tively. The values of $(f/A^*)_r$, and thus also $E_r$, are somewhat higher for the tetrafunctional networks, which is consistent with the expectation that the stress should increase with increase in junction functionality. The larger the number of chains emanating from a junction, the more firmly embedded it is within the network structure, and this partially suppresses the fluctuations which diminish the stress.[11]

Both $(f/A^*)_r$ and $E_r$ are seen to go through a maximum with decrease in the number of short chains. A composition of approximately 95 mol % short chains avoids excessive brittleness from having too few long chains and also having so many long chains as to preclude reinforcing effects from the limited extensibility of the short chains.[3] At this composition, which corresponds to 35–40 wt % short chains, the ultimate properties are apparently as high as can be achieved in an unfilled PDMS network.

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## References and Notes

(1) Mark, J. E. *Adv. Polym. Sci.* **1982**, *44*, 1.
(2) Mark, J. E. In "Elastomers and Rubber Elasticity"; Mark, J. E., Lal, J., Eds.; American Chemical Society: Washington, D.C., 1982.
(3) Mark, J. E.; Tang, M.-Y., submitted to *J. Polym. Sci., Polym. Phys. Ed.*
(4) Mark, J. E.; Sullivan, J. L. *J. Chem. Phys.* **1977**, *66*, 1006.
(5) Llorente, M. A.; Andrady, A. L.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 621.
(6) Llorente, M. A.; Andrady, A. L.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2263.
(7) Treloar, L. R. G. "The Physics of Rubber Elasticity"; Clarendon Press: Oxford, 1975.
(8) Mark, J. E. *Rubber Chem. Technol.* **1975**, *48*, 495.
(9) Andrady, A. L.; Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1980**, *72*, 2282.
(10) Andrady, A. L.; Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1980**, *73*, 1439.
(11) Flory, P. J. *Proc. R. Soc. London* **1976**, *351*, 351.

# Synthesis of Polyacetylene Block/Graft Copolymers

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ABSTRACT: Graft/block copolymers of polyacetylene and polyisoprene or polystyrene have been prepared by intercepting a growing polyacetylene chain with a polymer-bound ketone or epoxide, thus forming a new carbon–carbon bond. The catalyst employed is a modification of the Shirakawa catalyst for acetylene polymerization. The molecular weight of the polyacetylene block was varied by changing the ratio of monomer to graft sites in the polymerization, thus generating a series of samples of increasing polyacetylene block lengths. These samples exhibit visible absorption spectra ranging from that characteristic of low molecular weight *trans*-polyenes to that of conventional *trans*-polyacetylene. Graft copolymers in which the polyacetylene block length is relatively long were shown in solution to form aggregates which appear to be amorphous. When longer block lengths were prepared, the polyacetylene blocks formed crystalline domains with a characteristic *trans*-polyacetylene structure. The graft copolymers contain unusually low spin densities (<1/300 000 polyacetylene C atoms). Addition of bromine to graft copolymer solutions initially results in the formation of a charge-transfer complex and subsequently bromination. The formation of these complexes could be partially reversed (compensated) by the addition of ammonia.

Conducting polymers have been the focus of considerable research in recent years due to their electrical and electronic properties.[1-4] Polyacetylene is the most widely studied of this class of polymers and serves as the prototype for other conducting polymers. In order to unravel the complicated problem of electrical conduction in the bulk material, it is first necessary to better understand the intrinsic electronic properties of polyacetylene. This requires the separation of intrachain properties from those induced by chain–chain interactions or defect sites. Unfortunately, such effects are complicated by the fact that polyacetylene is insoluble and decomposes prior to melting.

One solution to this problem has been to prepare random copolymers of acetylene with other acetylenic monomers,[5-7] which can yield a more tractable material. These copolymers not only exhibit inferior electrical properties but also are inadequate models for the electronic properties of polyacetylene due to their greatly altered chemical structure. An alternative approach to synthesizing random copolymers is to prepare a block copolymer from acetylene and a suitable comonomer. With this method, the integrity of the polyene chain is maintained, allowing studies of the electronic properties of individual polyacetylene chains. Block copolymers exhibit phase diagrams characterized by elevated critical points[8] and phase structures which are limited to a microregime (e.g., $10$–$10^3$ Å).[9,10] Thus, block and graft copolymers potentially offer a method by which the intrinsic properties of polyacetylene can be retained in an experimentally tractable form.

The combination of a highly crystalline and inherently insoluble polymer (e.g., polyacetylene) with an amorphous, soluble polymer in the form of a block or graft copolymer should result in a spectrum of phase states which is strongly dependent on composition. When the polyacetylene segment represents a minor fraction of the polymer, the block copolymer solubility should be dictated by the solubility characteristics of the "carrier" block. In the limit of a low carrier polymer composition, the phase behavior of the composite should be similar to that of pure polyacetylene, which has been shown to form a fibrous

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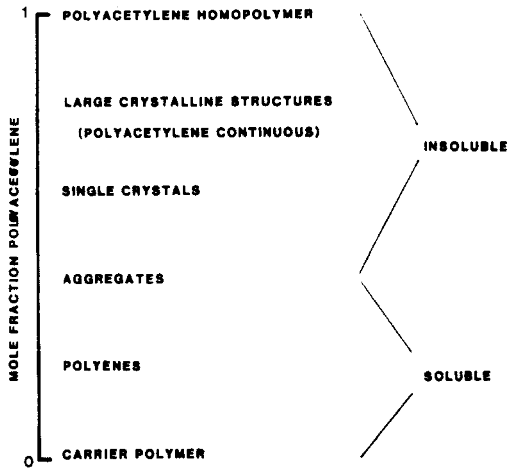

**Figure 1.** Expected spectrum of materials for a block or graft copolymer of polyacetylene and a soluble carrier polymer.

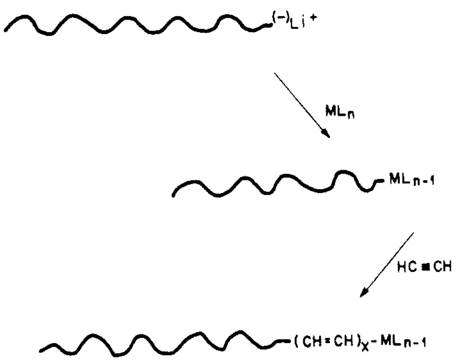

**Figure 2.** Block copolymer synthesis via the anion-to-Ziegler–Natta transformation reaction.

network. Intermediate compositions are expected to exhibit morphologies between these extremes, as depicted schematically in Figure 1.

