may be discerned. The T_g decreases in the series $T_{g_{syndio}} > T_{g_{atactic}} \gg T_{g_{isotactic}}$. This exactly parallels the trend observed with poly(methyl methacrylate),[1,10] where again the isotactic configuration is characterized by a significantly lower T_g. The results are in contrast with earlier predictions[11] that monosubstituted polymers such as polypropylene should show no significant dependence of T_g stereoregularity. The difference in glass transition temperature (ΔT_g) between the syndiotactic and isotactic forms of polypropylene of ~14 K is, however, much smaller than that for poly(methyl methacrylate),[10] $\Delta T_g \sim$ 81 K.

These results also cross correlate with the recent observation[8] that ^{13}C NMR spin-lattice relaxation times, T_1's, are considerably longer for isotactic than for syndiotactic PP sequences. Taken together, these findings appear to indicate a greater freedom in the segmental motion of the isotactic polymers.

The T_g value reported here for atactic polypropylene (267 ± 1 K) is close to the value recorded earlier[2,3] by DSC measurements for high molecular weight atactic polypropylene (266 K), but the isotactic T_g value (255 ± 2 K) is at variance with the earlier[2] value of 272 K. The discrepancy may be due to inadequate characterization or quenching of the PP samples in the earlier work, since the presence of crystallinity tends to increase the T_g of the sample.

Registry No. Syndiotactic polypropylene, 26063-22-9; atactic polypropylene, 9003-07-0; isotactic polypropylene, 25085-53-4.

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Communications to the Editor

Soluble Polyacetylene Graft Copolymers[†]

Polyacetylene, a semiconducting organic polymer, undergoes dramatic changes in conductivity upon appropriate doping. Inspired by the expectation of producing a commercially viable conducting plastic, various workers have devoted extensive study to this polymer for more than 2 decades.[1] Among known conductive polymers, polyacetylene exhibits the potentially most useful electrical and electronic properties; however, all previously reported forms of the material have undersirable physical properties such as complete insolubility and decomposition without melting.[2]

Recent experimental work has focused primarily on silvery, free-standing films prepared by polymerizing gaseous acetylene on a layer of concentrated Ziegler-Natta catalyst solution, as reported by Shirakawa in 1971.[3,4] While macroscopically homogeneous, such films are microscopically inhomogeneous, consisting of a tangled mat of fibers approximately 15 nm in diameter, in which polymer chains reportedly orient along the fiber axis.[5-7] Film densities are typically ~0.4 g/cm^3.[8,9]

Understanding the fundamental electronic properties of polyacetylene necessitates the separation of intramolecular, or single chain, effects from those induced by intermolecular, or chain-chain interactions. Attempts to solve this problem, usually by modifying the monomer, have in all cases resulted in materials with inferior electrical properties.[10-12] We have prepared a new type of polyacetylene which is soluble in various common organic solvents by incorporating the polyacetylene into a graft copolymer.

It has been known for over 2 decades that block and graft copolymers exhibit unique properties, unlike those of homopolymer blends. In particular, these systems exhibit significantly altered phase diagrams, characterized by an elevated critical point[13] and phase morphologies that are restricted in size to molecular dimensions.[15,16] With this in mind, we have prepared several copolymers containing a single block of polyacetylene grafted to various carrier polymers in an effort to exploit the solubility that results from block or graft copolymerization.[17] Two such graft copolymers are discussed in this communication, one prepared with polyisoprene (80% cis 1,4, 15% trans 1,4, 15% 3,4) at −78 °C and the second with polystyrene at 25 °C, denoted PI_{200}-PA and PS_{200}-PA, respectively. Both the polyisoprene and polystyrene carrier polymers are nearly monodisperse with a molecular weight of 2×10^5 and have been modified through oxidation to contain electrophilic sites.

The graft copolymers were synthesized by polymerizing acetylene with a $\mathrm{Ti(OC_4H_9)_4/Al(C_2H_5)_3}$ catalyst[3] in a toluene solution containing the carrier polymer. Intensely maroon or blue solutions were formed, characteristic of the cis and trans isomers of polyacetylene, respectively. These solutions are stable but sensitive to degradation by oxygen. We believe the grafting step to be the result of nucleophilic attack of the growing polyacetylene chains on electrophilic sites on the carrier polymer, which also terminates polyacetylene chain growth. These sites can be introduced onto polyisoprene with molecular oxygen to give aldehydes and ketones or, more selectively, with *m*-chloroperbenzoic acid, which introduces epoxides without chain scission. Unoxidized polyisoprene is ineffective as a carrier polymer. During the polymerization of the polystyrene carrier chains a small proportion of butadiene was introduced to provide sites for subsequent oxidation or epoxidation. The epoxidized styrene-butadiene copolymer is particularly useful for morphological work since polyacetylene can be selectively stained with osmium tetraoxide.[16]

The molecular weight of the polyacetylene units was estimated by infrared analysis on samples that had been

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[†] Presented in part at the International Conference on Low Dimensional Conductors, Les Arcs, France, Dec 11, 1982.

