROSPECTS

INTRODUCTION

Objectives

This report assesses the benefits of new materials based on fully deuterated polymers. A literature search was conducted to

(a) discover each area of science in which deuterated polymers have been used,

(b) identify the purpose and results of such work, and

(c) abstract pertinent data on chemical and physical properties from these studies.

The goals of this review are to highlight any reported differences in properties between deuterated and undeuterated polymers. In some cases, the potential benefits of these differences will be clear. Indeed, some work has been carried out with a specific application in mind. In other cases, it is expected that the data will serve to suggest further development or to provoke imaginative response to existing materials needs.

Methods and Scope

Often, an observation made in the course of research in one topic will raise implications in another area of research. For this reason, a thorough examination has been made of every area that used polymers, whether they were completely deuterated or deuterated at specific sites. In many instances, deuterated polymers have been prepared and studied for a number of different purposes.

The body of data that was uncovered has been organized so that implications for the future may be most readily discerned. Data pertaining to the properties of each specific polymer have been brought together for discussion. Although it has not been necessary to present every study that has used a deuterated polymer or to discuss in detail the principal results of each study that has measured properties of deuterated polymers, the potentially more significant work is discussed in some depth, and, if worthwhile, the background information has been provided to help illuminate the more suggestive research. Data from more than 100 primary literature sources have been included.

It is beyond the scope of this report to make proposals for further work based on the information presented; however, there are many factors that need to be considered before any specific application can be pursued reasonably. They include demand, cost, and possible alternatives. The reader is encouraged to interpret the data according to pertinent background information. Specific conclusions should not be drawn, although suggestions or conclusions already reported in the literature are presented. The intention of this report is to make the significant information accessible to research and development planners in materials science.

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Theoretical Basis for Isotope Effects

Effect of Mass Change on Vibrational Frequencies

When deuterium replaces protic hydrogen in a chemical bond, the stretching vibrational frequencies of the bond are affected directly, and since deuterium has a greater mass, the vibrational frequencies are reduced. The reduction is by a factor almost exactly proportional to the ratio of the square root of the masses, or about 1.4. Those molecular vibrations that involve hydrogen to any extent, will usually have frequencies greater than 2×10^{13} s^{-1} (700 cm^{-1}) [1]. Deuteration has been applied extensively to polymers to help interpret the infrared spectra by measuring the shift in vibrational frequencies.

Effect of Vibrational Frequency Shift on Bond Strength and Reaction Rate

The lowest energy level for any bond, called the zero-point energy, is $E_0 = 1/2(h\nu)$, where h is Planck's constant and ν is frequency. The zero-point energy may be understood as the vibrational energy of the bond at 0 K. At room temperature, typically >99% of bonds are at the zero-point energy. Because the vibrational frequencies for carbon-deuterium (C-D) bonds are lower than for carbon-hydrogen (C-H) bonds, the zero-point energy is lowered by substituting deuterium. The difference in the zero-point energies may be calculated by using the frequencies obtained by infrared spectroscopy which may be of 1.2 to 1.5 kcal/mole [1]. The dissociation energy is the difference between the zero-point energy and the energy of the two dissociating moieties at infinite distance; hence, the dissociation energies of C-D bonds are greater than C-H bonds, and the bonds are more stable.

Deuterium substitution can also have an impact on rate processes [1]. The absolute rate theory describes the rate of reaction as a function of the concentration of the activated complex and its rate of passage over the potential energy barrier. The potential energy curves of C-H and C-D bonds are similar; therefore, the lower zero-point energy of C-D bonds will result in a lower rate of reaction. The ratio of rate constants can be described in simplified terms by the following Eq. (1),

$$\frac{k_H}{k_D} = e^{(h\nu_H - h\nu_D)/2RT}, \tag{1}$$

assuming that

(a) nonreacting bonds are not affected in the reaction,

(b) the activated complex involves no bonds to H or D, and

(c) temperatures are below 400° to 500°C.

The theoretical maximum isotope effect can thus be calculated at various temperatures (see Table 1). The values shown in Table 1 are the maxima because according to assumption (b) above, the rupturing bond is completely broken in the activated complex. Often experiments find, in contrast to assumption (b), that deuterium remains partly bound in the activated complex; therefore, the maximum isotope effect on rate processes is not observed.

A third contribution to the general lower reactivity of bonds to deuterium is the possibility of nonclassical tunneling through the potential energy barrier. As predicted, tunneling occurs less probably for deuterium than for hydrogen [1]. It has been shown that a large isotope effect exists in the tunneling of the α-CD_3 group of poly(methylmethacrylate-d_8) (PMMA-d_8) compared to that of α-CH_3 in PMMA [3].

From the values of deuterium isotope effects shown in Table 1, it is clear that the effect on reaction rates may be greater than the proportional shift in vibrational frequencies, which is about 1.4.

Table 1 — Maximum Value of the Deuterium Isotope Effect for One Stretching Vibration as a Function of Temperature

Bond	ΔE_0, cal	Temperature (°C)	k_H/k_D
C-H	1150 (1100-1200)	0	8.3
		25	6.9
		100	4.7
		200	3.4
		300	2.7
		500	2.1 (approaches 1.4 in high temperature limit) [1]

However, at temperatures of 400° to 500°C and above, the theoretical isotope effect k_H/k_D will approach 1.4; this has been experimentally shown [1].

Deuterium isotope effects may be applied to advantage. It has been determined, through experiments, that isotope effects can yield important information about reaction mechanisms, and deuteration has been applied extensively in this area. Experiments have also determined that kinetic isotope effects can be large when the rate determining step of the reaction being studied involves loss of hydrogen. An example of this type of reaction is the oxidation of hydrocarbons by O_2 which is called autoxidation. Deuterium substitution has thus been applied to increase the stability of lubricants [2]. Observations of large deuterium isotope effects have been reviewed to stimulate potential industrial applications [4]; those observations involve polymers and are discussed in this report.

PROPERTIES OF DEUTERATED POLYMERS

Visible and Infrared Transmission

The vibrational frequencies of carbon-deuterium bonds are lower than the frequencies of carbon-hydrogen bonds by a factor of about 1.4. Thus deuterium substitution changes the vibrational absorption of light. The effect of deuteration on optical properties of polymers can be viewed in two different ways, and each of the two has practical significance:

a. Absorptions are shifted to longer wavelengths. The absorption of a specific bond can be identified by observing its shift after deuterium has been substituted.

b. A new transmission window is opened in the red and near infrared region. Absorptions are shifted farther into the infrared region, so that deuterated polymers have better optical transmission in the 500 to 900 nm region.

Recently, the latter effect has been applied in the preparation of plastic optical fibers (POFs) with low-transmission loss. To use POFs effectively in data transmission applications, the transmission should be increased in the 600 to 900 nm region, where some high output power light-emitting diodes (LEDS) operate [5]. It is possible that new materials for optical windows, coatings, or lenses can be similarly developed to take advantage of the increased infrared transmission of deuterated polymers.

The increased transmission (or reduced attenuation) of plastic optical fibers is one of the most dramatic examples of a deuterium isotope effect on polymer properties. Attenuations can be reduced by a factor of 10 or more, depending on the choice of wavelength and manufacturing precision. Of all

the potential materials applications of deuterated polymers, this application is the one whose development shows the most progress to date.

Optical fibers transmit light through the length of a transparent filament by multiple internal reflections of light. Fibers made entirely of glass, of glass clad with plastic or of plastic have been designed and tested. The core material must be designed to minimize losses due to absorption or scattering, while the cladding material is chosen to have a lower refractive index than the core to produce internal reflections. The light transmitted via an optical fiber might come from a light-emitting diode, a laser, or from an infrared-emitting diode.

Optical fiber transmission is ideal for voice signals, video signals, and analog or digital data signals in high-capacity information systems. Wide bandwidths can be transmitted with low loss. In 1966 the best fibers were made of glass; however, these showed attenuations of 1000 decibels per kilometer (dB/km) or more. At that time, 20 dB/km was thought to be the limit of achievable attenuation [6]. (A decibel is a dimensionless measure of signal transmission through a conductor; it may also refer to signal loss. The measured signal is compared to a reference signal, and the base 10 logarithm of their ratio is multiplied by 10 to yield the decibel value).

Fiber manufacturing methods have improved to the point where glass fibers that have attenuation of less than 10 dB/km are commercially available. In experimental work, attenuations of less than 1 dB/km have been achieved [7]. At present, fibers must have attenuations of less than 10 dB/km to be competitive with conventional transmission systems [8]. Glass fibers are made of high silica-content glass or multicomponent systems. The region of greatest interest for achieving low attenuations lies between 500 to 1400 nm, where economical semiconductor and laser light sources operate [9]. Glass fibers have their lowest attenuations in the 1000 to 1200 nm region [10].

