A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

MASTER

Received by OSTI

JUN 0 6 1986

CONF-8606133--3

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

LA-UR--86-1744

DE86 011218

TITLE PHYSICAL CHARACTERISTICS OF DIBLOCK POLYACETYLENE COPOLYMERS:
PROCESSABILITY-CONDUCTIVITY CORRELATION

AUTHOR(S) M. Aldissi, MST-7
M. Hou, P-10
J. Farrel, P-10

SUBMITTED TO ICSM'86 Conference
Kyoto International Hall
Kyoto, Japan
June 1-6, 1986
to be published in Synthetic Metals

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government, retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

PHYSICAL CHARACTERISTICS OF DIBLOCK POLYACETYLENE COPOLYMERS:
PROCESSABILITY-CONDUCTIVITY CORRELATION

M. ALDISSI
Materials Science and Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87545 (U.S.A.)

M. HOU, and J. FARRELL
Physics Division
Los Alamos National Laboratory
Los Alamos, NM 87545 (U.S.A.)

ABSTRACT

The physical properties of polyacetylene diblock copolymers containing polystyrene (PS) or polyisoprene (PI) blocks of various compositions are studied using electron spin resonance, resonance raman scattering, and room temperature conductivity measurements. This study is performed to investigate the processability-conductivity correlation in these materials and their viability as conducting systems.

INTRODUCTION

Due to the intractability of most conjugated (conducting) polymers, we have investigated in the past the synthesis of soluble polyacetylene, $(CH)_x$, as diblock copolymer networks in their conducting and non-conducting forms. The process involves a coordination polymerization of acetylene by a polymeric catalyst formed by the reaction of $Ti(OBu)_4$ with poly(isoprenyl)lithium or poly(styryl)lithium of various chain lengths [1,2]. One advantage of using this procedure is the combination of flexible sequences and rigid ones (polyene) in one chain, and thereby the modification of their individual physical characteristics, particularly in this case, processability.

RESULTS AND DISCUSSION

1) Electrical conductivity

Room temperature conductivity measurements on the various materials, heavily doped with iodine or AsF_5 , showed that the extent and regime of conductivity depends strongly upon the relative amount of the active material (polyene). Their characteristics depend upon the nature of the flexible chain.

In the case of PI copolymers, soluble materials whose content of polyene is below 10 weight % are insulating. In the 10-20 weight % range, the soluble materials exhibit conductivities up to $1\text{-}10\ (\Omega\text{cm})^{-1}$. Above 20 weight %, insoluble materials are obtained and increasing conductivities with the relative amount of doped polyene are measured. The ranges are, however, different in the case of PS copolymers. In general, lower amounts of polyene in these materials than in PI copolymers are required, in order to obtain soluble materials. In this case, the amount of the non-active component (PS) is predominant, and therefore, insulating materials are obtained. In the insoluble range of PS copolymers, the conductivity varies drastically with composition, in a similar manner to that of filled polymers (conducting composites). We have explained this type of behavior, correlated with the morphology of the materials, by percolation [2], with a threshold at 0.16-0.18 volume fraction of polyene.

Resonance raman scattering (RRS)

The RRS spectra were recorded using incident lines with excitation wavelengths in the visible absorption range of the materials. The maximum absorption in the visible (bandgap) of polyene particles varies between 600 nm ($\sim 2\text{ eV}$) for the soluble copolymer, and 700 nm ($\sim 1.8\text{ eV}$) for $\text{trans}-(\text{CH})_x$. However, the absorption spectrum for the copolymers is relatively wider than for $(\text{CH})_x$, due to bending effects caused by the interaction of the polyene blocks with the flexible ones [3]. The enhancement of the RRS effect can be measured by using incident lines in the violet to red range, where each line corresponds to a certain length range of conjugated sequences. The features characteristic of a $\text{trans}-(\text{CH})_x$ sequence consist of two relatively sharp peaks around approximately 1100 cm^{-1} for C-C and 1500 cm^{-1} for C=C. The anomalous resonance raman effect observed in $(\text{CH})_x$ [4,5] is also observed, but less extensively, in the copolymers. This result can be explained by the existence of narrower distributions of the conjugated sequences. Figure 1 shows that the raman shift of the $\nu_{\text{C}=\text{C}}$ mode from the violet line to the red line is approximately 80, 55, and 50 wavenumbers for $(\text{CH})_x$, a soluble, and an insoluble PI copolymer respectively. It is however, important to note that on the other hand, the difference in the distribution between the two copolymer samples is observed principally in the low energy region, and on the other hand, the length of the sequences involved when the yellow/red lines are used (1.9 eV 2.0 eV) seems to be comparable for the three samples. The

determination of the polyene length for each excitation wavelength can be attempted by using the Kuzmany model [5], as shown below.

