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on the dibenzyl glucose was 41%. $[\alpha]_D^{25}$, +5.3° (*c*, 1.0 g/dL in chloroform). Anal. Calcd for $C_{54}H_{56}O_{10}$: C, 70.37; H, 6.20. Found: C, 70.36; H, 6.16.

^{1}H NMR: *J*(H′-1,H′-2), 11.6 Hz. ^{13}C NMR (CDCl$_3$): 138.5, 138.4, 138.2, 138.1, 137.7, and 137.5 (phenyl ipso); 127.9, 127.5, and 127.3 (phenyl ortho, meta, and para); 103.8 (C′-1); 100.0 (C-1); 81.8 (C′-3); 78.9 (C′-2); 76.2 (C-2); 76.0 (C-4); 75.2 (C-3); 74.6 (C′-5); 74.4 (C′-4); 74.2 (C-5); 73.4, 73.3, 73.2, 72.9, 72.1, and 70.8 (benzyl CH$_2$); 68.6 (C′-6); 64.7 (C-6). (The primed protons and carbons are of the β-galactopyranose moiety and the nonprimed ones of the β-glucopyranose moiety.)

Polymerization. 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**6**) was prepared according to the prescribed method.[9,10,17] Purification of *p*-chlorobenzenediazonium hexafluorophosphate and dichloromethane was followed by usual methods.[17] Polymerization was carried out by using high-vacuum techniques.[17]

Debenzylation. Polymer was debenzylated with sodium in liquid ammonia according to the method described previously.[17]

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Registry No. **1**, 125076-61-1; **1** acetylated analogue, 125076-60-0; **2**, 125076-63-3; **4**, 125076-62-2; **5** debenzyl derivative, 14241-58-8; **6**, 10548-46-6; **6** 3-debenzyl derivative, 33208-48-9; 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide, 3068-32-4.

Chemical Nature of Conduction in Iodine-Doped *trans*-1,4-Poly(buta-1,3-diene) and Some of Its Derivatives: The Presence of I$_3^-$ and the Effect of Double-Bond Configuration

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Received July 31, 1989;
Revised Manuscript Received October 2, 1989

Conductive polymers have been extensively studied following the discovery of Shirakawa et al.[1,2] that polyacetylene (PA) could be prepared as films having a metallic luster and conductivity. This conductivity can be increased by 9–13 orders of magnitude by doping with various donor or acceptor species to give p-type and n-type semiconductor and conductor charge-transfer complexes. Many modifications of PA have been prepared including substitutions[3] and conjugation length variations.[4,5] Conjugation of the polymer backbone was thought to be a prerequisite for the formation of a conductive charge-transfer complex upon doping.[6]

Recently it was found that several 1,4-poly(butadiene) polymers having a nonconjugated backbone could be halogen doped to form semiconductors.[7] Both *cis*- and *trans*-1,4-poly(2-methylbuta-1,3-diene) (natural rubber and gutta percha or synthetic rubber) and *cis*-1,4-poly(2,3-dimethylbuta-1,3-diene) became dark and conductive when treated with iodine but *cis*-1,4-poly(buta-1,3-diene), without methyl substitution at the double bond, did not change color on doping or become conductive. This difference was proposed to be due to an inductive effect of the methyl substituent. It was proposed that radical cation polaron formation is responsible for the increased conductivity and that the electron transports through interchain hopping. These results have received editorial comment[8] because they call into question basic assumptions concerning the mechanism of conductivity in doped polymers. The simplicity of polybutadiene backbone deserves more study to clarify the physical and chemical nature of this system as the results will likely help us gain more insight into polymer conduction mechanisms.

The technique of inclusion polymerization[9–11] has been applied to synthesize poly(butadiene) and its methyl and chloro derivatives. The product from inclusion polymerization has well-characterized trans stereochemistry and crystal structure[9,10] that have long been recognized as important to characterize the chemical and physical properties of conductive polymers. The availability of *trans*-poly(butadiene) and its derivatives from inclusion polymerization permits us to extend the work of Thakur[7] so as to investigate the effect of stereochemistry on conductivity. The availability of chloro as well as methyl derivatives permits further examination of inductive effects.