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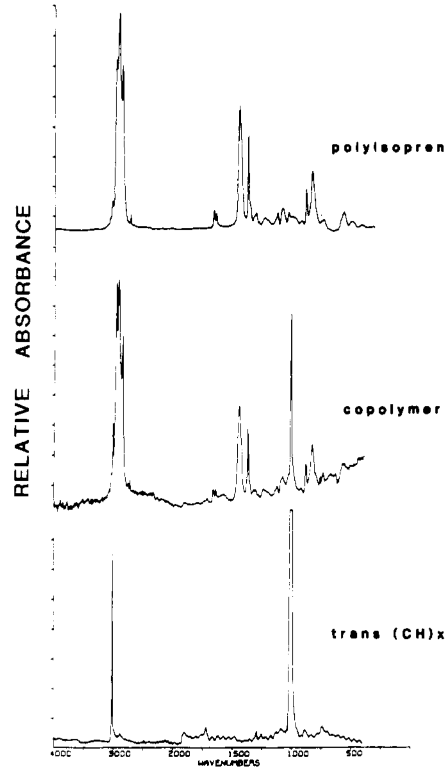

Figure 1. IR spectra of polyisoprene homopolymer (top), extracted PI_{200}-PA graft copolymer (middle), and conventional *trans*-polyacetylene prepared by the method of Shirakawa et al.[3,4] and isomerized at 190 °C (bottom).

separated from residual homopolymer.[18] These graft copolymers are expected to contain no more than one polyacetylene block per chain since the grafting reaction was carried out in the presence of excess carrier polymer. Figure 1 illustrates the IR spectra obtained from bulk homopolyisoprene, extracted PI_{200}-PA, and *trans*-polyacetylene film. The absorption at 1013 cm^{-1} is unique to *trans*-polyacetylene. Polyisoprene and polyacetylene IR absorptivities will be reported elsewhere.[18] Based on the compositions measured by IR and the known carrier molecular weights, the polyacetylene molecular weights are estimated to be between 3×10^4 and 6×10^4.

Several hours after preparation, samples PI_{200}-PA and PS_{200}-PA, both in toluene, were found to contain exclusively *trans*-polyacetylene, as demonstrated by their spectra (Figures 1 and 2). Infrared analysis confirmed a complete lack of *cis*-polyacetylene absorption bands (446, 741, and 1328 cm^{-1}) and the visible absorption spectrum, while shifted to higher energy with respect to conventional polyacetylene (see below), exhibited none of the features associated with the cis isomer.

Samples of PI_{200}-PA in $CDCl_3$ (5% w/v) were examined by ^{13}C and ^1H NMR spectroscopy. These results are presented in Figure 3. The ^1H spectrum was also determined in CCl_4 in order to eliminate the residual $CHCl_3$ resonance and verify the chemical shift of the *trans*-polyacetylene protons. Both the ^1H and ^{13}C polyacetylene resonances exhibit line widths comparable to that of the polyisoprene carrier polymer, which is known to be in solution. Previously, NMR studies of polyacetylene have required magic-angle spinning and such spectra have exhibited the relatively broad lines characteristic of a solid material. The origin of the ^{13}C doublet in *trans*-polyacetylene will be discussed below. The graft copolymer composition, determined by IR spectroscopy (Figure 1), is higher than that observed in the NMR spectrum, since the homopolyisoprene was not separated from the graft copolymer for this measurement.

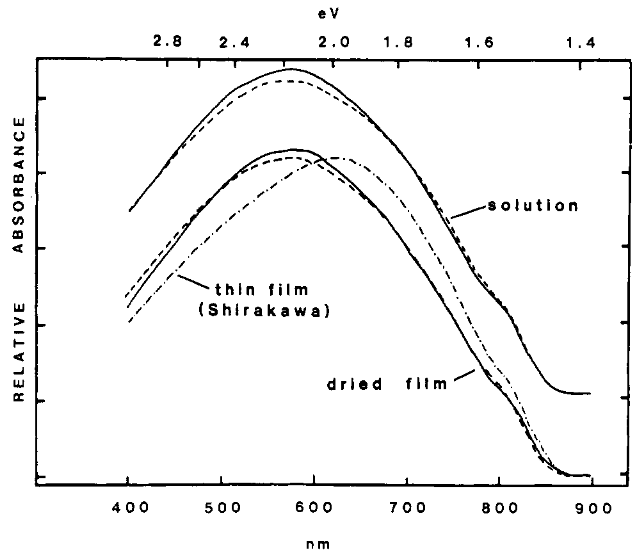

Figure 2. Visible absorption spectra of samples of PI_{200}-PA (—) and PS_{200}-PA (---). Solution spectra were taken as a dilute solution in toluene and have been shifted vertically. The thin film of conventional polyacetylene was prepared by the method of Shirakawa et al.[3,4] and isomerized at 190 °C (-·-).