TABLE 1

Length of conjugated sequences in polyacetylene and copolymers for the various excitation wavelengths

Polymer	Polyene length/ $\nu_{C=C}$ at Excitation wavelength/Å				
	4579	4880	5145	5682	6471
(CH) _x	9	11	14	64	>100
PI insoluble					
copolymer	12	22	29	44	64
PI soluble					
copolymer	10	17	22	33	44

Electron spin resonance

The already trans-rich polyene copolymers are thermally treated under vacuum at ~ 150°C to complete the cis-trans transformation for a more accurate comparison between the ESR characteristics of the various materials. Lorentzian lines are in general obtained at g values near that of the free electron, and with room temperature linewidths in the range 1 - 4 gauss. This indicates that the defects on the polyene segments have a high mobility. We have found that the linewidth (ΔH_{pp}), and therefore the carrier mobility, depend upon the composition of the copolymers.

TABLE 2

ESR linewidth of polyacetylene diblock copolymers at 20°C

Polymer	(CH) _x weight%	ΔH_{pp} /gauss
Polyacetylene	100	1.0
PI copolymers	30	1.7
	25	2.5
	15*	2.1
PS copolymers	50	3.5
	60	3.2
	50**	2.1

* Soluble sample.

** After compression at 10 Kbars.

The number of spins is usually about 10^{18} spins/gram and increases slightly as the polyene weight % increases.

A temperature dependant study in the range 100 - 400°K has been carried out to determine the behavior of the diffusing magnetic defect in the various polymeric networks. In Fig. 2 are displayed the changes of the linewidth as a function of temperature for $(CH)_x$ and some selected copolymer samples. In all cases, a line narrowing upon warming is observed, suggesting that the defect mobility is thermally activated. The temperature dependence of the linewidth changes at approximately 100°K, which indicates that different mechanisms govern the defect mobility in the polyene network in its various forms. The fact that the linewidth varies with the relative amount of polyene segments at all temperatures, suggests that the spin lattice interaction is affected by the presence of the non-active components (PI, or PS) and the interaction between the latter and the polyene chains. In fact, the decrease of the slope above 100°K in the case of a $(CH)_x$ /PS copolymer sample, in addition to the narrowing of the line after it is subjected to compression at 10 Kbars, supports this hypothesis. Note that the lines at 300°K are narrower than at 100°K by a factor of approximately 3, 1.9, and 1.6 for $(CH)_x$ /PI with $(CH)_x$ weight % of 100, 30, and 25 respectively. The ratio for the $(CH)_x$ /PS sample before and after compression is approximately 1.7, and 1.2 respectively. These results indicate that the spin motion is affected more drastically by the composition of the system at lower temperatures. This is related to the interaction between the two different components of the material. It would be interesting to continue this study down to the helium temperature, to check whether the motion of the paramagnetic center will be drastically reduced or even frozen in the more diluted polyene materials. Dysonian lines are obtained upon doping with iodine in all cases, indicating that the systems become conducting. The A/B ratio variation is in agreement with conductivity measurements. It increases with increasing amounts of polyene segments in the copolymer, and the doping level of these segments [$1.0 < A/B < 1.75$], ratios which are lower than for $(CH)_x$ [$A/B \geq 2$].

CONCLUSIONS

We have shown in this study that, similarly to conducting composites, conduction by percolation in polyacetylene block copolymers depends upon the relative amount of the active component. The ESR results showed that the spin

lattice interaction is strongly correlated with dilution of the polyene in the non-active component, and that the systems become conducting upon doping with a Dysonian lineshape, the dissymmetry of which depends upon that dilution. The RRS results indicate that shorter polyene chains than in $(CH)_x$ are sufficient to result in conducting systems, and that the distribution of the polyene segments is narrower than in pristine $(CH)_x$. Finally, we have shown that high conductivity is achieved when soluble block copolymers of polyacetylene with the proper composition and morphology are doped.

ACKNOWLEDGMENTS

This work is supported by the Materials Science Division of the Basic Energy Sciences, the Centers for Materials Science, and for Non Linear Studies of the Los Alamos National Laboratory.

REFERENCES

- 1 M. Aldissi, J. Chem. Soc., Chem. Commun., (1984) 1347;
and U.S. Pat. 4,554,093.
- 2 M. Aldissi, and A.R. Bishop, Polymer, 26(4), (1985) 622.
- 3 M. Aldissi, Synth. Met., 13, (1986) 87.
- 4 S. Lefrant et al., Sol. St. Commun., 29 (1979) 191.
- 5 H. Kuzmany, Pure and Appl. Chem., 57, (1985) 235.

Fig. Captions

Fig. 1: Raman shift as a function of the excitation wavelength for $(CH)_x$ (1), soluble $(CH)_x/PI$ (2), and insoluble $(CH)_x$ (3).

Fig. 2: ESR linewidth temperature dependence for $(CH)_x$ (1), $(CH)_x/PI$ -30% (2), $(CH)_x/PI$ -25% (3), $(CH)_x/PS$ -50% before (4), and after compression at 10 Kbars (4').

Fig. 1.

Fig. 2.