Two new approaches to the preparation of block copolymers in which one block is synthesized by Ziegler–Natta catalysis have been identified. In the first method, termed "anionic-to-Ziegler–Natta transformation" (Figure 2), the anionic center of a living polymer prepared by standard anionic polymerization methods is converted to a transition-metal alkyl, which either is an active polymerization catalyst or is a suitable intermediate. Polymerization at the catalyst site should yield a block copolymer in which the segments are joined end-to-end. This procedure has been employed to prepare block copolymers of polystyrene and polybutadiene with polyethylene[11-13] and has recently been applied to block copolymers of polyacetylene.[14]

The second method is a new approach to block and graft copolymer synthesis in which a growing polymer chain initiated by a Ziegler–Natta catalyst is intercepted by a suitable graft site on a carrier polymer, thereby forming a new carbon–carbon bond (Figure 3). The graft site can be located anywhere on the carrier polymer, including the terminus, which would then yield the copolymer identical with that obtained from the transfer reaction.

In this report, we describe the practical synthesis of polyacetylene block/graft copolymers by employing termination reactions as the key step in graft/block copolymer formation.

## Results and Discussion

The chief advantage of the grafting procedure over the anion-to-Ziegler–Natta transformation reaction is the simplicity of these polymerizations, which can be carried out in standard air-free reactors using common syringe techniques. We have reproducibly prepared large quantitites of graft copolymers by this technique with some control over polyacetylene molecular weight (see below).

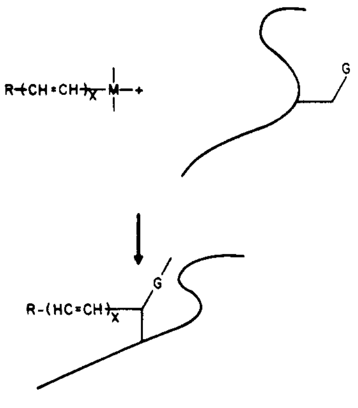

**Figure 3.** Graft copolymer synthesis via termination of a growing Ziegler–Natta chain.

Polymerizations are carried out by adding a solution of triethylaluminum in toluene to a solution of acetylene, titanium tetrabutoxide, and the carrier polymer, containing graft sites, in toluene. Graft sites are typically epoxides or ketones as discussed below. The polymerization commences almost immediately as indicated by a color change; at room temperature the reaction is complete in several minutes. The point at which the polyacetylene block is attached to the carrier polymer can be varied along the chain, depending upon the graft site(s) location. In most cases, the grafting reaction was enhanced by randomly incorporating numerous (15–50) graft sites on each carrier chain. The presence of excess carrier polymer favors the incorporation of one grafted polyacetylene chain per graft copolymer molecule and a large amount (>95%) of unreacted carrier homopolymer.

Unfortunately, no method has yet been devised by which the solubilized graft copolymer can be separated from the carrier homopolymer. (In this context we use the term "solubilized polyacetylene" to denote polyacetylene copolymers which are able to pass through filters with pore sizes as small as 2000 Å and are not readily separated from carrier homopolymer by centrifugation.) Thus, standard techniques such as elemental analysis or spectroscopy cannot be used to directly determine the composition of the copolymer in these mixtures. When the size of the polyacetylene block became sufficiently long, the copolymer precipitated from solution. These materials were isolated by filtration or centrifugation and, after thorough washing, were analyzed by IR spectroscopy to determine the composition of the block. Like homopolyacetylene, block copolymers which precipitated during synthesis were intractable.

Solubilized copolymers were analyzed by IR and UV–vis spectroscopy to determine both the trans isomer content and the total amount of polyacetylene in each sample. For such studies, the carrier polymer is an inert diluent. Since the IR spectrum of a block copolymer is merely the sum of that for the two blocks, the characteristic 1013-cm$^{-1}$ absorption for the *trans*-polyacetylene portion of the copolymer is clearly revealed when a standard spectrum of the homopolymer is subtracted from that of the copolymer (Figure 4).

The composition of each sample was calculated by comparing the intensity of the 1013-cm$^{-1}$ absorption band with that of a characteristic band found in the IR spectrum of the carrier polymer and applying the measured extinction coefficients. When working with solutions, it was

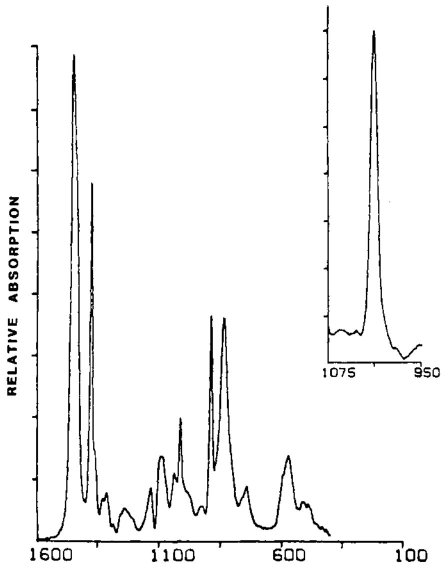

**Figure 4.** FTIR spectrum of polyacetylene/polyisoprene graft copolymer. Note that subtraction of the spectrum for polyisoprene from that of the copolymer (inset) cleanly reveals the characteristic 1013-cm$^{-1}$ absorption for *trans*-polyacetylene.

**Table I**
**Absorptivities for *trans*-Polyacetylene**

| energy (wavelength) | $\epsilon \times 10^{-3}$, cm$^3$ g$^{-1}$ cm$^{-1}$ |
|---|---|
| 1013 cm$^{-1}$ (9.68 μm) | 4.6[a] |
| 3010 cm$^{-1}$ (3.32 μm) | 1.8[b] |
| 12000 cm$^{-1}$ (833 nm) | 100[c] |
| 17240 cm$^{-1}$ (575 nm) | 80[d] |

[a] Calculated from the measured value of $\epsilon_{3010}$ and the ratio $\epsilon_{1013}/\epsilon_{3010}$, which was independently determined for 11 polyacetylene graft copolymers. [b] Measured using a thin (55 μm) free-standing film of *trans*-polyacetylene. [c] Calculated from the reported value[15] of $\alpha$ for a thin *trans*-polyacetylene film on glass without density corrections. [d] Measured for solubilized polyacetylene.

far more convenient to use UV–vis spectroscopy to determine the polyacetylene content in samples of solubilized polyacetylene. This technique was verified by examining a sample by both IR and UV–vis spectroscopy; $\epsilon_{575}$ was calculated to be 80 × 10$^3$ cm$^3$ g$^{-1}$ cm$^{-1}$, a value comparable to that reported for thin films of crystalline *trans*-polyacetylene.[15]. A complete listing of the extinction coefficients for *trans*-polyacetylene appears in Table I.