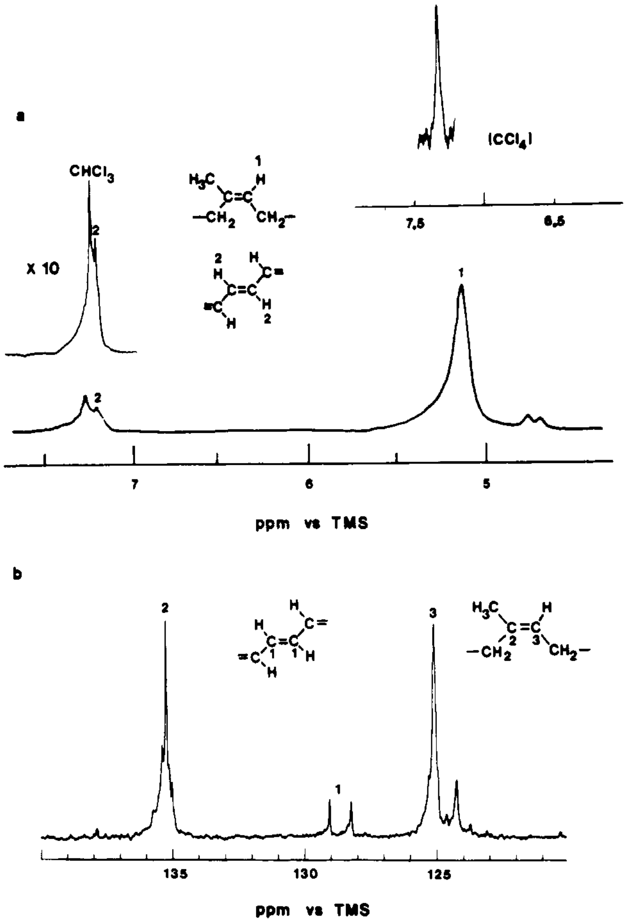

Figure 3. (a) ^1H NMR spectra of sample PI_{200}-PA taken in $CDCl_3$ and CCl_4 (inset). (b) ^{13}C NMR spectrum of PI_{200}-PA in $CDCl_3$. These spectra do not reflect the actual graft copolymer compositions since the solutions contained a significant amount of homopolyisoprene.

Solvent-free films of PI_{200}-PA and PS_{200}-PA were cast from toluene and examined by visible absorption spectroscopy and transmission electron microscopy (TEM). As shown in Figure 2, removal of the solvent had little effect

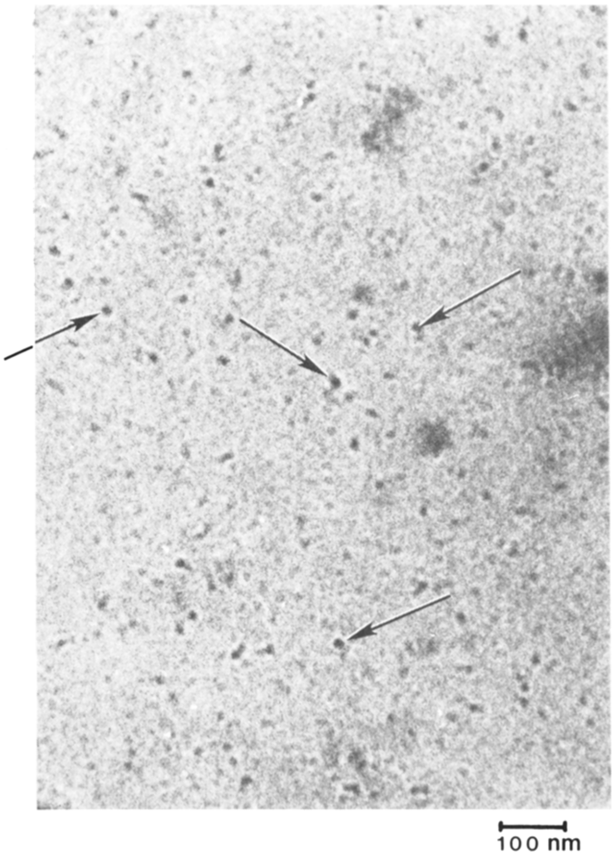

Figure 4. Transmission electron micrograph of a sample of PS_{200}–PA stained with OsO_4. Several stained polyacetylene microdomains (black areas) are indicated by the arrows. The apparent polyacetylene density does not reflect the actual graft copolymer composition since this sample contained a considerable amount of homopolystyrene.