Optical fibers prepared from plastic offer some important advantages over glass fibers:

(a) ease in handling due to light weight and good ductility;

(b) ease of splicing to light sources and other fibers due to large core diameters and high numerical aperture; and

(c) lower cost (hydrogenated) [5].

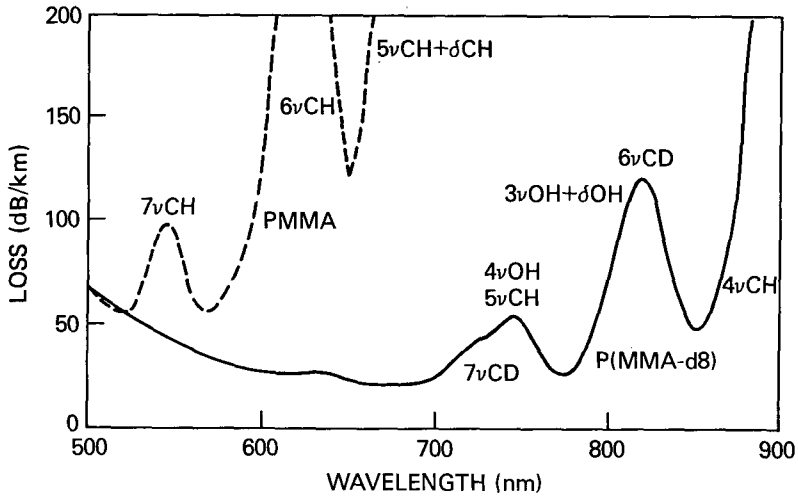
Polystyrene (PS) and polymethylmethacrylate (PMMA) have been used as core materials of plastic optical fibers. These materials are optically transparent but tend to attenuate light more strongly than glass. Both PS and PMMA show attenuation levels above 300 dB/km. Of the two, PMMA has superior mechanical properties and chemical resistance to environmental conditions [11] and has received more attention for its potential as a deuterated POF.

The factors which contribute to the transmission loss are presented in Table 2. Control of extrinsic factors has been instrumental in lowering the attenuation of both glass and plastic fibers. The greatest single factor in transmission loss of the POFs is the vibrational absorption of C-H bonds. Therefore, by substituting deuterium, this absorption in the near infrared region can greatly be reduced or eliminated. A new optical window is created for hydrocarbon polymers at about 650 nm, which is near the peak output wavelength of the high output power GaAlAs LED. Figure 1 shows the shift in vibrational frequencies caused by substituting deuterium.

Figure 1 compares the transmission loss spectra of PMMA and PMMA-d_8 in the 500 to 900 nm region. Figure 2 shows that adjacent to the $7\nu_{CH}$ peak of PMMA there is no vibrational component in the loss spectrum. In the corresponding region of the PMMA-d_8 loss spectrum, at 650 to 680 nm, there will be virtually no vibrational loss. Only Rayleigh scattering and structural imperfections will contribute to transmission loss.

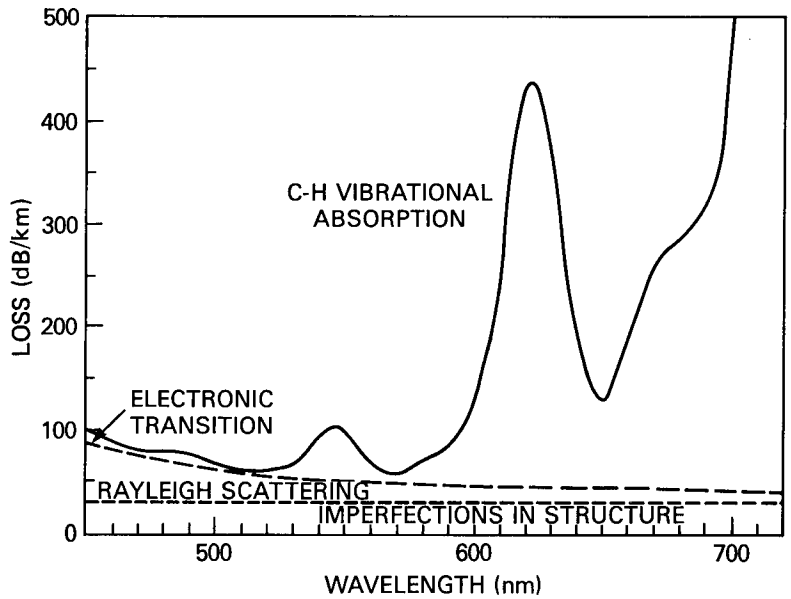
Table 2 — Loss Factors for Plastic Optical Fibers

Factors	Transmission Loss	
	Intrinsic	Extrinsic
Absorption	Higher harmonics of C-H vibration	Transition metals
		Organic contaminants
Scattering	Rayleigh scattering	Dust and microvoids
		Fluctuation in core diameter
		Orientation birefringence
		Core-cladding boundary imperfections
	adapted from Ref. 5	



FROM APPLIED PHYSICS LETTERS VOL. 42, 1 APRIL 1983, NO. 7 BY T. KAINO, FIGURE 2 ON p. 568, COPYRIGHT © 1983, USED BY PERMISSION.

Fig. 1 — Transmission loss spectra of PMMA and PMMA-d_8, 500 to 900 nm [11]



FROM APPLIED PHYSICS LETTERS VOL. 42, 1 APRIL 1983, NO. 7 BY T. KAINO, FIGURE 1 ON p. 567, COPYRIGHT© 1983, USED BY PERMISSION.

Fig. 2 — Loss factors for PMMA core plastic optical fibers [5]

Reports of the attenuations shown by normal and deuterated POFs are compiled in Table 3. To date, four patents for the preparation of deuterated POFs have been issued: three by Japan and one by the United States.

Plastic Optical Fibers (POF) manufacturing processes can be expected to improve in a fashion similar to the manufacture of glass fiber, so that POF transmission loss will approach the theoretical limit imposed by Rayleigh scattering. Loss limits for PMMA optical fibers are listed in Table 4.

It is of interest to note that deuteration has contributed to the very low attenuations of glass fibers achieved experimentally [7]. The absorption by O-H bonds also contributes to the transmission loss; therefore, it is very important to exclude H_2O from glass fibers and POFs. A patent has been issued to prepare glass fibers from deuterated silicates [12]. It has also been shown that absorbed water can reduce the transmission in PMMA-d_8 in the 650 to 750 nm region. Soaking the fiber in D_2O, however, can actually increase transmission slightly [13].

The use of POFs, now available, is limited; they are employed as light monitors and displays in automobiles, and image guides in endoscopes (instruments used to visualize the interior of body cavities) [11]. The use of POFs for data transmission applications covering 10 to 50 m or more, such as computer-terminal links, is made possible by substituting deuterium for hydrogen in the fiber core [11]. By the use of PMMA-d_8 core POFs, data transmission up to 1000 m is feasible in combination with economical connections and light sources [5].

New infrared absorption bands are created by incorporating deuterium into a compound. Carbon-deuterium absorption bands enable a deuterated material to be identified in complex mixtures. A new patented method for the determination of sulfonate surfactants in the complex petroleum and brine mixtures found in enhanced oil recovery efforts makes use of the new absorption band at 6.45×10^{12} s^{-1} (2150 cm^{-1}) [21]. The sulfonate surfactant is based on oligomeric polyethylene oxide to which a partially deuterated hydrocarbon moiety is bonded. No other component of the mixtures in which this surfactant is to be used shows infrared absorption at 2150 cm^{-1}. The other components include

Table 3 — Attenuation of Light by Plastic Optical Fibers

Basic Research				
Fiber Core Material	Wavelength (nm)	Attenuation (dB/km)	Maximum Data Transmission Distance (m)	Ref.
PMMA	518 567 650	57 55 128[a]	N/A	[5]
PMMA-d_8	650	<300[a]	100	[14]
PMMA-d_5[b]	565 646	41 55	400	[15]
PMMA-d_8	650,680 780 850	20[a] 25 50	1300	[5,11,16]
PMMA-d_8	647	18	N/A	[13]
PS	762	114	N/A	[5]
PS-d_8 (reduced attenuation reported, unpublished results)				[15]
Patents for Deuterated POFs				
PMMA-d_8	690 790	150-200 150-200	N/A	[17] (U.S.)
PS-d_8	575-855	<250	N/A	[18] (Japan)
PMMA-d_8	650	50	N/A	[19] (Japan)
PMMA-d_8	660	30	N/A	[20] (Japan)

[a] Extrinsic factors in fiber manufacture have resulted in different attenuations observed for the same wavelength region.
[b] The methoxy group is undeuterated.