We unambiguously demonstrated that grafting occurs during these polymerizations by comparing the polymerization of acetylene in two nearly identical reactions, differing only in the locations of the chain termination sites. The first polymerization was carried out in a 10% solution of polyisoprene which had graft sites in the form of ketones (15 per molecule) bound to the polyisoprene. In the second polymerization, an equivalent amount of methyl ethyl ketone was substituted for the graft sites in a 10% solution of nascent polyisoprene. Both solutions contained an equivalent amount of acetylene and titanium tetrabutoxide. Initiation with a solution of triethylaluminum quickly produced a blue solution in the first reaction, while the second rapidly developed macroscopic black particles. The black particles were collected by filtration and were exhaustively washed with toluene and methanolic HCl. Less than 10% of this sample was found to be polyisoprene as measured by infrared spectroscopy. The product of the first reaction also eventually precipitated from solution, but in this case as finely divided blue particles, which were isolated by filtration and exhaustively washed as before. In these samples a considerable amount of carrier polymer (~50%) could not be separated from the polyacetylene portion, owing to the graft copolymer nature of this product. As discussed below, the final composition and physical state of the copolymer is directly related to the reaction conditions.

This grafting procedure can in principle be extended to polymers other than polyacetylene, providing a method for the preparation of a wide range of interesting materials. In the following sections, the choice of reaction parameters for the preparation of graft copolymers of polyacetylene is described.

**Catalyst.** Although many transition-metal catalysts polymerize acetylene to give a high molecular weight polymer,[1] the most commonly used catalyst is prepared by combining triethylaluminum and titanium tetrabutoxide at low temperatures. When free-standing films are prepared, the catalyst solution (4:1 triethylaluminum–titanium tetrabutoxide in toluene, ~0.2 M) is often aged[16] at room temperature for approximately 1 h in order to obtain a catalyst solution of maximum activity. The resulting high concentration of active centers leads to a highly, intertwined polymer network upon addition of the monomer, giving a tough, mechanically stable film.[17]

The graft polymerization requires a different state of catalyst. While the same chemical species can be employed, it is important that the concentration of active sites remains relatively low, in order to suppress crystallization of the growing polyacetylene chains during polymerization. In practice, we found that the addition of a previously prepared solution of catalyst to the carrier polymer solution produced an inhomogeneous precipitate. Presumably this results from an inability to disperse the reactants prior to catalyst formation and polymerization.

The ideal catalyst is one which is homogeneous and dilute at all times. This was effected with the titanium tetrabutoxide/triethylaluminum system by preparing the catalyst in situ, e.g., by adding a dilute solution of triethylaluminum to a well-mixed solution of carrier polymer, acetylene, and titanium tetrabutoxide in toluene. In this way, the rate of formation of catalyst is limited by the addition and diffusion of triethylaluminum, which can be readily controlled. Thus dilute catalyst solutions were prepared which resulted in a reproducible and efficient means of initiating graft polymerization.

IR spectroscopic analyses revealed only the trans isomer in samples of the solubilized polyacetylene prepared at room temperature. Typical preparations of polyacetylene films with the Shirakawa catalyst at room temperature result in a 40% trans content.[17] One explanation for these different results is that the polymerization consists of three discrete steps: chain growth by cis insertion of acetylene monomer, cis–trans isomerization, and crystallization. The formation of graft copolymer may suppress the crystallization step and allow the complete isomerization to the trans isomer. This mechanism cannot fully explain the results since control polymerizations containing no carrier polymer also had a higher trans isomer content than expected, occasionally even 100% trans.

A second explanation is that the catalyst prepared by the above procedure (slow addition of triethylaluminum to titanium tetrabutoxide) is not identical with the Shirakawa catalyst. Previously it had been shown that the trans content of polyacetylene films increased when the ratio of triethylaluminum to titanium tetrabutoxide decreased[17] from the typical value of 4/1. In solubilized polyacetylene polymerizations, a low Al/Ti ratio was used, and thus a high trans isomer content might be expected, although a 100% trans product under the reaction conditions employed has never been reported. A complete explanation for these results requires further experimental work.

**Graft Sites.** Graft sites for a polyacetylene graft polymerization can easily be chosen with some knowledge of the reactivity of the active site of the catalyst. Unfortunately, little is known about the nature of the active catalyst in the titanium tetrabutoxide/triethylaluminum system or any other Ziegler–Natta catalyst. Two distinctly different intermediates are expected depending upon whether an insertion mechanism[18,19] or an analogue of the olefin metathesis reaction[20] is operating. Titanium alkylidenes are expected from a metathesis mechanism, while insertion mechanisms postulate the formation of a titanium alkyl.

Fortunately, the reactivity of these intermediates is similar toward a variety of reagents yielding new carbon–carbon bonds. For example, the reaction of $Cp_2TiCH_2$ with acid chlorides and ketones represents high-yield approaches to the synthesis of methyl ketones[21] and allenes,[22] respectively. The reactivity of titanium–carbon alkyls toward carbonyls[23,24] and epoxides is similar, the product resulting from an insertion of the reagent into the titanium–alkyl bond. In both cases a new carbon–carbon bond would be formed between the graft site and the growing polyacetylene chain.

Although many reagents could be used as graft sites, ketones and epoxides are particularly useful since they can be introduced onto carrier polymers by standard chemical techniques. In addition, their reactivity toward the triethylaluminum/titanium tetrabutoxide catalyst is high, making the graft step relatively efficient at room temperature. As reaction temperatures were lowered, it was observed that epoxides became less useful as their reactivity lessened relative to the rate of polymerization, while ketones remained active. Therefore, at low temperatures (−40 °C), ketones are the graft sites of choice.

Ketones and epoxides not only are very active toward catalytic sites with a growing polyacetylene chain but may also react with the initial catalyst or catalyst precurosors. A demonstration of this reactivity was the conversion of methyl ethyl ketone to 3-methyl-3-pentanol in >95% yield in less than 5 min under typical polymerization conditions. Alkylation by triethylaluminum alone was at least 10 times slower, demonstrating that the transfer of an ethyl group from aluminum to titanium to ketone (or from an aluminum–titanium complex to ketone) is extremely facile. Thus, graft polymerizations carried out at a ratio of graft sites to catalyst of >1 should eventually cease as the graft sites quench all available catalyst sites, those with growing polyacetylene chains and those without.