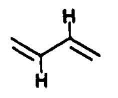
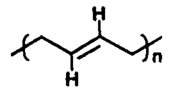
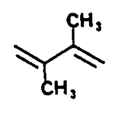
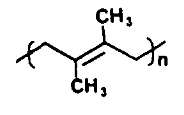
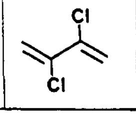
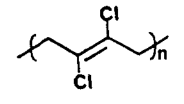
Experimental Section

Synthesis of Polymers. Monomers were of commercial origin and were used without further purification except 2,3-dichlorobutadiene which was synthesized following a published procedure.[12] *trans*-1,4-Poly(buta-1,3-diene) (PBD) was obtained through urea inclusion polymerization while deoxycholic acid (DCA) inclusion polymerization was applied to synthesize *trans*-1,4-poly(2,3-dimethylbuta-1,3-diene) (PDMBD) and *trans*-1,4-poly(2,3-dichlorobuta-1,3-diene) (PDCBD).[13] γ-Ray irradiation was provided by a ^{60}Co source for 15 h with a dose rate of 40 Mrad/h. The sample was maintained at −78 °C. The polymer structures were verified by infrared spectra.

Doping with Iodine and Conductivity Measurements. For initial evaluation, the pressed pellet of synthesized polymer was

0024-9297/90/2223-1886$02.50/0

Table I
Polymers Synthesized Using Inclusion Polymerization and Their Conductivities[a]

Name	Monomer	polymer	Conductivity (Ω.cm)$^{-1}$
PBD			1×10^{-5}
PDMBD			3.5×10^{-4}
PDCBD			—

[a] The conductivities have been measured by the four-probe method under vacuum after heavy doping with iodine.

left in the iodine tank overnight. The development of a metallic luster indicated that the polymer reacted with iodine. The conductivity of a pellet (pressure 1500 psi, diameter 1.3 cm, thickness 0.3 mm) was measured by using the conventional four-probe method under vacuum.[14,15] Electrodac 504 colloidal silver (Acheson Colloids) was used to make contact between the platinum electrodes and the polymer sample. The results are given in Table I.

Infrared Spectral Measurements. The infrared (Nicolet DX-FTIR) and far-infrared (NICOLET 8000) spectra were obtained for both pristine and doped polymers in pure pellet form. The far-infrared spectrum was done under vacuum with TGS as detector.

Results

Three types of polymers have been synthesized (Table I). The FTIR spectra of these samples demonstrate the high trans configuration content. It is known that polymers obtained by inclusion polymerization are high molecular weight, non-cross-linked, and crystaline in form.[9-11] Upon being treated with iodine both *trans*-1,4-polybuta-1,3-diene (*trans*-PBD) and *trans*-1,4-poly(2,3-dimethylbuta-1,3-diene) (*trans*-PDMBD) become metallic black in color; *trans*-PDMBD changes color more rapidly than *trans*-PBD. Note that *cis*-1,4-poly(buta-1,3-diene) has previously been shown to be undopeable.[7] *trans*-PDCBD does not show significant color change when exposed to iodine and does not show appreciable conductivity. The conductivity has been measured for *trans*-PBD and *trans*-PDMBD when heavily doped with iodine (Table I). The lower conductivity of *trans*-PDMBD compared to Thakur's value for *cis*-PDMBD may be due to retention of considerable domain resistance.

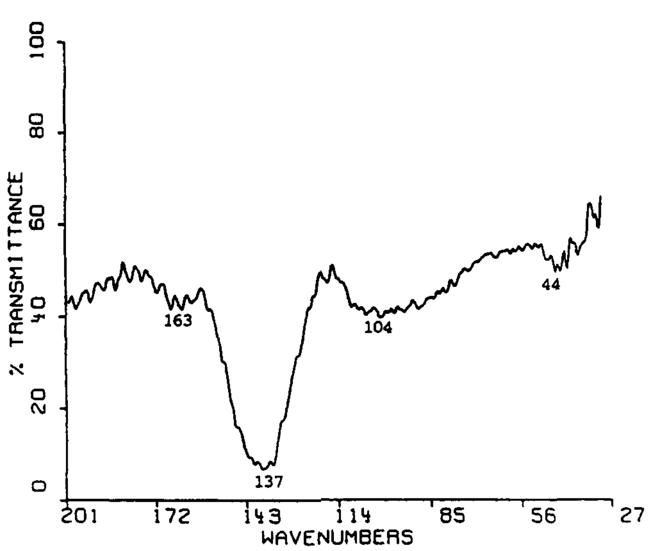


Figure 1. Far-infrared spectrum of heavily doped *trans*-1,4-poly(2,3-dimethylbuta-1,3-diene) (PDMBD) with iodine. The unreacted sample does not have any absorption in this region. *trans*-1,4-Poly(buta-1,3-diene) (*trans*-PBD) has the same features when similarly treated with iodine.