on the visible absorption spectrum of either sample. Since both carrier polymers and polyacetylene have similar mass densities, TEM examination required staining with osmium tetraoxide.[16] This method is ineffective with PI_{200}–PA but well suited to PS_{200}–PA, as demonstrated in Figure 4. Polyacetylene microdomains, 10–15 nm in diameter, are clearly evident as indicated by the arrows. Such microphase separation is dictated by the molecular structure of these graft copolymers.[15,16]

These results clearly demonstrate that block or graft copolymerization of acetylene with an appropriate carrier polymer can render polyacetylene soluble, thereby providing the opportunity to investigate the single-chain characteristics of this polymer. The optical absorption results presented in Figure 2 illustrate our initial results for single-chain polyacetylene. Recent measurements of the dependence of the optical absorption in solid-state samples as a function of pressure have led to the prediction[19] of a shift in the band gap to higher energies by approximately 0.3 eV for isolated one-dimensional trans chains. This shift corresponds to the loss of chain–chain coupling in solid-state polyacetylene and should be accompanied by a sharpening of the absorption envelope.

Determination of the band gap energy from the spectra shown in Figure 2 is complicated by broadening due to phonon coupling.[20] However, the absorption peaks in PI_{200}–PA and PS_{200}–PA are clearly shifted to higher energy and the edges are broader than in the thin film. This is the opposite effect to that expected for the linear one-dimensional chain.[19,21] We believe these results indicate some flexibility in the polyacetylene chain and that the shift in the absorption spectrum is caused by rotation about single bonds. Such bond rotations would decrease the effective conjugation from that expected for the trans-transoid conformation. Interestingly, the spectra of solvent-cast films of PI_{200}–PA and PS_{200}–PA are nearly identical with those in solution. We believe this indicates the presence of amorphous polyacetylene, trapped in the microdomains as identified in Figure 4. Indeed, it would seem unlikely that these polyacetylene microphases would exist in a crystalline form, considering their size and the spatial constraints associated with graft function placement at the domain interface.[15]

The ^1H and ^{13}C NMR spectra (Figure 3) are also consistent with a flexible-chain model. Recent calculations[22,23] have suggested that the trans-transoid and a distorted trans-cisoid conformation of isolated polyacetylene chains differ only slightly in energy, with a significant barrier between these conformations. The observation of two peaks, nearly identical in area, may be the result of a slow exchange between the predicted energy minima at room temperature.

Forthcoming papers will describe the polymerization procedures, solution behavior, and solid-state characteristics of this new form of polyacetylene.

Acknowledgment. We are indebted to numerous people for providing both experimental and conceptual assistance in this work. H. Schonhorn determined the IR spectra and F. C. Schilling obtained the NMR spectra. Our ongoing collaboration with J. Orenstein has been very beneficial in this work. F. Padden, A. Lovinger, H. D. Keith, and E. A. Chandross have also been particularly helpful.

Registry No. Acetylene–isoprene copolymer, 37702-88-8; acetylene–styrene copolymer, 84824-32-8.

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Stereochemical Evidence for the Participation of a Comonomer Charge-Transfer Complex in Alternating Copolymerizations

The question of the participation of a comonomer charge-transfer complex in alternating copolymerizations has long been debated. Although considerable data have been amassed over the years, several authors[1,2] have suggested that there has been no unambiguous experimental proof of participation of the complex in the reaction. In order to clarify the mechanism of alternating copolymerization, a new source of data was deemed necessary.

Mulliken theory[3] predicts that maximum amount of charge-transfer stabilization is attained if the conformation of the complex is that in which there is maximum overlap between the HOMO of the donor and the LUMO of the acceptor. It is therefore conceivable that if a comonomer charge-transfer complex adds to the radical chain end in a concerted manner, then a certain amount of stereoregularity may be induced into the copolymer chain. The degree of stereoregularity may be related to the amount of complex participation in the propagation steps.