The second function of the graft site is to form a basis for controlling molecular weight. Without some method to reliably control the molecular weight of a block, this preparation of graft copolymers becomes less useful since each preparation must be treated as a special case. A demonstration of the utility of ketones as modifiers of molecular weight was the preparation of oligomers of acetylene. Low molecular weight polymers are soluble in organic solvents and exhibit a distinctive four-peak electronic absorption envelope.[25] A room-temperature polymerization was carried out at a low ratio of acetylene to acetone in the absence of carrier polymer. As the polymerization was initiated by the addition of triethylaluminum, it was quickly quenched by acetone. The UV–vis spectrum of the isolated product (Figure 5) shows a broad absorption envelope with a periodic fine structure, which is the expected result for a mixture of polyenes varying from $n = 1$ to $n \simeq 10$, where $n$ is the number of conjugated double bonds. By varying the ratio of acetylene to acetone, the average molecular weight and conjugation length of the polyenes can be manipulated. Since a mixture of products is produced, this procedure does not represent a useful preparative synthetic method for discrete polyenes. A determination of the structure of the chain ends, however, may yield information on the initiation of acetylene polymerization as well as the termination step during grafting.

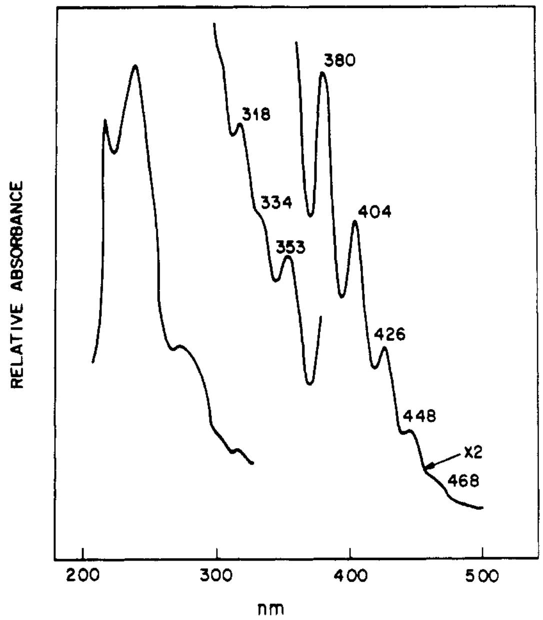

**Figure 5.** UV–vis spectrum of a polyene mixture prepared by termination reactions. The spectrum from 200 to 300 nm was obtained by diluting the polyene solution by an arbitrary amount.

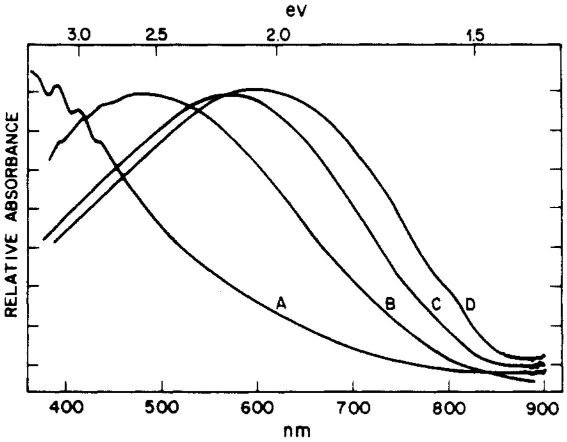

**Figure 6.** UV–vis spectra of polyacetylene graft copolymers prepared by the described procedure with the following amounts of acetylene: A, 65 $cm^3$ at 10 torr; B, 65 $cm^3$ at 30 torr; C, 65 $cm^3$ at 100 torr; D, 65 $cm^3$ at 1 atm.

When a polyisoprene carrier polymer ($M_n$ = 200 000) containing 50 graft sites per chain is substituted for the acetone used in the previous polymerization, higher molecular weight polyenes can be prepared and analyzed. Figure 6 illustrates the products obtained with four different ratios of acetylene to graft site. In curve A, the typical polyene absorption envelope is observed, similar to that of Figure 4. Based upon the position of the peak in the absorption curve, the average molecular weight of the polyene segment can be roughly estimated to be 216 ($n = 6$). By tripling the amount of added acetylene, curve B was obtained, indicating a further increase in conjugation length and molecular weight. A small portion of the polyene fine structure remains, although the absorption envelope now more closely resembles that of *trans*-polyacetylene. By using 10 times as much acetylene, a blue product (curve C) was produced, with all the spectral features of *trans*-polyacetylene. This preparation may represent limiting behavior for this series of polymerizations, in that further increases in acetylene (curve D) yielded products which contained a fraction of crystalline polymer as verified by electron diffraction. These solids could be removed by centrifugation, and the spectrum of the supernatant closely matched that of spectrum C. Suspensions of crystalline polyacetylene gave spectra shifted to even lower energies ($\lambda_{max} \simeq 685$). This shift may be due to either interchain coupling in the crystalline state, or higher effective conjugation lengths.

**Carrier Polymers.** The primary purpose of the carrier polymer is to impart the desired physical properties of the carrier to the copolymer. These properties may be solvent resistance, impact resistance, or, for an insoluble block, solubility. A wide variety of polymers can be employed, but several obvious requirements must be fulfilled. The polymer either must be relatively inert toward the catalyst or be inherently reactive toward the catalyst in a way which yields graft copolymer, as in the case of poly(methyl vinyl ketone) and its copolymers. The carrier must be functionalizable, preferably to yield epoxides or ketones in the desired amounts, and be amenable to characterization so that the resulting block copolymer might also be characterized.

Using these guidelines, we have employed polyisoprene and polystyrene as carrier polymers. These polymers were prepared by anionic polymerization to give well-defined monodisperse carriers ($M_n \simeq 2 \times 10^5$). When epoxides were desired as graft sites, polyisoprene was epoxidized with *m*-chloroperbenzoic acid in benzene to the desired extent. Random copolymers of styrene and a few percent butadiene were treated in the same way to yield a polystyrene carrier with epoxide graft sites. Ketone-containing carriers were prepared from the epoxidized carriers by treating them with $BF_3$ etherate in benzene. A typical number of graft sites for a 200 000 molecular weight polyisoprene carrier was 15–50 per chain. Multiple grafting of growing polyacetylene to a single carrier polymer was avoided by carrying the grafting reaction to a low conversion (>95% of the carrier chains have no graft).