Table 4 — PMMA Core Optical Fibers; Loss Factors and Loss Limits at 646 to 680 nm

Core Material	Wavelength (nm)	Absorption (dB/km)	Rayleigh scattering	Loss Limit (dB/km)	Ref
PMMA	650	88	12	100	[5]
PMMA-d_5[a]	646	24	12	36	[15]
PMMA-d_8	680	0	10	10	[11]
PMMA-d_8	680	0	10	10	[5]

[a] The methoxy group is undeuterated.

crude oil, lignosulfonates, salts, water, petroleum sulfonates, and alcohol. This method for the infrared determination of deuterated sulfonate surfactants in enhanced oil recovery fluids [21] demonstrates the potential analytical application of deuterated materials.

Stability Against Degradation

It has been well established that deuterium substitution results in greater bond strength, because of the lower zero-point energy of bonds to deuterium. In principle, therefore, the stability of a deuterated polymer can be greater than that of its hydrogenated counterpart. To investigate this possibility, a number of studies have been conducted to measure deuterium isotope effects on various degradation processes. Also, researchers have used selective deuterium substitution to make the degradation mechanisms clear. Many observations of isotope effects on polymer stability have been reported.

Measurements of isotope effects on thermal, oxidative, photolytic, and radiolytic processes in deuterated polymers have been compiled and are presented in Table 5. The data was obtained through an exhaustive search of the literature on the reactive stability of deuterated polymers.

Table 5 — Isotope Effects on Polymer Stability[a]

(a) Thermal Stability

Isotope Effect	Measured Quantity	Deuterated Polymer	Reaction Conditions	Ref.
1.7	HCl elimination	PVC-d_3	180°C, N_2	[32]
2.7	HCl elimination	PVC-d_3	180°C, N_2	
6	HCl elimination	PVC-d_3	180°C, N_2	[25]
6	HCl elimination	PVC/PS-d_8	N/A	[27]
≈ 1	(pyrolysis	PS(α-d)	350-390°C	[33]
≈ 1	products)	PS(β-d)	350-390°C	
≈ 2	molecular weight	PS(α-d)	350-390°C	[33]

[a] Notation:

- Sites on polymer backbone:

  $-(-\overset{\beta}{\underset{\beta}{|}}-\overset{R}{\underset{\alpha}{|}}-)\underset{n}{-}$; $d_3 = \alpha, \beta, \beta$

- PVC Polyvinylchloride
  PS Polystyrene
  PP Polypropylene
  PE Polyethylene
  PMMA Polymethylmethacrylate
  PVA Polyvinylalcohol

- Isotope Effect = k_H/k_D for rate processes,
  Q_D/Q_h for time of induction period.

Table 5 — Isotope Effects on Polymer Stability (Continued)

(b) Oxidative Stability

Isotope Effect	Measured Quantity	Deuterated Polymer	Reaction Conditions	Ref.
≈5	UV absorption at 340 nm	PS($\alpha - d$)	60°C, air, UV radiation	[34]
≈4 ≈4	UV absorption at 340 nm	PS($\alpha - d$ vs $\beta - d$) PS($\alpha - d$)	60°C, air, post-UV dark reaction	[35]
1 1 2.5 3 7 20	Time of induction period; by carbonyl infrared absorption	PS PS($\beta - d$) PS($\alpha b - d_2$) PS($\beta\beta - d_2$) PS($\alpha - d$) PS($\alpha\beta\beta - d_3$)	175-230°C, O_2 also 65-154°C, O_3	[36]
5.8 ± 0.8	Uptake of O_2	PS($\alpha\beta\beta - d_3$)	210°C, O_2	[37]
2.5	Time of induction period	PP($\alpha - d$)	100-140°C	[38]
4.26 3.88 3.50	Carbonyl Infrared absorption	PP($\alpha - d$) PP($\alpha - d$) PP($\alpha - d$)	100°C 115°C 130°C	[38]
2	Uptake of O_2	PVC-d_3	180°C, O_2	[26]
17	HCl elimination	PVC-d_3	180°C, O_2	[26]
1.6	HCl elimination	PVC-d_3	180°C, O_2, w/1.0% free radical scavenger	[25]
3.4	HCl elimination	PVC-d_3	180°C, O_2, w/1.0% free radical initiator	[25]
4.4	Autoxidation rate	PVC/PS-d_8	N/A	[27]
7.5	Induction period	PVC/PS-d_8	N/A	[27]

Table 5 — Isotope Effects on Polymer Stability (Continued)

(c) Photolytic Stability

Isotope Effect	Measured Quantity	Deuterated Polymer	Reaction Conditions	Ref.
1.9 ± 0.2	Autoxidation rate	PS($\alpha\beta\beta - d_3$)	80°C, UV	[37]
2.1 1.8	Yield of free radicals	PE-d_4 PP-d_6	UV radiation	[39]
2.4	Rate of radical transformation	PE-d_4, PP-d_6	230-310 K, post-UV dark reaction	[39]
≈5	UV absorption at 340 nm	PS($\alpha - d$)	60°C, air, UV radiation	[34]
≈4	UV absorption at 340 nm	PS($\alpha - d$ vs $\beta - d$) PS($\alpha - d$)	60°C, air, UV radiation	[35]

(d) Radiolytic Stability

Isotope Effect	Measured Quantity	Deuterated Polymer	Reaction Conditions	Ref.
1.5 ± 0.1	Autoxidation rate	PS($\alpha\beta\beta - d_3$)	γ-radiation	[37]
4.3 4.0 5.9	Evolution of HD gas	PS($\alpha - d$)/PMMA PS($\beta - d$)/PMMA PS($p - d$) PMMA	γ-radiation γ-radiation γ-radiation	[40]
5-7	Evolution of all D gases	PS($\alpha, \beta, p - d$)/PMMA	γ-radiation	[40]
2 2	Yield of free radicals	PP-d_6 PE-d_4	γ-radiation, 77°K	[41]
1.6	Yield of D vs H	PE-d_4	16 MeV electons	[42]
1	Yield of D vs H	PVA(O-d)	γ-radiaion, 12°C	[43]
2.27	Yield of D vs H	PVA(O-d)	γ-radiation, −196°C	[43]

Table 5 — Isotope Effects on Polymer Stability (Continued)

(e) Summary of Observations

1.	Reactivity $\alpha > \beta$ position toward free radical H abstraction	[35,36]
2.	Isotope effect on autoxidation rate is cumulative	[36]
3.	γ-radiation not selective for reactivity	[40]
4.	PS, PP, PE induction periods for onset of autoxidation: 2.5-7.5 times	[36,38,27]
	20 times	[36]
5.	PS, PP, PE autoxidation rates 1.5-6 times lower:	
	Initiation by exposure to O_2	[37,26]
	UV radiation	[35,34,37]
	γ-radiation	[37]
	high temperature	[33]
6.	Free radical production: UV, γ, e- 1.5-2 times less	[41,42,43,39]
7.	Uptake of O_2 by PVC 2-4.4 times less	[26,27]
8.	Elimination of nonmonomer moieties:	
	HCl by PVC 2-6 times less	[32,25,27]
	17 times less	[26]
	D-containing gas, 4-7 times less under γ-radiation	[40]
	Yield of D, 1.6 times less under γ-radiation	[42]

Degradation Processes

All polymers are susceptible to degradation initiated by a host of environmental factors and agents. To improve the resistance of synthetic polymers to degradation is of utmost importance for many applications, and the prevention of degradation has been the focus of extensive research. The aim of this research has been to elucidate degradation mechanisms and to devise means to inhibit or counteract those mechanisms. Very often, several processes may be at work simultaneously in a complex combination that is difficult to resolve.

The transfer of energy from a number of sources can cause degradation of polymer properties. The input of energy can be from heat, light (especially ultraviolet radiation), high-energy radiation (x-rays, γ-rays, fast particles), mechanical processes, and supersonic and ultrasonic waves. Polymers can react chemically with solvents, atmospheric oxygen, gaseous pollutants, and ozone, and they can be attacked by microorganisms. Other processes that have been studied recently include ignition, flame propagation, and ablation.

The loss of important structural properties may proceed through different mechanisms:

(a) random chain scission leading to a drop in molecular weight;

(b) depolymerization, releasing monomer units;

(c) carbonization, or elimination of small nonmonomer moieties; and

(d) reaction of side chain groups [22].

The processes of thermal and oxidative degradation have been studied intensively. Deterioration from these causes can take place in actual applications and during polymer processing at elevated temperatures. Attack by molecular oxygen, called autoxidation, is known to proceed through free radical chain reactions and generalized as [23]:

Initiation	production of free radicals	(1)
Propagation	$R\cdot + O_2 \rightarrow RO_2\cdot$	(2)
	$RO_2\cdot + RH \rightarrow ROOH + R\cdot$	(3)
	$RO_2\cdot + RH \rightarrow ROORH\cdot$	(4)
Termination	$RO_2\cdot + RO_2\cdot \rightarrow$	(5)
	$R\cdot + RO_2\cdot \rightarrow$	(6)
	$R\cdot + R\cdot \rightarrow$	(7)

(5)–(7): nonradical products

Because the absorption of light or the irradiation with high-energy rays or particles can produce free radicals, photolytic and radiolytic processes can be very important considerations in stabilization against autoxidation. Thermal decomposition in the absence of other reactants or pyrolysis, is also an important aspect in the study of polymer degradation.