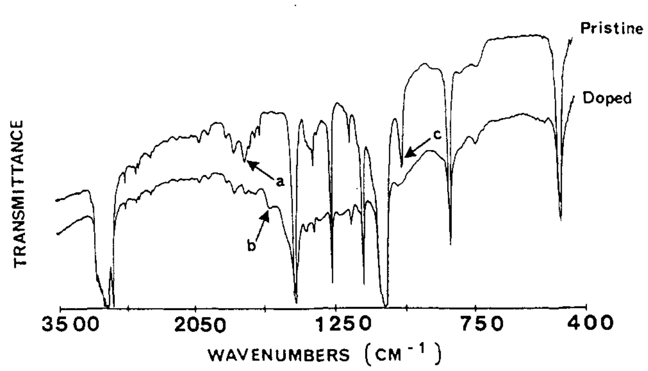
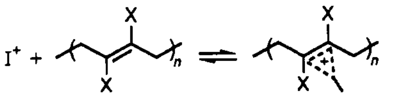


Figure 2. FTIR spectrum of *trans*-1,4-poly(buta-1,3-diene) (PBD) before (pristine) and after extensive reaction with iodine. (a) and (b) label the C=C stretching region; (c) labels a C–H bending vibration.

The far-infrared spectrum of iodine-doped *trans*-PDMBD (Figure 1) shows three peaks at 137, 104, and 44 cm^{-1}. These bands demonstrate the presence of I_3^- by comparison with the far-IR spectrum of solid $(Bu)_4NI_3$ crystal.[16] The small peak at 163 cm^{-1} is identified as being due to I_5^- by its diminution under prolonged evacuation. The absorption spectrum obtained for these samples in the visible and near-UV range is also consistent with the presence of I_3^-.[17] The changes observed upon doping in the near-IR spectrum for *trans*-1,4-poly(buta-1,3-diene) are identical with those reported for *cis*-1,4-poly(2-methylbuta-1,3-diene) (*cis*-polyisoprene) by Thakur.[7] In each case there is a red shift of about 100 cm^{-1} of the double-bond stretching frequency near 1700 cm^{-1} and loss of the sharp CH wagging mode at 914 cm^{-1} upon doping. The modest change in the C=C stretch indicates only a slight weakening of the double bond.

Discussion

The visible and near-UV spectra observed for these samples are very similar to those recently reported by Elman and Thakur for *cis*-1,4-polyisoprene.[18] This further confirms the similarility of the doping processes in these two cases. At very low doping levels the primary absorption features are seen at about 300 and 370 nm. These features correspond quite closely in wavelength, shape and relative intensity to those reported for I_3^-.[17] At higher doping levels the bands broaden with a peak near 400 nm. The following reaction scheme[19,20] is proposed to explain the visible, IR, and far-IR results and is consistent with the lack of any observed paramagnetism for these samples:



According to this scheme, molecular iodine formally dissociates in the polymer matrix to form cationic and anionic species:

$$2I_2 \rightarrow I^+ + I_3^- \qquad I_3^- + I_2 \rightleftarrows I_5^-$$

The formation of a complex of the cationic iodine with the double bond of the polymer stabilizes this species. This complex formation influences the vibrational spectrum in a characteristic fashion. Specifically, the decreased frequency of the double-bond stretching vibration and the loss of intensity of the C–H wagging vibration have been noted for similar π-bridged complexes formed by Ag^+ and Pd^{2+}.[21-23] These observations provide a direct spectral comparison with a known structural type.