When unsaturated polymers are used as carriers, it is possible that vinyl groups may participate in the polymerization and yield cross-linked materials or unwanted copolymers. Model reactions showed that the polymerization of simple $\alpha$-olefins by the titanium tetrabutoxide/triethylaluminum catalyst was exceedingly slow, if they polymerized at all. A more important side reaction is the polymerization of epoxides by residual catalyst or triethylaluminum after the graft polymerization. This too was found to be a slow reaction on the time scale of the polymerization (days vs. minutes), and could be eliminated by the addition of dilute acid to destroy residual catalyst at the end of the graft reaction. No gelation was observed for acid-treated samples.

## Properties of Solubilized Polyacetylene

One of the most important problems in polyacetylene research is the difficulty in adequately characterizing samples. Due to its tractibility, solubilized polyacetylene can be analyzed by a variety of techniques, and the results for a typical sample (corresponding to curve C, Figure 6) will be described. A typical polymerization is carried out to low grafting conversion (based on carrier polymer) and yields a polyacetylene content of a few percent based on total polymer. These solutions are opaque, but dilution of the sample with solvent yields a clear purple solution comprised of graft copolymer and carrier polymer. Dilute solutions of solubilized graft copolymer pass through filters with pore sizes as small as 2000 Å and are stable for at least many months under an inert atmosphere. A short exposure to oxygen initiates a rapid oxidation process, with the sample changing from purple to red to yellow in a few days.

A major point of controversy in polyacetylene research has been the nature of the free spins found in the homopolymer. These spins have been claimed to be highly mobile[27] and have been implicated in the conduction mechanism at low doping levels.[28] These spins are found at a level of ~1/3000 carbon atoms in *trans*-polyacetylene[29] and appear in the ESR spectrum as a narrow (~0.5 G) singlet at the free electron *g* value. Solubilized polyacetylene is essentially spin free (<1/300 000 polyacetylene carbon atoms) showing a broad (~5 G) residual signal at the free electron *g* value. This low-spin material should prove particularly useful in doping and photoexcitation experiments, since the spin state of the excited state can be readily determined against a low background spin level.

The most difficult characterization question is the microscopic state of solubilized polyacetylene. Small amorphous aggregates, microcrystals, or single chains are all possible states for the system. Although these should differ considerably in molecular weight from unreacted homopolymer, it was not possible to separate solubilized polyacetylene from the homopolymer by ultracentrifugation since both apparently have a similar sedimentation coefficient (see below). The most powerful technique for identifying the size of molecules in solution is light scattering. A recent study[30] of sample C (Figure 6) found the persistence length of the polyacetylene block(s) to be ~350 Å while the hydrodynamic radius of the entire copolymer was ~1050 Å. These values are consistent with the domain sizes obtained in microphase-separated block copolymers and suggest that this sample consists of aggregates of graft copolymers in solution, although the arrangement of the polyacetylene segments within the aggregate has yet to be determined.

NMR spectroscopy is a powerful tool for determining the microstructure and state of a polymer in solution. Recent experiments with 100% $^{13}C$-labeled solubilized polyacetylene have indicated that our previous assignment[26] of resonances centered at 128 ppm vs. $Me_4Si$ to solubilized polyacetylene to be in error. Careful measurements have failed to detect a $^{13}C$ NMR signal from solutions of solubilized polyacetylene. This result is not surprising when the light scattering results are considered. Previous solution NMR experiments[31] on styrene–butadiene block copolymers in hexane (a poor solvent for polystyrene) have revealed that the styrene portion of the copolymer escapes detection due to the restricted motion of the chains. Similarly, the polyacetylene segments in solubilized polyacetylene may have restricted motion within the aggregate, resulting in an extremely broad signal. When dried samples of solubilized polyacetylene were examined by magic angle spinning techniques, a signal attributable to *trans*-polyacetylene[32-34] was observed at 138 ppm relative to $Me_4Si$ in addition to the spectrum for the carrier polymer. Due to 100% $^{13}C$ enrichment, the *trans*-polyacetylene resonance was broadened to 1–2 kHz by dipole–dipole interactions of the $^{13}C$ nuclei.

Inferences concerning the phase state of solubilized polyacetylene can be made by considering the striking differences between it and a sample prepared with a higher acetylene content. As described earlier, an increase in the amount of acetylene charged into a polymerization leads to an increase in the molecular weight of the polyacetylene block. Thus this sample (D, Figure 6) has a visible absorption spectrum shifted to significantly lower energies (longer conjugation length) than that of solubilized polyacetylene (C, Figure 6). By a simple filtration or centrifugation step, this sample was separated into two distinct fractions: a mixture of solubilized polyacetylene and unchanged carrier polymer, and a fraction composed of particles >2000 Å in size free of unreacted carrier polymer. The visible absorption spectrum of the filterable fraction is identical with that of solubilized polyacetylene, but the absorption peak corresponding to the particles is shifted to even lower energy. Ultracentrifugation failed to separate the solubilized fraction from the residual homopolymer, implying a similarity in sedimentation coefficients. We believe that this result is a reflection of a similarity in buoyancy factors.

The fact that sample D could be cleanly separated into two distinct fractions suggests a fundamental difference in the phase states of these fractions. Samples of solubilized polyacetylene unfortunately contained too low a polyacetylene content to be examined by electron diffraction. The particulate fraction was highly crystalline and exhibited an electron diffraction pattern identical with that of *trans*-polyacetylene. A shift of the absorption envelope to lower energies is consistent with an enhanced conjugation length due to a more planar arrangement of the $\pi$ system or an increase in the coupling between chains, both consquences of a transition from a noncrystalline to crystalline state. Finally, the large observed difference in sedimentation rates is consistent with solubilized polyacetylene being amorphous and of a lower density than the crystalline particulate fraction; i.e. crystalline and amorphous polyacetylene would have very different buoyancy factors.

The doping of polyacetylene films to high conductivity has initiated much of the current interest in conducting polymers. Since the polyacetylene content in dried samples of solubilized polyacetylene is but a few percent and is present in isolated domains within an insulating matrix,[26] it was not surprising that the oxidation of these samples with typical doping agents such as halogens did not lead to an increase in the bulk conductivity. The chemical process of doping, however, can be examined in solution by spectroscopic techniques. For example, a solution of solubilized polyacetylene changes from purple to gray when bromine is added, corresponding to a decrease in absorption in the visible region (Figure 7) and a concurrent increase in absorption in the infrared, just as is observed for thin films of polyacetylene. When ammonia is added (compensation) a portion of the original spectrum is restored, but there is a shift of the absorption to higher energy, indicative of shorter conjugation lengths.