Current methods for stabilizing polymers against autoxidation include the addition of chain-breaking antioxidants that react with peroxy radicals, preventive antioxidants that decompose peroxides, or synergistic combinations of the above. Crystallinity will decrease the diffusion of oxygen and thus inhibit autoxidation, but isotacticity can increase fast intramolecular propagation of free radical reactions. Branching and cross-linking increase the rate of oxidation by increasing the number of reactive tertiary hydrogens. In nonoxidative degradation, however, cross-linking and copolymerization are effective stabilizing schemes [23].

The effects of light can be reduced by incorporating ultraviolet absorbers, antioxidants, excited-state quenchers or by using light-screening compounds. Radiolytic processes are nonspecific because of their high energy, relative to bond energies, and they cannot be inhibited directly [24].

It has been well established that hydrogen atom abstraction from the substrate by peroxy radicals (Reaction 3 above) is the most important, and the rate-limiting step in autoxidation [23]. The kinetic isotope effect from deuterium substitution can thus increase a polymer's stability against autoxidation, because C-D bonds do not rupture as easily as C-H bonds. Structure modifications that replace weak C-H bonds with nonisotopic substituent bonds of higher dissociative energies, for example C-F, do improve thermal stability but lead to changes in polymer properties [24].

Discussion: Trends in the Data

Table 5 shows all the currently published (to our knowledge) reports of kinetic isotope effects on polymer stability. The principle of improving polymer stability by deuteration has been shown with polystyrene (PS), polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC) and polymethylmethacrylate (PMMA). The observations are summarized in Table 5e.

The largest improvements in thermal and oxidative stability come from deuterium substitution at tertiary sites (α-substitution). However, complete deuteration of polystyrene resulted in even larger isotope effects. Some trends are evident in the study of polystyrene and polyolefins:

- In temperature ranges of 60°C to approximately 200°C, induction periods for the beginning of autoxidation are lengthened by roughly 3 to 7-fold. One report of an increase of 20-fold is described.
- Rates of oxidative degradation proceeding by free-radical propagation are reduced by roughly 1.5 to 6-fold. These effects may be seen during exposure to oxygen, γ-rays or elevated temperature, or during post-reactions, which follow exposure to ultraviolet (UV) radiation.
- Generation of free radicals due to irradiation by UV light, γ-rays, or high-energy electrons is reduced by roughly 1.5 to 2-fold. (It is known that high-energy radiation is not selective, so the greater the degree of deuteration the greater the effect [22].)

Deuterium isotope effects are temperature dependent. For example, when temperatures were raised from 100° to 130°C, the relative autoxidation rate of poly(propylene-d_6) decreased from 4.26 to 3.50. At temperatures 350°C (662°F) or higher, isotope effects on thermal and oxidative stability of polystyrene were reduced to insignificant levels.

The thermal and oxidative stability of polyvinylchloride (PVC) has been improved by perdeuteration. The rate of oxygen uptake is reduced by a factor of 2. The rate of HCl elimination is reduced by roughly 2 to 6-fold in nitrogen atmosphere and by 17-fold in an oxygen atmosphere.

An important study was conducted on PVC and PVC-d_3. The rates of HCl elimination from films containing either 1% of free radical initiator (benzoperoxide) or 1% of free radical inhibitor (hydroquinone) were measured in oxygen atmosphere at 180°C [25]. Without additives, the ratio of HCl elimination from PVC compared to PVC-d_3 was 17 [26]. In the presence of a free radical initiator, both HCl elimination rates went up, while the ratio of rates was reduced to 3.4. In the presence of a free radical inhibitor, HCl elimination was reduced in the normal PVC to a far greater extent than in the PVC-d_3; the isotope effect was still evident, but it was reduced to 1.6. The elimination of HCl is the principal decomposition pathway in PVC. However, many of the factors involved in the thermal degradation of PVC have not been elucidated or are the subjects of controversy even after years of study [24]. The benefits of adding antioxidant to PVC to reduce rates of HCl elimination are comparable to the benefits obtained by substituting deuterium for hydrogen in PVC-d_3. This observation suggests that deuterium substitution might be comparable to antioxidant incorporation as a means of stabilizing polymers.

Deuterated polymers might offer benefits in cases where the chemical properties of a hydrogenated polymer are required, but not where incorporation of additives in the material is not desirable. For example, deuteration might fill a need where antioxidants cannot be employed.

The presence of hydrogenated sites or hydrogenated chain segments does not necessarily eliminate the benefits of deuteration toward thermal and oxidative stability: vinylchloride-h_3 copolymerized with styrene-d_3 or styrene-d_8 showed reduced rates of HCl elimination similar to those in PVC-d_3 [27].

The principle of improving stability via deuteration could be applied to any vinyl polymer whose backbone has secondary or tertiary hydrogen sites. Resistance to free-radical initiation and propagation, as well as resistance to elimination of labile substituent groups or atoms, will result. For example, it has been asserted that poly(vinylidene-d_2 fluoride) (PVF_2-d_2) will prove to be more stable toward dehydrofluorination than PVF_2 [28].

Deuterium substitution as a new method of improving polymer stability has been the basis of a few patents. A patent was issued by the Deutsch Democratic Republic (East Germany) in 1971 for the improvement of the thermal stability of polyvinylchloride-polystyrene graft copolymers by using styrene-d_3 or styrene-d_8 as a comonomer [27]. The deuterated copolymers that resulted showed a 6-fold reduction in rate of splitting off HCl, a 4.4-fold reduction in autoxidation rate, and a 7.5-fold longer induction period for the uptake of O_2.

Dibenzyl succinate, a model lubricant or model plastic material, was used to demonstrate the improved stability by deuteration at specific sites [29]. An autoxidation rate reduced by a factor of 5 is reported for two selectively deuterated compounds. The addition of a conventional antioxidant resulted in an overall reduction of oxygen uptake rate by 40-fold. A patent for improving stability, as shown in this work, was granted by Romania in 1968 [29]. A similar patent was granted to the same researchers by East Germany in 1965 [30].

The work with dibenzyl succinate indicates that deuteration may be effective in improving polyester stability. The major isotope effect would be exerted through β-substitution, as in succinate compounds:

$$-CD_2CH_2-OOCCH_2CH_2COO-CH_2CD_2-$$

It is known that in the degradation of polyesters, of which dibenzyl succinate is a model compound, stability is increased by replacing the β-hydrogens of the alcohol moiety [31].

Pyrolysis Studies

Pyrolysis, the thermal degradation of polymers in the absence of other reactants, is a process that can be studied effectively with deuterated materials. The transfer of a deuterium label during pyrolysis reactions can be determined by mass spectrometry (MS), infrared (IR) or nuclear magnetic resonance (NMR) spectroscopy, and other methods. The results can be used to infer pyrolysis mechanisms. In general, these investigations do not concern themselves with isotope effects; it is an important assumption that bonds to H and D behave similarly. It is significant to note that at high temperatures, 400° to 500°C (750° to 930°F) or more, theoretical maximum kinetic isotope effects of H vs D reduce to a value of 1.4 [1].

Table 6 summarizes some examples of pyrolysis studies that use deuterated polymers. Isotope effects on the reactions were not reported.

Secondary Isotope Effects: Coupling with C-C Bonds

Only kinetic isotope effects on hydrogen abstraction reactions have been considered until now. These are called primary isotope effects, because the isotopic label is directly involved in the reacting bond. Because of their importance in the autoxidation processes, hydrogen abstraction reactions have necessitated numerous measurements of the primary isotope effects.

It is a known fact that vibrational coupling takes place between adjacent bonds; therefore, when deuterium is substituted for hydrogen in a polymer, the vibrational behavior of the adjacent carbon-carbon bond of the polymer backbone may be affected. As a result, the bond strength of the C-C bond may be increased, because the effective mass of the CD group at one end of the rupturing bond has

Table 6 — Deuterium Substitution in Polymer Pyrolysis Studies

Polymer	Analytical Method	Temperature (°C)	Ref.
Poly(propylene-d_3)	MS, IR, NMR	340	[44]
Poly(acrylonitrile α-d)	IR	200	[45]
Poly(methylmethacrylate-d_5	MS	180	[46]
Polyurethane based on poly(propylene-d_3 oxide)	MS	800	[47,48]
Methylmethacrylate-d_5 copolymer with α-methyl styrene	GC-MS	480	[49]
Styrene-d_8 copolymer with styrene	GC[a]	510	[50]

[a] GC: Gas Chromatography

been increased. A so-called secondary isotope effect on C-C bond stability may result from deuterium substitution.