The nature of the interaction of cationic halogens with double bonds has been the subject of extensive study.[24] In low nucleophilicity solvents at low temperature ("stable ion conditions"[24]), ethylenehalonium ions are often stable species. These are probably best described as cyclic structures involving two σ-bonds (σ-complex). It has been proposed that the initial attack of the halide group on the double bond results in a π-complex (analogous to that formed by Ag^+) and that this is a precursor to the σ-complex.[24] Under normal solution conditions, attack of the nucleophilic trihalide anion on the halonium ion results in addition to the double bond to form the saturated dihalide. If the double bond is sufficiently sterically hindered, this addition reaction does not occur.[24,25] In one case[24,26] (adamantylideneadamantane) a complex with halogen forms reversibly. The structure of this complex[26] shows that it is an ionic compound with the formula (ethylenehalonium)$^+$ $(X_3)^-$. We propose that similar structures form in the polymer matrix when it is doped with iodine. The relatively small shift of the C=C frequency indicates that the species present in the polymer is better described as a π-complex (similar to the known Ag^+ species) than as a σ-complex. Steric hindrance in the polymer matrix presumably inhibits the later steps of the addition reaction, halting the process at the stage of π-complex formation.

I_3^- has been previously reported to be present in large amounts in iodine-doped PA.[27-32] Some I_5^- is also present in equilibrium with I_2 and I_3^-.[31,32] The proposed cationic complex would not be expected to form with polyacetylene because PA is a much stronger electron donor due to stabilization of the cation by delocalization. It is interesting to note in this regard that when PA is doped with silver perchlorate, silver atoms are formed demonstrating direct electron transfer.[19] In contrast, Ag^+ is known to form cationic complexes with species containing isolated double bonds.[21] Parallel behavior is expected for halogen doping.

Thakur and Elman[17] have recently reported the observation of an ESR signal and a temperature-dependent magnetic susceptibility for iodine-doped 1,4-poly(2-methylbuta-1,3-diene). We were unable to detect any ESR spectral signal or any magnetic susceptibility above the diamagnetic level for the polymers we studied. In our case the samples had excess iodine removed by pumping. This treatment does not remove the tightly bound iodine involved in the "doping" process resulting in sample coloration and conduction. It should be noted that the level of paramagnetism reported by Thakur and Elman[18] is very low, corresponding to only one unpaired electron for roughly 500 iodine atoms in the sample. The difference between the results of our magnetic measurements and those of Thakur and Elman may be due to differences in the sample preparation. The level of paramagnetism reported by these workers is so low that species with unpaired spins may be unrelated to the conduction mechanism. More specifically, our samples, with very similar spectral and conductivity properties to those previously reported, have no unpaired spins. From this we conclude directly that unpaired spins are not associated with the observed conductivity whatever the origin of the differences in the samples.

The species proposed by Thakur[7] to be responsible for the ultraviolet, infrared, and conductivity properties of doped *cis*-1,4-poly(buta-1,3-diene) is a radical cation. Such species are unknown in chemistry. They are apparently very unstable relative to a variety of other structures. Because of this there is no spectroscopic evidence to confirm the assignments made by Thakur.

As an alternative to radical cation formation,[7] we propose the formation of the cationic iodine complex shown above. The inductive effect of a methyl group on the double bond is to stabilize the cationic structure while that of chloro substitution would be expected to destabilize such a structure. The observed conductivity should be similar in mechanism to that of organic molecular crystals.[33] The weak interaction between double bonds infers a very narrow band with highly localized holes. The holes move through electron hopping (tunneling) between neighboring double bonds. Nonconjugated polymers are expected to have low conductivity due to the intrinsic low carrier mobility (hopping is a high barrier process), but both interchain and intrachain hopping are probable since neighboring double-bond distances within and between chains are similar in the crystal structure. Furthermore, there may be participation of I_3^- or higher aggregates in the conduction chain.

The differences observed between the *trans*-butadiene polymers studied here and the *cis*-polybutadiene polymers discussed previously and the effect of substituents in terms of color change and conductivity upon treatment with iodine may be related to differences in packing in the solid state rather than being related to unimolecular properties. Thus, solid-state packing is likely to influence iodine permeability and to affect the nature of the complex formed.

Acknowledgment. This research was supported by a grant from the Office of Naval Research.

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Intrinsic Dynamic Viscoelasticity of Polystyrene in Good Solvent. A Test of the Nonuniform Expansion Theory

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Received July 19, 1989;
Revised Manuscript Received September 2, 1989

Introduction

Experimental and theoretical studies on the structure and dynamics of long-chain polymers in solution are critical to understanding the relaxation processes of macromolecules that lead to their characteristic and extraordinary physical properties. Dynamic viscoelastic (VE) and oscillatory flow birefringence (OFB) experiments focus on the relaxations associated with the response of polymers in solution, which are subjected to a small shear.[1,2] Data from these experiments have been successfully treated[3] with the Rouse–Zimm bead–spring theory,[4,5] which models Gaussian chain configurations and includes hydrodynamic interactions by a preaveraged Oseen tensor. In comparison to this ideal chain model, infinite dilution dynamic storage and loss moduli, $[G'(\omega)]_R$ and $[G''(\omega)]_R$, of high molecular weight polymers in Θ solvents are in clear agreement with theory in the limit of nondraining polymer coils.[6,7]