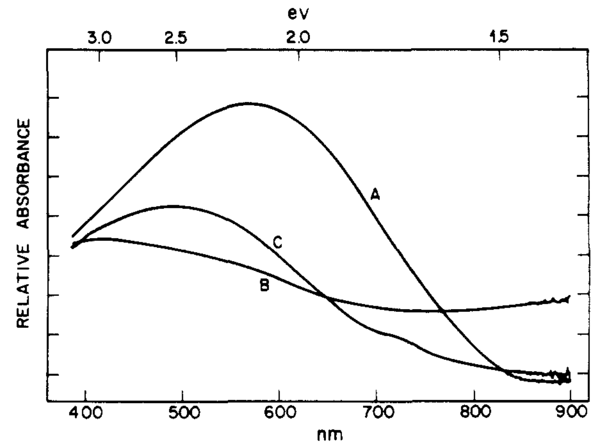

**Figure 7.** UV–vis spectrum of solubilized polyacetylene (A). After treatment with $Br_2$ curve B is obtained. Treatment with ammonia partially restores the absorption curve (compensation) and gives spectrum C.

Charge-transfer complexes of olefins and bromine are well-known and represent an intermediate step in the bromination of olefins.[35] If the subsequent addition step can be suppressed, a stable charge-transfer complex can be formed. For example, the formation of the charge-transfer complex of tetrakis(*p*-methoxyphenyl)ethylene with bromine[36] is accompanied by an increase in absorbance at $\sim {}^1/_2$ the energy of the $\pi$–$\pi^*$ transition. Addition of bromine to form the dibromide is unfavorable, and thus the original olefin can be regenerated by adding a reagent which irreversibly reacts with bromine. Halogenation is a competing process when solubilized polyacetylene is treated with bromine, and eventually the polymer is converted to poly(1,2-dibromoethylene). The basic spectral features of doped polyacetylene, charge-transfer complexes of olefins, and the intermediates in the bromination of solubilized polyacetylene are similar, suggestive of similar chemical interactions in each system.

## Conclusions

Block/graft copolymers of polyacetylene can be prepared by intercepting a growing Ziegler–Natta polymer with a suitable graft site on a carrier polymer. The molecular weight of the polyene segment can be varied by adjusting the relative amounts of monomer and termination sites, yielding copolymers with different compositions and properties. Solubilized polyacetylene solutions have been shown by light scattering to be composed of aggregates on a molecular scale. These materials serve as models for polyacetylene since several solid-state properties of polyacetylene (e.g., doping) have also been observed for solubilized polyacetylene. Future work will exploit this similarity, in an effort to explain the properties of polyacetylene.

## Experimental Section

All manipulations of products containing polyacetylene were carried out in an oxygen-free Vacuum Atmospheres HE series glovebox filled with helium or on a vacuum line using standard vacuum line techniques. Toluene and hexane were dried and distilled from sodium benzophenone ketyl dianion prior to use. Acetylene (Matheson) was passed through two dry ice–acetone cold traps and then through a column of activated $Mn^0$ supported on vermiculite and into a 500-mL storage bulb. The bulb was isolated and the acetylene was condensed by cooling with liquid nitrogen. After evacuating the bulb to 50 mtorr to remove contaminating noncondensible gases, the bulb was warmed to room temperature. **Caution**: Acetylene has been reported to be explosive when condensed.[37] We experienced no problems in handling acetylene in this manner, but we were careful to always use acetylene at reduced pressure to limit the possibility of explosion. Titanium tetrabutoxide (Alfa) was distilled under reduced pressure and was then diluted with dry deoxygenated toluene to yield a 0.13 M stock solution. Triethylaluminum (25 wt. % solution in toluene, Aldrich) was used as received. Monodisperse samples of polyisoprene and poly(styrene-*co*-butadiene) used for carrier polymer synthesis were prepared by standard anionic polymerization techniques[38] and were stored in an oxygen free glovebox.

Samples of solubilized polyacetylene for ESR and solid-state $^{13}C$ NMR spectroscopy were transferred as solutions to the appropriate sample tube in the drybox. The samples were dried and evacuated to remove the residual solvent and then were sealed *in vacuo*. ESR spectra were obtained on a Varian X-band spectrometer with DPPH as the reference. The $^{13}C$ NMR spectrum of 100% $^{13}C$-enriched solubilized polyacetylene was obtained on a Varian XL-200 spectrometer equipped for CP/MAS measurements. Optical spectra of solutions of solubilized polyacetylene were measured with a Perkin-Elmer 559 spectrophotometer. These solutions were prepared in the drybox, and were sealed in air-free cells.

**Analysis of Copolymers by IR Spectroscopy. Determination of Cis–Trans Isomer Content.** Samples for IR analysis were prepared by removing an aliquot of the copolymer from the reactor and drying the film on a silicon wafer. The residual solvent was removed *in vacuo*, and the total exposure time to atmospheric oxygen was 5 min or less. Spectra were obtained on a Nicolet MX-1 or 10DX FTIR spectrometer under a nitrogen atmosphere. The cis isomer content of the samples was determined by comparing the integrated area of the 1013-cm$^{-1}$ (trans) absorption with that appearing at 740 cm$^{-1}$ (cis) as previously described.[39] When the 740-cm$^{-1}$ band was obscured, the trans isomer content was determined by measuring the increase in intensity of the 1013-cm$^{-1}$ absorption relative to a characteristic band for the carrier polymer after the sample had been thermally isomerized (180 °C, 5 min) to the trans isomer.