Secondary isotope effects are not as important as primary isotope effects, and experimental experience has shown that their effects on reaction rates are generally small. For example, secondary deuterium isotope effects on solvolysis reactions do not exceed 1.25 [51]. No secondary isotope effects were reported in the studies of polymer reactivity listed in Table 5.

Vibrational coupling with adjacent bonds can be measured through the study of infrared spectra of labeled polymers. Such studies infer increases in C-C bond strength. In some studies, researchers have reported that deuterium substitution affects C-C bond behavior. Vibrational coupling with C-C bonds have been reported in the infrared spectra of poly(acetylene-d_2) [52], and in selectively deuterated polybutadienes [53].

Quenching of the Fluorescence of a Dissolved Probe Compound

A new method for the study of surface temperature profiles uses deuterated polymethylmethacrylate [54]. The technique is expected to be useful in the design and test of integrated circuits, since it can give detailed information about local power dissipation in these devices. The PMMA-d_8 acts as a support film for a fluorescent probe (Europoium Thenoyltrifluoroacetonate, EuTTA) whose fluorescence quantum efficiency depends on temperature.

The temperature dependence of fluorescence intensity from excited EuTTA molecules is increased by a factor of 2 after substituting PMMA-d_8 for PMMA-h_8. The deuterated polymer allows a greater change in fluorescence intensity to result from the changes in surface temperature. The sensitivity of temperature measurements is thus increased by a factor of 2. The authors do not describe the reasons for this difference.

The EuTTA has a strong UV absorption band centered at 350 nm. Fluorescent radiation is emitted in a narrow line at 612 nm. This wavelength is in the region where PMMA-d_8 absorbs less strongly than PMMA. However, it is not clear whether the diminished quenching of PMMA-d_8 is due to an isotope effect on collisional fluorescence quenching or to a lower level of absorption of the emitted radiation.

This method of surface temperature measurement has been used to prepare fluorescent images for commercial MOSFET devices with and without applied voltages. The images were used to evaluate the operation of the integrated circuits. Spatial resolution of 15 μm and temperature resolution of 0.01°C were reported.

The authors assert that this technique offers better resolution, simpler procedures, and simpler interpretation than other currently available methods for surface temperature methods. In an experiment with an extremely thin metal strip on a glass surface, spatial resolution was reduced to 0.7 nm at a temperature resolution of 0.08°C. This resolution approaches, for the first time, the dimensions of state-of-the-art integrated circuits [55].

The authors consider the fluorescence-based technique to be the basis for a new photothermal microscopy with unprecedented sensitivity. Future work will use fluorescent compounds with nanosecond relaxation times in an attempt to make time-resolved temperature measurements.

Microstructure Imparted by Isotope Effects on Polymerization Mechanisms

A decrease in sequence defects in the polymer chain [28] was caused by an isotope effect on the polymerization of vinylidene-d_2 fluoride. Normal polyvinylidene fluoride (PVF_2) may have 3.5 to 6% of its monomer units reversed, thus creating head-to-head and tail-to-tail defects, which is experienced because of a free radical addition mechanism that is not regiospecific. In PVF_2-d_2, however, monomer reversal was found to be 2.84%, because the radical structure $-CD_2CF_2$ is preferred. This may be the first observation of an isotope effect on sequence distribution in a polymer chain [28].

The piezoelectric and pyroelectric behavior of PVF_2 have prompted considerable interest in this polymer. It is anticipated that PVF_2 with no sequence defects, or a decrease in this number, will show changes in its electronic properties. At this point, physical properties of PVF_2-d_2 such as melting point, density, and molecular weight have been measured, and the NMR spectra have been used to demonstrate the decrease in sequence defects. However, comparison of electronic properties has not been reported yet. The data on the physical properties of PVF_2-d_2 are presented in Table 7.

Table 7 — Properties of Poly(vinylidene-d_2 fluoride)

	1.0% Initiator		0.1% Initiator	
	PVF_2-d_2	PVF_2	PVF_2-d_2	PFV_2
Melting Point, by DSC[a]	185.1	109.9	188.3	179.5
Intrinsic Viscosity, in DMF 125°C	2.8	0.45	4.1	2.6
Density	1.840	1.792	1.860	1.770
Temperature (°C) of 10% Weight Loss by TGA[b]	—	490	497	—
Percent Reversal, by ^{19}F NMR	2.86	3.45	2.83	3.46

[a]DSC: Differential Scanning Calorimetry [28]
[b]TGA: Thermogravimetric Analysis

The average molecular weights of PVF_2-d_2 were significantly higher when calculated from the intrinsic viscosity. After compensating for the mass of deuterium in PVF_2-d_2, the density was still 1.80 compared to 1.78 for PVF_2, suggesting a higher degree of crystallinity due to a more regular chain structure. The increase in melting point on deuteration is interpreted as evidence for higher crystallinity.

Thermodynamic Quantities

Changes in thermodynamic quantities resulting from deuteration are presented in Table 8. Properties of polymers in both the solid phase and in solution have been measured. In general, the greater the carbon-deuterium bond strength is, the weaker CD····DC interactions are. Reduced melting points, flow temperatures, and glass-transition temperatures are attributed to weaker Van der Waals forces in the deuterated material [56]. These reductions are in the order of 5° to 9°C. Polymer solubility in solvents is increased for the same reason.

Since C-D bond energies are greater than C-H bond energies, quantities such as heat capacity, enthalpy, and entropy are increased by deuteration. The heat capabilities of both poly-(styrene-d_8) and poly(ethylene-d_4) show increases of about 20% over a broad temperature range.

The relationship between glass-transition temperatures of normal and deuterated polystyrene reverses when the film is subjected to stress. The significance of this observation is not clear [57]. Without stress, the PS-d_8 shows a lower glass-transition temperature, as it is expected.

Hydrogen Bond Strength

Hydrogen bonding plays an important role in stabilizing the α-helix of polypeptides. In the study of helix-coil transformations of dissolved poly(β-benzyl L-glutamate) (PBLG), as it has been shown, N-deuteration results in an overall increase of about 5% in polymer stability [64], (see Table 7). The same factors that increase covalent bond strength to deuterium also result in greater hydrogen bond strength following deuterium substitution.

Solutions of PBLG have been important model systems for the study of liquid crystalline polypeptides. At high concentrations in selected solvents, the rigid, extended α-helical conformation is reordered to a liquid crystalline phase that shows distinctly different properties [68]. Because of the participation of hydrogen bonding along the amide backbone in forming the α-helix, N-deuteration has been used as a means for studying the conformational changes. Isotope effects in this phenomenon are detected as changes in the temperature of transition. The isotope effect is more pronounced when a protic solvent is used, because the solvent must interact with the labile deuterium bond to disrupt the helical structure [64].

Neutron Scattering Power

The coherent neutron scattering length of hydrogen (a_H) is -0.374×10^{12} cm, while that of deuterium (a_D) is $+0.667 \times 10^{12}$ cm. The scattering power K^2 is found from the equation:

$$K^2 = a_D - a_H(V_D/V_H); \quad V \text{ is the partial molar volume.}$$

The value of K^2 is a measure of the contrast that can be obtained between deuterated and hydrogenated polymers in small angle neutron scattering experiments. The scattering power of deuterated polystyrene, for example, is 700 times larger than that of normal polystyrene in carbon disulfide solution [69].

Table 8 — Thermodynamic Quantities of Deuterated Polymers

(a) Solid Phase

		Ref.
Melting Point (°C)		
PE-d_4: 130.4	PE: 135.2	[58]
PE-d_4: 122.5	PE: 126	[56]
PS-d_8: 209.5	PS: 215	[59]
PVF-d_2: 185.1	PVF_2: 180.9[a]	[28]
Flow Temperature (°C)		
PE-d_4: 116	PE: 120	[56]
Heat Capacity		
PE-d_4 > PE by ≈20%, 80-310°K		[60]
PE-d_8 > PS by ≈20%, 7-330°K		[61]
Enthalpy		
PS-d_8 > PS by 3.5 kJ/mol		[61]
Entropy		
PS-d_8 > PS by 20 kJ/mol		[61]
Free Energy		
PS-d_8 > PS by 2.5 kJ/mol		[61]
Enthalpy of Mixing		
PBD-d_6 > PBD mixed with PS, by 0.2 kJ/mol styrene, 1:1 mixture		[62]
Side-Chain Conformational Energy		
PMMA-d_8 > PMMA, by 600 cal/mol, at temperatures below glass transition		[63]

Notation:

[a] PVF_2-d_2 shows greater regiospecificity than PVF_2, probably resulting in greater crystallinity and an anomalously high melting point.