The same is not true for polymers in good solvent. One method of modeling these results has been to allow the hydrodynamic interaction paramter h^* to vary from its nondraining limit of 0.25 toward the free-draining limit of 0. Allowing h^* to vary as a fitting parameter indicates that the introduction of excluded volume for the polymer chain shifts experimental data, including intrinsic viscosity, in the direction of the free-draining Rouse limit.[1,6] By this method dynamic VE, OFB, and intrinsic viscosity results have been treated with effective h^* values.

It has long been recognized[8] that this application of the Rouse–Zimm model is inconsistent because polymer chains in good solvent are expanded beyond the Gaussian configuration assumed by the calculation. Thus, despite the widespread success of the method in fitting data, it does not establish that an adjustable h^* corresponds to the correct physical interpretation of the data. Ptitsyn and Eizner[9] addressed the problem by introducing non-Gaussian chain statistics into the bead–spring theory and solving for the case of dominant hydrodynamic interaction. This model includes excluded volume with a uniform expansion as $\langle r_{ij}^2 \rangle = \sigma^2 |i-j|^{1+\epsilon}$ where $\langle r_{ij}^2 \rangle$ is the mean-square separation between the ith and jth bead. $\langle r_{ij}^2 \rangle$ is not a linear function of $|i-j|$, but expands according to the excluded-volume parameter ϵ, which ranges from 0 in Θ condition to 0.333 in good solvent cases. Tschoegl extended this approximate treatment to include arbitrary hydrodynamic interaction because it was found that the addition of ϵ alone could not account for the experimental results; an adjustable h^* was also required.[10] Equally good comparisons to data were obtained by setting $\epsilon = 0$ and varying h^* alone.[8]

In a recent paper[7] both the original Gaussian model and Tschoegl's extension have been applied to data from dilute solution VE experiments ($[\eta]$, $[G'(\omega)]_R$, and $[G''(\omega)]_R$ for polystyrenes of molecular weights from 1.79×10^5 to 2.06×10^7 in toluene). Generalized programs for calculation of eigenvalues and VE properties using the bead–spring model (Hookean springs) were provided by Sammler and Schrag.[11,12] For the original Zimm theory, h^* was determined from the Houwink–Mark–Sakurada (HMS) molecular weight exponent for $[\eta]$ and used to fit $[G'(\omega)]_R$ and $[G''(\omega)]_R$ vs $\omega\tau_1$. For the uniform expansion model ϵ was fixed from radius of gyration measurements by light scattering, the value of h^* consistent with this ϵ was determined from $[\eta]$, and the resulting calculations were compared to $[G'(\omega)]_R$ and $[G''(\omega)]_R$ vs $\omega\tau_1$. For PS in toluene both fits were excellent with the following parameters:[7] Gaussian ($\epsilon = 0$), $h^* = 0.04$; uniform expansion, $\epsilon = 0.192$, $h^* = 0.06$. These values of h^* are surprisingly small, tending toward the Rouse limit of $h^* = 0$.

Nonuniform Expansion Model

It has been shown by neutron scattering[13] and by direct perturbation calculations[14,15] that even the uniform expansion assumption is incorrect for real excluded-volume chains. These studies demonstrated that if $\langle r_{ij}^2 \rangle$ is cast in the Ptitsyn and Eizner form, ϵ depends on $|i-j|$. Descriptions of chain expansion in good solvents, which should provide a more accurate representation, are given by the renormalization group calculations of Miyake–Freed[16,17] and by the perturbation calculations of Barrett.[18] Recently Sammler and Schrag[12] have compared results obtained under the Gaussian, uniform expansion, and (Miyake and Freed) nonuniform expansion models. The eigenvalues in each model are dependent, in complicated ways, on the same hydrodynamic interaction parameter, $h^* = (\zeta/\eta_s)(1/12\pi^3 b^2)$, where ζ, η_s, and b are the monomeric friction factor, solvent viscosity, and equilibrium bead length, respectively. The calculations

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0024-9297/90/2223-1889$02.50/0