**Determination of Copolymer Composition.** Extinction coefficients were determined for characteristic absorptions in polyacetylene and the carrier homopolymers. The IR spectrum of a thin (55 $\mu$m) film of *trans*-polyacetylene was measured. From the observed intensity of the C–H stretching mode at 3010 cm$^{-1}$ and the measured density, $\epsilon_{3010}$ was calculated to be $1.8 \times 10^3$ cm$^3$ g$^{-1}$ cm$^{-1}$. The value of $\epsilon_{1013}$ was calculated by using the ratio $\epsilon_{3010}/\epsilon_{1013}$ determined by averaging the results from 11 independent graft copolymer samples, giving a value of $4.6 \times 10^3$ cm$^3$ g$^{-1}$ cm$^{-1}$. The value of $\epsilon_{1013}$ was not directly determined on films of crystalline *trans*-polyacetylene since optically thin films were too thin for accurate density measurements, and the line shape of the 1013-cm$^{-1}$ absorption varies with the trans content and degree of crystallinity in the sample. For both polyisoprene and polystyrene, the IR spectra of polymer solutions in $CCl_4$ of known concentration were measured. The value of $\epsilon_{1600}$ for polystyrene was calculated to be $2.15 \times 10^2$ cm$^3$ g$^{-1}$ cm$^{-1}$ and $\epsilon_{1447}$ for polyisoprene was found to be $6.02 \times 10^2$ cm$^3$ g$^{-1}$ cm$^{-1}$.

The total polyacetylene content in samples of copolymer mixed with homopolymer was determined by preparing films of the mixture on a silicon wafer as before and thermally isomerizing (180 °C, 5 min) the sample to ensure that only the trans isomer was present. The IR spectrum was measured and using the values of $\epsilon$ and the measured intensities, the composition was calculated. Alternatively, the spectrum of the copolymer was subtracted from that of the mixture by the interactive subtraction routine of the 10 DX spectrometer until only the *trans*-polyacetylene spectrum remained (Figure 4). This procedure was especially useful when the 1013-cm$^{-1}$ band of *trans*-polyacetylene was partially obscured.

**Epoxidation of Carrier Polymers.** The following procedure, as exemplified for poly(styrene-*co*-butadiene), was also employed for the epoxidation of polyisoprene. A random copolymer containing 3 wt % butadiene and 97 wt % styrene was prepared by standard techniques.[33] The copolymer had a molecular weight of approximately 200 000 and a polydispersity of 1.04. To a solution of 10 g of copolymer dissolved in 200 mL of benzene was added 0.15 g (0.74 mmol) of 85% *m*-chloroperbenzoic acid. After stirring 48 h at room temperature, the solution was twice washed with 10% aqueous $NaHCO_3$ and three times with distilled water. The polymer was precipitated into methanol and was dried under vacuum at 11 °C for 12 h. The polymer was stored under helium prior to use. Due to the low level of epoxidation in the polymer, the epoxides were converted to ketones for analysis by IR spectroscopy. The polymer was dissolved in benzene and a 10-fold excess of $BF_3$ etherate (Aldrich) was added. After stirring for 24 h, the polymer was washed with water, with 10% aqueous $NaHCO_3$, and again with water. The polymer was precipitated into methanol and was dried under vacuum for 24 h. The ketone content was calculated by measuring the absorption at 1716 cm$^{-1}$ due to cabonyl and applying an appropriate value for the extinction coefficient[40] ($1.4 \times 10^4$ cm$^3$ g$^{-1}$ cm$^{-1}$).

**Preparation of Polyacetylene Oligomers.** To a 500-mL flask containing 200 mL of dry, deoxygenated toluene was added 6.9 g of titanium tetrabutoxide. The flask was cooled in a dry ice–acetone bath and was evacuated to a pressure of 100 mtorr. A 1070-mL storage bulb containing acetylene at 1 atm was connected to the flask, and the acetylene was transferred into the reactor by cooling it in a liquid nitrogen bath. When the manometer indicated that all of the gas had been condensed, the storage bulb was disconnected. The reactor was allowed to warm to room temperature, and 1.3 g of acetone was added via syringe. With vigorous stirring, 33 mL of a 1.88 M solution of triethylaluminum in toluene was added over a period of 10 min. The color changed from clear to yellow and finally to brown. When the last of the triethylaluminum had been added, the reaction was quenched by adding 10 mL of methanol followed by the careful addition of 100 mL of 2 N HCl. The product was filtered to remove the precipitated salts. After the salts had been washed with toluene, the filtrate was successively washed with water, $NaHCO_3$, and finally distilled water. The organic layer was dried over $MgSO_4$. Evaporation of the solution to dryness yielded a yellow oil with the spectrum shown in Figure 5. The UV–vis spectrum for this mixture of polyenes did not change over the course of several days of oxygen exposure, indicative of the greater stability of short polyenes relative to polyacetylene.

**Preparation of Solubilized Polyacetylene.** To a 50-mL flask were added 10 mL of a 10 wt % solution of epoxidized polyisoprene (~50 epoxides per chain, $M_w = 200\,000$) and 500 $\mu$L of a 0.13 M solution of titanium tetrabutoxide in toluene. The solution was cooled in a dry ice–acetone bath and was then evacuated to ~100 mtorr. A 65-cm$^3$ storage bulb containing acetylene at a pressure of 100 torr was connected to the flask. When the transfer of acetylene was complete, the flask was warmed to room temperature, and 85 $\mu$L of a 1.88 M solution of triethylaluminum in toluene was added to the vigorously stirred reaction mixture. The solution rapidly developed a purple color and subsequently became opaque. After 5 min, the polymerization was terminated by adding 100 $\mu$L of a degassed mixture of 9/1 methanol–acetic acid, and the product was then transferred into and stored in a drybox prior to use.

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## References and Notes

(1) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361.
(2) Street, G. B.; Clarke, T. C. *IBM J. Res. Dev.* **1981**, *25*, 51.
(3) Etemad, S.; Heeger, A. J.; MacDiarmid, A. G. *Annu. Rev. Phys. Chem.* **1982**, *33*, 443.
(4) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.
(5) Chien, J. C. W.; Wnek, G. E.; Karsaz, F. E.; Hirsch, J. A. *Macromolecules* **1981**, *14*, 479.
(6) Deits, W.; Cukor, P.; Rubner, M.; Jopson, H. *Synth. Met.* **1982**, *4*, 199.
(7) Deits, W.; Cukor, P.; Rubner, M.; Jopson, H. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1981**, *22*, 197.
(8) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(9) Cohen, B. E.; Ramos, A. R. *Macromolecules* **1979**, *12*, 131.
(10) (a) Goodman, I., Ed. "Developments in Block Copolymers"; Applied Science Publishers: London, 1982. (b) Ceresa, R. J., Ed. "Block and Graft Copolymers"; Wiley: London, 1973.
(11) Siove, A.; Fontanille, M. *Makromol. Chem.* **1980**, *181*, 1815.
(12) Cohen, P.; Abadie, M. J. M. Schué, F.; Richards, D. H. *Polymer* **1981**, *22*, 1316.
(13) Soum, A; Siove, A.; Fontanille, M. *J. Appl. Polym. Sci.* **1983**, *28*, 961.
(14) Galvin, M. E.; Wnek, G. E. *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.* **1983**, *24*, (2), 14.
(15) Tanaka, M.; Watanabe, A.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3430.
(16) Aldissi, M.; Schué, F.; Giral, L.; Rolland, M. *Polymer* **1982**, *23*, 246.
(17) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.
(18) Boor, J., Jr. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979.
(19) A recent study (Clarke, T. C.; Yannoni, C. S.; Katz, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 7787) has shown that the synthesis