Table 8 — Thermodynamic Quantities of Deuterated Polymers (Continued)

Glass Transition Temperature (°C) with Stress [57]					
Stress (kg/cm^2)	0	30	70	120	180
PS-d_8	91	85	80	70	60
PS	100	91	83	66	45

(b) Solution Phase

Temperature of Helix-Coil Transition in $CHCl_2COOH/Cl_2Et$	
PBLG(N-d): 297°C PBLG(N-h): 272°C	[64]
Enthalpy of Helix-Coil Transition in $CHCl_2COOH/Cl_2Et$	
PBLG(N-d) > PBLG, by 42 ± 5 cal/mol Residues (5% relative to PBLG)	[64]
Interaction Coefficient, in Toluene	
PI-d_8: .415 PI: 398	[65]
Temperature in C_6H_{12} (°C)	
PS-d_8(115,000 MW): 30 PS (130,000 MW): 35	[66]
Solubility in Solvents	
PS-d_8 more soluble; showed higher R_f in TLC using solvent	[67]
Notation:	
PE: Polyethylene PVF_2: Polyvinylidene fluoride PS: Polystyrene PBD: Polybutadiene PMMA: Polymethylmethacrylate PBLG: Poly(β-benzyl L-glutamate) PI: Polyisoprene	

Recently, many deuterated polymers have been prepared to take advantage of this difference in neutron scattering power. These materials serve as solvents that provide high neutron scattering contrasts for dissolved hydrogenated polymer analogs. Small angle neutron scattering (SANS) analysis can provide information about conformation of polymers in solution and in the bulk state. The SANS technique gives direct insights of the many aspects of polymer morphology that have been inaccessible until now. For this reason, the preparation of new deuterated polymers will continue. For example, a new synthesis of poly(ethylene-d_2 oxide) with narrow molecular weight distribution was developed primarily for SANS applications [70]. It is possible that new materials applications could evolve following such syntheses, if new properties are observed in the new deuterated polymers.

Segregation of Isotopically Labeled Chains

During small angle neutron scattering (SANS) analyses of single polymers and polymer blends, it was discovered that segregation of isotopically labeled chains takes place [71]. In SANS methods, a material is "dissolved" at 5% or lower levels in its deuterated analog. In many cases, deuterated and undeuterated polymer chains are found to be inhomogeneously dispersed in the blended solid phase. SANS is very sensitive to inhomogeneity of dispersion, and interpretation of data is made more difficult by the segregation or clustering phenomenon.

The origin of these clusters is now under study and is being debated intensely because of the analytical implications. The dominant view is that they arise strictly from thermodynamic differences acting on crystallization rates during phase separation from melts or solutions [58, 72, 73, 74]. A theoretical examination found that partial miscibility between deuterated and undeuterated chains is a distinct possibility, but that it would depend on the polymer used and should only begin to appear for very large molecules. This second-order effect would be different than the larger first-order effect of selective partitioning between phases. The effect would be maximized in equimolar solutions. The lower vibrational frequencies of C-D bonds may cause a larger stabilization energy for C-H than for C-D in the polymer solutions. Hydrogen-hydrogen interactions would be slightly more stable than deuterium-deuterium interactions (shorter distances CH···HC than CD···DC) [75]. This hypothesis was concluded from the data obtained from the mixing of poly(butadiene-d_6) and polybutadiene with polystyrene [62] (see Table 7). The enthalpy of mixing was found to be 0.2 kJ/mol lower for PBD, thus indicating more stable CH···HC than CH···DC interactions.

Most studies of isotopic clustering have been conducted with polyethylene. Deuterated polyethylene is known to have a lower melting point and can be expected to crystallize at a different rate. Zones of isotopic enrichment have been observed in polyethylene through various techniques. These reports are noted in Tables 9 and 10. It has been shown that rapid cooling from the melt can retard the formation of isotopic clusters [73], as can cross-linking induced by irradiation prior to crystallization [72]. These data support the view that isotopic clusters form during polymer crystallization.

Table 9 shows the principal results from studies of polymer blend systems involving deuterated polymers. Cases where isotopic clustering was observed are also indicated. The SANS technique has great implications for the study of polymer blends. To help assess the potential of blends, composites, and graft copolymers composed of deuterated and undeuterated polymers, a more detailed discussion of SANS methods may be found in the appendix of this report. In Table 10, representative SANS studies of single polymer systems are shown. Cases of isotopic clustering are likewise indicated.

Conductivity

Polyacetylene, a long chain polyene, is being studied intensively as a result of its remarkable electrical properties. The electrical conductivity of polyacetylene films can be increased over twelve orders of magnitude by doping. Depending on the choice of dopant (electron acceptors or donors), both p-type and n-type semiconductors can be prepared [89]. Many experimental studies have been

Table 9 — Neutron Scattering Studies of Polymer Blends

Blend System	Isotopic Clustering	Principal Results and Comments	Ref.
PS*/PαMS		Direct evidence for statistical distribution of two polymers in a compatible system (SANS)	[76]
PS*/PXE		Study of the effect of bromination of the aromatic ring on the compatibility of a system known to be compatible (SANS)	[77]
PS/Noryl		Demonstration of true compatibility at the chain segmental level (SANS)	[78]
PBD*/PS	X	Difference in heat and entropy of mixing between PBD-d_6 and PBD blended with PS was observed (by pulse induced critical light scattering apparatus)	[79]
PS*/PVME	X	Cloud point curves showed different stability parameters for PS-d_8 vs PS blended with PVME	[80]
PS*/PBD		Cloud point curves practically identical for PS-d_8 and PS blended with PBD.	[81]

* — This component is a mixture of perdeutero and normal polymer

Notation:

PS — polystyrene

PαMS — poly (α-methyl) styrene

PXE — poly(xylenylether); (2,6-dimethyl-1,4-phenylene oxide)

Noryl — commerical name for poly(2,6-dimethyl-1,4-phenylene oxide)

PBD — polybutadiene

PVME — poly(vinyl methylether)

Table 10 — Neutron Scattering Studies of Single Polymer Systems

Polymer	Isotopic Clustering	Principal Results and Comments	Ref.
PS		Radius of gyration determined	[82]
PMMA		Dependence of radius of gyration on temperature and concentration determined	[83]
PS		Conformation in bulk polymer compared to conformation in solvent	[84]
isotactic and atactic PS		Dimensions, conformation, and behavior in bulk solution were studied	[59]
PE		Mechanisms of deformation on compression and annealing studied at various temperatures	[85]
PEO	X	Found evidence for inhomogeneous regions in PEO-d_4/PEO crystallized from the melt	[86]
PS,PE	X	Demonstration of capability of SANS technique	[71]
PE	X	Solution and melt-grown crystals differ; evidence for chain folding into lamallae with adjacent reentry; segregation phenomena described as "not an insuperable hindrance"	[72]
PE	X	Segregation attributed to phase diagram of PED/PEH on melt crystallization; rate of crystallization affects degree of segregation	[73]
PE,PEO,PS		Examination of several aspects of scattering theory	[87]
PDMS		Determination of second virial coefficient and radius of gyration	[88]

Notation:

PS: polystyrene
PE: polyethylene
PEO: polyethylene oxide
PDMS: polydimethylsiloxane
PMMA: polymethylmethacrylate

carried out to more fully characterize the electronic structure of polyacetylene. Vibrational spectra have been very important for the identification of molecular structures in polyacetylene.

Deuterated polyacetylene has been prepared for a variety of spectroscopic analyses aimed at characterizing its electronic structure. Shifts in the infrared [90-92], Raman [52, 92, 93], visible, electron spin resonance (ESR) [94], and nuclear magnetic resonance (NMR) [95] spectra have been studied in pristine and doped poly(acetylene-d_2). Vibrational absorptions, which are shifted by deuterium substitution, are considered to be closely connected with electrical conductivity in doped polyacetylene [92]. However, measurements of conductivity in poly(acetylene-d_2) have not been reported. The principal results of spectroscopic studies on poly(acetylene-d_2) are compiled in Table 11.

Several different theories concerning the electronic states in conjugated polymers have been put forth, but the issue has not yet been completely resolved. The molecular orbital theory, which involves overlap of π orbitals, has been applied. Localized bond alternation defects have been postulated. Also, extended lattice defects or solitons have been described. These are considered to be spread over a number of -CH- units. At the center of the soliton domain, the sign of the bond alternation is reversed, thus forming an electronic kink. The soliton model, though it explains some phenomena well, has not yet gained universal acceptance and is undergoing considerable investigation. Neutral defects are present in pristine polyacetylene; dopants induce a larger number of charged defects; and the transport mechanism responsible for the conductivity is not yet clear [98].