Various N-substituted maleimides were shown to copolymerize alternatively with several vinyl ethers. Chloride and nitrogen elemental analysis of *N*-phenylmaleimide (NPM)-2-chloroethyl vinyl ether (CEVE) copolymers prepared by conventional free radical initiation (AIBN, CH_2Cl_2, 60.0 °C) in degassed, sealed tubes indicated that the copolymers contained nearly an equimolar amount of comonomers regardless of the comonomer ratio in the original monomer feed (Figure 1). The NPM–CEVE copolymerization rate (measured gravimetrically) exhibited a maximum at nearly a 1:1 initial comonomer mole ratio, where the comonomer charge-transfer complex concentration would be maximum (Figure 2). Rate profiles such as this are typical of comonomer pairs that polymerize in an alternate manner.[1] Reactivity ratios derived from the composition data by the Kelen–Tüdös[4] method were r_1 = 0.275 (NPM) and r_2 = 0.000 (CEVE).

Figure 3 shows the ^{13}C NMR spectrum of an NPM–CEVE copolymer prepared by using light-induced decomposition of AIBN at low temperature (−78 °C) and a large excess of CEVE (initial mole fraction of NPM (χ_M) = 0.1) in the feed. Copolymers prepared under these conditions possessed totally alternating sequence distributions. The ^{13}C NMR spectra of NPM–CEVE copolymers were found to be markedly dependent on such copolymerization conditions as temperature, initial comonomer ratio, solvent, total monomer concentration, and the relative donor and acceptor strengths of the comonomers. This effect is illustrated in Figure 4, which shows the expanded carbonyl regions of several NPM–CEVE copolymers prepared under similar conditions (AIBN, 60.0 °C, CH_2Cl_2, M_T = [NPM] + [CEVE] = 0.5), except for the initial mole fraction of maleimide in the feed (χ_M). The most obvious variation in these spectra is the change in relative intensity of the peaks at 176.4 and 177.1 ppm from Me_4Si. The upfield peak grows at the expense of the intensity of the downfield peak as χ_M increases. That the aforementioned changes were due to stereochemical differences in the copolymers was established by copolymer epimerization studies. Treatment of solutions of NPM–CEVE copolymers in Me_2SO with 2,2,6,6-tetramethylpiperidine at 60 °C or with potassium *tert*-butoxide at room temperature caused the relative intensities of the carbonyl peaks at 176.4 and 177.1 ppm to change with time. Indeed, the intensity of the peak at 177.1 ppm eventually becomes less than that of the peak at 176.4 ppm. Copolymer epimerization with lithium diisopropylamide in tetrahydrofuran at −78 °C resulted in

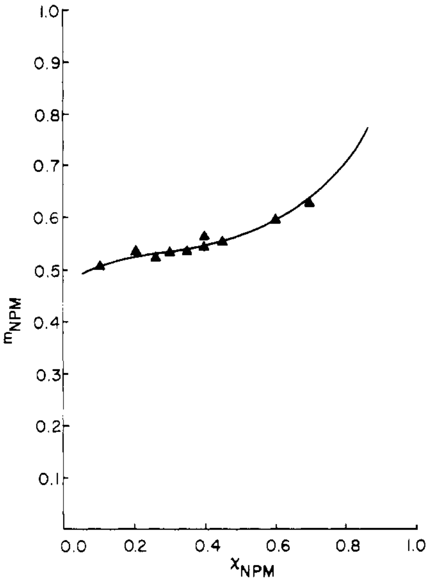

Figure 1. Copolymer composition diagram for the NPM–CEVE system (m_{NPM} = mole fraction NPM in the copolymer, χ_{NPM} = initial mole fraction of NPM in the feed).

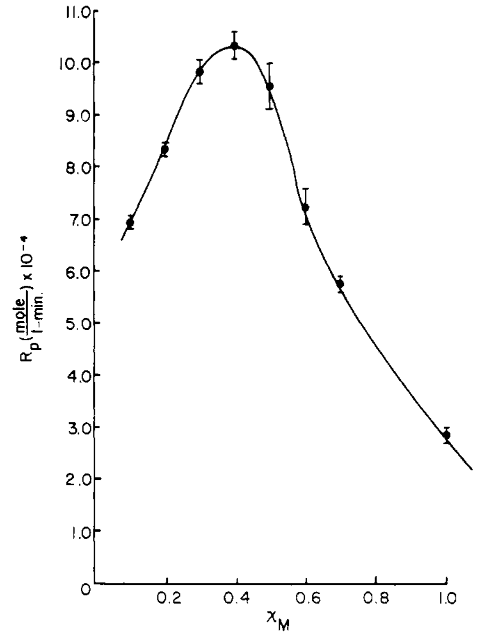

Figure 2. Initial copolymerization rate vs. χ_M for the system NPM, CEVE, AIBN, CH_2Cl_2, 60 °C.