of *cis*-polyacetylene proceeds by an insertion mechanisms when the Shirakawa catalyst is employed.
(20) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.
(21) Stille, J. R.; Grubs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664.
(22) Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490.
(23) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1983**, *105*, 651.
(24) Ikeda, Y.; Furuta, K.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1982**, *104*, 7663.
(25) Sondheimer, F.; Ben-Efraim, D. A.; Wolovsky, R. *J. Am. Chem. Soc.* 1961, *83*, 1675.
(26) Bates, F. S.; Baker, G. L. *Macromolecules* **1983**, *16*, 704.
(27) Nechtschein, M.; Devreux, F.; Green, R. L.; Clarke, T. C.; Street, G. B. *Phys. Rev. Lett.* **1980**, *44*, 356.
(28) Kivelson, S. *Phys. Rev. B* **1982**, *25*, 3798.
(29) Goldberg, I. B.; Crowe, H. R.; Newman, P. R.; Heeger, A. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1979**, *70*, 1132.
(30) VanNice, F. L.; Bates, F. S.; Baker, G. L.; Carroll, P. J.; Patterson, G. D. *Macromolecules* **1984**, *17*, 2626.
(31) Spevacek, J. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 697.
(32) Maricq. M. M.; Waugh, J. S.; MacDiarmid, A. G.; Shirakawa, H.; Heeger, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7729.
(33) Mehring, M.; Weber, H.; Miiller, W.; Wegner, G. *Solid State Commun.* **1983**, *45*, 1079.
(34) Gibson, H. W.; Pochan, J. M.; Kaplan, S. *J. Am. Chem. Soc.* **1981**, *103*, 4619.
(35) DuBois, J.; Garnier, F. *Chem. Commun.* **1968**, 241.
(36) Buckles, R. E.; Womer, W. D. *J. Am. Soc.* **1958**, *80*, 5055.
(37) "Beilstein's Handbuch der Organischen Chemie"; Prager, B., Jacobson, P., Eds.; Springer: Berlin, 1918; Vol. 1, p 233.
(38) Szwarc, M. "Carbanions, Living Polymers and Electron Transfer Processes"; Wiley-Interscience: New York, 1968.
(39) Gibson, H. W.; Weagley, R. J.; Prest, W. M., Jr.; Mosher, R.; Kaplan, S. *J. Phys. Colloque C3* **1983**, *44*, 123.
(40) Fleet, M. St. C. *Spectrochim. Acta* **1962**, *18*, 1537.

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# Light Scattering from Solubilized Polyacetylene

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ABSTRACT: A solubilized form of polyacetylene (PA) has recently been created by grafting polyacetylene chains onto a polyisoprene carrier chain. The product of this grafting reaction is stable in toluene solution indefinitely. In the present paper static and dynamic light scattering is used to characterize the particles that exist in solution. Polyisoprene is nearly isorefractive in toluene so that nearly all the scattered intensity is due to the PA part. Also, the scattering from the polyacetylene is strongly resonance enhanced. This allowed PA concentrations near $10^{-7}$ g/mL to be studied. The excess depolarized (HV) Rayleigh scattering from the solutions is intense. This means that there is a high degree of orientation correlation between PA subunits in the particles. From the angular dependence of the scattered intensity a characteristic length for the polyacetylene part of the particles is calculated (350 Å). This is a lower bound for the radius of gyration for the PA subunits. Dynamic light scattering studies of the depolarized intensity allowed both the translational and rotational diffusion coefficient to be determined ($D_0 = 3.45 \times 10^{-8}$ cm$^2$/s) ($\Theta = 153$ s$^{-1}$). The overall shape was determined by solving the Perrin equations and gave a prolate ellipsoid with major axis $a = 1800$ Å and axial ratio $\rho = 0.4$. The present results suggest that the graft copolymer molecules form a micellar aggregate in solution. The polyacetylene subunits are highly ordered in the aggregate, but the degree of order has not yet been quantitatively determined.

## 1. Introduction

Polyacetylene was first synthesized in 1958 by Natta et al.[1] as an intractable black powder. In 1971 Shirakawa et al.[2] demonstrated that films of polyacetylene could be grown on the surface of a concentrated Ziegler–Natta catalyst solution. In 1978 it was demonstrated[3] that these films could be doped to obtain near-metallic conductivity. These films consist of a mat of insoluble polyacetylene fibers. Characterization of the individual molecules of polyacetylene is still not possible.

Bates and Baker[4] recently reported the first synthesis of a solubilized form of polyacetylene created by grafting the polyacetylene onto a polyisoprene carrier polymer. When the ratio of the polyacetylene molecular weight to the polyisoprene molecular weight was in the right range, the product of the grafting reaction was stable in solution indefinitely. The visible absorption spectrum of the solution was characteristic of *all-trans*-polyacetylene. However, the macroscopic state of the polyacetylene in solution was not determined. In the present work the state of the polyacetylene graft copolymer in toluene solution is examined by static and dynamic light scattering.

## 2. Theory

The classical theory of light scattering from polymer solutions is well-known.[5] The excess scattered intensity extrapolated to zero angle and zero concentration is proportional to the molecular weight of the polymer. The angular dependence of the scattered light at zero concentration yields the radius of gyration. For polyacetylene, the classical theory is not sufficient to understand the results. For most polymers there is no absorption of visible light so that the excess scattered intensity is simply proportional to the square of the refractive increment $dn/dc$, where $n$ is the refractive index and $c$ is the polymer concentration. In the case of polyacetylene (PA) visible light is strongly absorbed. This leads to intense scattering even at very dilute concentrations, but the magnitude of the excess polarizability associated with the polyacetylene molecules is not known. Also, at the point when the solution is dilute enough to measure a refractive increment at all there is so little polyacetylene present that a direct measurement of $dn/dc$ is not possible. Since the polyacetylene examined in this work is in fact a block copolymer, the simple theory for homopolymers or random

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