In general, isotope effects are non-electronic in nature [99]. One would not expect the electronic distribution of poly(acetylene-d_2) to be significantly different than that of polyacetylene. Although there is a complicated interplay between nuclear and electronic motions, to a good approximation these are resolved into separate energies [12]. It is conceivable that an isotope effect could be present in doped polyacetylene, if dopant-induced electronic oscillations couple with C-D vibrations differently than with C-H vibrations, as has been asserted [97]. But whether or not an isotope effect on conductivity can occur, it is likely that the effect would be small compared to the effect of p-type or n-type dopants, which can vary the conductivity over many orders of magnitude.

Poly(acetylene-d_2) is not the only deuterated conducting polymer whose properties have been investigated. The conductivity of deuterated poly(p-phenylene) was measured after doping with AsF_5, and it was found to be lower than that of normal doped PPP by a factor of 14 [100]. However, the authors attribute this difference entirely to the substantial difference in molecular weight of the two polymers. An isotope effect on polymerization lowered the molecular weight of the PPP-d_6.

Mechanical Properties

Poly(isoprene-d_8), deuterated synthetic natural rubber, was prepared with the aim of comparing its various performance properties to those of polyisoprene [65]. The physical properties of the deuterated rubber were measured, and, based on the differences in boiling point and interaction coefficients in solution, better dynamic behavior for the deuterated material was predicted [65]. Less polymer-polymer interaction was expected. However, tensile strength and percent elongations at break were found to be nearly identical [101]. Studies on properties such as thermal and oxidative stability, gas permeability, and reinforcement by pigments were proposed, but results were not reported. X-ray diffraction studies showed the crystal structures to be identical [65, 101].

A series of model poly(ester urethanes) was N-deuterated to study the effect on mechanical properties. However, the stress-strain diagrams of the N-D materials were not altered from the corresponding N-H stress-strain diagrams [102].

Table 11 — Spectroscopic Studies of Deuterated Polyacetylene

Polymer[a]	Analytical Method	Principal Results and Comments	Ref.
C_2H_2/C_2D_2 copolymers	IR	Dopants induce perturbed domains over more than one monomer unit. Calculations based on soliton theory account for IR shifts very well.	[91]
$(CH)_x$, $(CH)_x$, C_2H_2/C_2D_2 copolymers	IR, Visible	Absorption bands due to charged soliton-induced vibrations were shifted in $(CD)_x$. At 160 K, new bands appeared; these were affected by deuteration.	[90]
C_2H_2/C_2D_2 copolymers	Raman, IR	Conjugation lengths of up to 100 C=C bonds were found in trans $(CH)_x$.	[92]
$(CD)_x$, $(CH)_x$	Raman	Most frequent C=C conjugation length is 30 bond lengths; broad distribution about this value. C-C stretching modes shifted due to large C-D contribution.	[52]
$(CD)_x$, $(CH)_x$	Raman	Conjugation lengths vary from 10 to 100 CH units.	[93]
$(CH)_x$, $(CD)_x$	ESR	Deuteration caused narrowing of line widths. Both polymers show $\approx$1 free electron per 6000 C atoms.	[94]
$(CD)_x$	NMR	Spin-lattice relaxation times in $(CD)_x$ similar to those in $(CH)_x$.	[95]
$(CD)_x$, $(CH)_x$	Raman, IR	Dopant-induced bands show isotopic shifts; dopants affect vibrations both at the dopant site and along the polymer chain.	[96]
$(CH)_x$, $(CD)_x$	IR	Dopant-induced band may result from interaction between charge oscillaton and molecular vibration.	[97]

[a] $(CH)_x$ = polyacetylene
$(CD)_x$ = poly(acetylene-d_2)

The glass transition temperature (Tg) of poly(styrene-d_8) was lower than that of polystyrene (91°C compared to 100°C—see Table 7). This is the expected result, based on thermodynamic considerations. However, as applied stress was increased to 180 kg/cm^2, the glass transition temperature of PS fell below that of PS-d_8 (45°C compared to 60°C). The authors draw no conclusion concerning isotope effects on mechanical properties from these data [57].

The viscoelastic relaxation of PMMA-d_8 was studied at temperatures between −200 and +50°C in an attempt to detect quantum mechanical tunneling of $-CD_3$ and $-CH_3$ groups on the polymer backbone [103]. Both PMMA-d_8 and PMMA were studied by high-precision torsional pendulum, vibrating reed, and ultrasonic techniques to obtain data on viscoelastic relaxations at vibrational frequencies of 0.2 to 10 Hz, 2×10^2 to 2×10^4 Hz, and 10^6 to 10^8 Hz, respectively. Evidence for methyl group tunneling was present in the methyl relaxation, and a large isotope effect in the methyl relaxation was also observed.

Viscoelastic relaxation in PMMA had previously been identified as due to rotational motion of the backbone methyl group. The temperature dependence of viscoelastic energy dissipation in PMMA yields information about quantum mechanical tunneling, and also about isotope effects on tunneling. The rotational tunneling frequencies of PMMA-d_8 were predicted to be shifted to lower frequencies at less than −100°C, and this was observed experimentally. At less than −200°C, CD_3 rotational tunneling frequencies are more than two orders of magnitude lower than CH_3 frequencies. If classical rotation were the only relaxation mode available, there would be no isotope effect observed. The researchers assert that this is the first observation of an isotope effect in the field of polymer mechanical properties [103]. This isotope effect, which is evident only below −100°C, is an alteration in the mechanical energy dissipation mode of stretched (vibrating) PMMA, and arises solely because of quantum mechanical tunneling.

Gas Permeability

The diffusion of gases through deuterated polymethylmethacrylate has been measured with a new technique [104]. The polymer film is irradiated by high-energy particles which cause splitting off of various small molecules and which then diffuse out of the film and are detected by a mass spectrometer. The technique has not yet been applied to normal PMMA, and the results have not been compared to diffusion rates for PMMA measured by other methods.

Measurement of the gas permeability of deuterated polyisoprene was a goal of the researchers who prepared this material [65], but results were not reported.

Density

Deuterium substitution increases the density of a polymer. The increase is usually due entirely to the greater mass of the $^2H_1$ isotope (see Table 12). After correcting for the greater mass of deuterium, poly(vinylidene-d_2) fluoride showed a slightly higher density than normal PVF_2 (1.80 vs 1.78 g/cm^3). This difference is attributed to a higher degree of crystallinity resulting from a fewer number of sequence defects in the PVF_2-d_2 chain [28].

Poly(ethylene-d_4) shows one of the highest deuteron densities of a variety of deuterium-containing compounds, including solid deuterium, D_2 [105]. Deuterium-containing polymer targets are used in applications where the main consideration is to have a high density of deuterium atoms in an appropriate support. These polymer films are used for particle bombardment to produce neutrons via the $D(d,n)^3He$ reaction. A number of studies discuss target films made from poly(ethylene-d_4) [106-108], poly(styrene-d_8) [107, 109, 110], and deuterated polyvinylchloride or polycaprolactam [110].

Table 12 — Densities of Deuterated and Undeuterated Polymers

Polymer	Densities, g/cm^3	Ref.
Polyisoprene	0.907	[65]
Poly(isoprene-d_8)	1.005	[65]
Polystyrene	1.047	[57]
Poly(styrene-d_8)	1.127	[57]
Polyethylene	0.95	[116]
Poly(ethylene-d_8)	1.092	[116]

Controlled fusion reactions may be feasible with specially designed microsphere targets irradiated by high-energy lasers [111]. Deuterated polyethylene has been studied for its potential in this area [112-114], and a U.S. patent has been granted for this application [115].

The neutron scattering power of a deuterated polymer is more than two orders of magnitude greater than that of an undeuterated polymer (see Neutron Scattering Power Section). Plastics can be used as radiation shields to protect from the harmful effects of high-energy particles. Although no quantitative comparison is presented here, it is possible that deuterium substitution can increase the neutron stopping power of a plastic material such as polyethylene.

SUMMARY

Summary of Findings

Substitution of deuterium for hydrogen in a polymer can alter a variety of chemical and physical properties. A broad and in-depth investigation of literature reports on the properties of deuterated polymers has been performed. The findings of this investigation are summarized from several viewpoints to encompass the scope of the studies involved, and to facilitate the interpretation of the data. The summary of findings consists of a tabulation of measured changes in polymer properties, a listing of current and potential applications as reported in the literature, and an overview of the features of deuterated polymers that may pertain to future applications.

The major objective of this report has been to highlight documented differences in properties between deuterated and undeuterated polymers. A quantitative comparison of such differences is presented in Table 13. Properties are tabulated in decreasing order of the magnitude of the isotope effect. Note that for the purposes of this report, the term "isotope effect" is used in a general way, mainly to mean the ratio of any measured property, Q, of a deuterated vs undeuterated polymer, i.e., Q_D/Q_h. This usage is different from the specific term "kinetic isotope effect," which is a ratio of reaction rates, i.e., k_H/k_D. In a general sense, an isotope effect implies any change that results from deuteration. To avoid confusion in discussing quantitative data, Table 13 consists of relative values Q_H and Q_D listed side by side. Also note that an isotope effect may be viewed as beneficial though its magnitude may be less than one, or its sign may be negative.

Table 14 lists the applications of deuterated polymers including applications currently in use, those undergoing development, and those clearly indicated by experimental data. Also included are analytical applications as well as materials application.

Table 13 — Properties of Deuterated vs Undeuterated Polymers

Property	Isotope Effect; Ratio of Properties, Q_D/Q_H	
	Q_D	Q_H
Neutron Scattering Power, Polystyrene	700	1
Visible and Infrared Transmission, 500 to 900 nm	≈10	1
Stability Against Autoxidation		
Polystyrene, Polyolefins, 60 to 200°C[a]		
Induction Period for Onset of Autoxidation	2-20[b]	1
Autoxidation Rate	1	2-7[b]
Polyvinylchloride, HCl elimination rate	1	1.6-17[b]
EuTTA Fluorescence Intensity, dispersed in Polymethylmethacrylate (612 nm)	2	1
Free Radical Production Rate, under UV light	1	1.5-2
Sequence Defects in Polyvinylidene fluoride	0.82	1
Heat Capacity	1.2	1
Density	≈1.1	1
Hydrogen Bond Strength, Polypeptides	1.05	1
Melting Point, Glass Transition Temperatures (K)	≈0.98	1
Mechanical Properties	no change	---
Conductivity, Polyacetylene	(not clear)	---
Gas Permeability	(not clear)	---

[a] Reactive stability is temperature dependent.
[b] Values shown are the lowest and highest of those reported.

Table 14 — Current and Potential Applications of Deuterated Polymers

Materials Applications
Plastic optical fibers for data transmission
Plastic with increased thermal, oxidative, and photolytic stability
Targets for controlled laser fusion
Targets for neutron bombardment in experimental physics
Neutron shield materials
Analytical Applications
Neutron scattering analyses of polymers and blends
Surface temperature profiling of integrated circuitry
Detection of deuterated materials in complex mixtures by infrared spectroscopy

A summary of the features of deuterated polymers which pertain to materials applications is found in Table 15. This is essentially a general, nonquantitative interpretation of the data presented in Table 13.

Table 15 — Features of Perdeuterated Polymers that Pertain to Materials Applications

Physical Properties
Increased light transmission, 500 to 900 nm
No vibrational component to light attenuation, 650 to 680, 790 nm
Increased deuteron density, for neutron scattering or neutron stopping applications
Small increase in hydrogen bond strength
Slight reduction in interchain interactions; weaker interchain forces
Tendency to segregate very slightly from hydrogenated chains in a blend
Decreased number of sequence defects in PVF_2 (a piezoelectric polymer used as a mechanical-to-electrical transducer, as in microphone pickups)
Chemical Properties
Lower reactivity with oxygen at elevated temperatures or under UV light
Lower rate of HCl elimination from polyvinylchloride

Future Prospects

Certain aspects of the behavior of deuterated polymers clearly indicate that such polymers will continue to play an important role in science. Small-angle neutron scattering studies involve deuterated polymers as a fundamental requirement. Related applications are based on deuteron density such as targets for laser fusion studies and particle bombardment targets in experimental physics. Deuterium will continue to serve as a tracer atom incorporated into polymers for infrared, NMR, and pyrolytic mass spectrometry studies.

A materials application that seems to have real potential for the future involves the improved light transmission of deuterated plastic optical fibers. Transmission loss from a deuterated POF in the red region of the visible spectrum is comparable to the transmission loss from commercially available glass optical fibers.

Some new applications of deuterated materials have recently been studied: PMMA-d_8 is used as a film support for a fluorescent, temperature sensitive probe compound in microscopic surface temperature imaging; it has been proposed that PVF_2-d_2 may show improved piezoelectric properties (PVF_2 is used as a mechanical-to-electrical energy transducer, as in microphone pick-ups); the infrared absorption band at 6.45×10^{13} s^{-1} (2150 cm^{-1}) can be used to detect deuterated materials in complex mixtures.

Several studies on deuterated polymers subjected to tension clearly show that perdeuteration does not alter significantly the mechanical properties of a polymer. Hydrogen bond strength in a polyamide may be slightly increased, but not by a factor with potential utility.

The influence of perdeuteration on conductivity in polyacetylene is not clear. Even if an effect is found to take place, it may be of interest only for fundamental studies; it is highly likely, on theoretical considerations, that deuterium substitution will result in a change that is not significant compared to the effects of doping with n-type or p-type dopants.

The potential increase in stability against degradation is one aspect of this investigation which is suggestive, and may be a matter for further discussion. The hypothesis that perdeuteration can lead to greater stability against polymer autoxidation has been confirmed by the studies presented here. However, it does not appear that any deuterated polymers have been used in practice as a longer lasting plastic. The data on the elimination of HCl from PVC in oxygen atmosphere make this issue more clear. It was found that incorporation of a conventional type of antioxidant (hydroquinone, a free radical inhibitor) reduced the rate of HCl elimination by nearly the same amount as substitution of deuterium in PVC-d_3. Deuterium substitution improved stability against autoxidation, but not to a greater degree than a well-established, widely used alternative method. The possibility of a synergistic combination of deuteration with antioxidants to improve stability against autoxidation has not been shown yet. Nevertheless, it is possible that a pristine, deuterated polymer could be useful in a case where additives cannot be employed with a hydrogenated plastic.

There are other physical and chemical properties of polymers that have not been discussed because literature reports of the effects of deuteration or because these properties were not found. A wide range of other aspects of polymer behavior were considered, including surface activity, biodegradation, and dielectric constant, as well as applications such as adhesives, drag-reducers, coatings and uses in laser ablation, and UV photolithography. Assessment of the prospects of deuteration in these and other areas requires comparison of known and projected properties of deuterated polymers with specific materials needs and requirements. These studies remain for future consideration.

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Appendix

SMALL ANGLE NEUTRON SCATTERING (SANS) APPLIED TO POLYMER BLENDS

In recent years, polymer blends have become the focus of a major research endeavor within the polymer science. Polymer blends have great practical importance analogous to the well-established role of copolymerization. Before the neutron scattering method was known, the critical and unambiguous examination of the thermodynamics of mixed polymer systems was limited. Small angle neutron scattering analysis has filled this gap. SANS depends on the contrast between the coherent scattering lengths of deuterium and hydrogen for neutron diffraction. Hence, deuterated polymers are prepared for studies of mixed systems as well as for conformational analysis of a single polymer in the solid state.

In general, polymer pairs are not miscible. In fact, miscibility is not desirable in some applications. The concept of compatibility has evolved, which is loosely defined as a desired or beneficial result from a combination of two polymers [117]. SANS offers the kind of clarification and quantitative information on the thermodynamics of polymer blends that are not obtainable by optical microscopy, differential calorimetry, preparation of cloud point curves, and other methods. It is analogous to classical light scattering, with one polymer "dissolved" in another, in typically a 1 to 5% ratio of deuterated-undeuterated polymer, or vice versa. In studies of polymer blend, either the solvent or solute might be a blend of deuterated and undeuterated polymers.

The mathematical principles of SANS are described in Ref. 118. The ratio of coherent scattering intensity from solved particles to the incident neutron radiation is given by an equation which depends on coherent scattering lengths of nuclei in the solvent and solute, partial molar volumes, wavelength, scattering angle, and other factors. Neutron wavelengths from cold sources ($\nu = h/m\mathrm{v}$; h is Planck's constant, m is mass, v is velocity) are on the order of 10 Å. Of great interest is the single particle scattering function, which can yield the radius of gyration and detailed knowledge of conformation from other calculations. In a nonideal interaction, one takes into account the virial coefficients of osmotic pressure. The influence of thermodynamic solution parameters on scattering has been described mathematically by Zimm or Zimm plots which can be prepared to evaluate data.

Information that can be obtained by SANS includes the molecular weight of the solute polymer, the size of the molecule, the radius of gyration and its dependence on molecular weight and meaningful second virial coefficients for miscible blends. SANS is the first analytical method to give direct evidence of miscibility of polymers.

In both areas of thermodynamic research, isotope effects have been observed which result in aggregation of isotopically similar chains. Research on this phenomenon exists, and the number of literature reports is significant; however, there is considerable discussion going-on about the causes of this nonstatistical distribution of deuterated chains and the dramatic impact of this behavior on SANS analysis. Normally, one assumes that labelled chains are distributed homogeneously. Neutron scattering is very sensitive to small deviations from statistical distributions; it depends on the degree of isotopic aggregation, and the number of average molecular weights determined by SANS that could vary over three orders of magnitude [78].

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