Oxygen doping of polyacetylene determined by dielectric techniques

J. M. Pochan, H. W. Gibson, F. C. Bailey and D. F. Pochan
Xerox Corporation, Rochester, NY, USA

(Received 31 December 1979)

Polyacetylene has been of intense interest[1–5] in the last few years primarily because its electrical conductivity can be varied by over 12 orders of magnitude[2] by doping. Electron acceptors such as bromine, iodine and arsenic pentafluoride are used typically. Molecular oxygen is also a good electron acceptor that will dope $(\text{–CH=CH–})_n$[6,7] and it is pervasive. Oxygen exposure is also known to affect the mechanical[8] properties of $(\text{–CH=CH–})_n$, but a systematic study of its affect on the dielectric properties of $(\text{–CH=CH–})_n$ has not been made previously.

Polyacetylene was prepared by the Shirakawa technique[1]. The sample was 160 μm thick; anal. calcd.: C, 92.26; H, 7.74; found: C, 91.64; H, 7.91. It was initially ~90% *cis* and 10% *trans*. The sample was stored *in vacuo* (10^{-4} Torr) at 195K. The sample was transferred in an oxygen-free dry box ($[O_2] < 0.8$ ppm) to an oxygen-free argon-filled flask and thence to a Balzar vacuum evaporation system where ~10^3 Å thick gold electrodes were evaporated onto the sample at 298K. During the electroding process, the film was exposed to air for approximately 3–5 min. The sample was transferred to a sample cell and the temperature lowered to ~90K under argon. Dielectric experiments were conducted at a scan rate of ~0.9K min^{-1} at a frequency of 1 kHz.

The experimental cell used was made of stainless steel with two ports installed to permit the circulation of desired gases past the sample. The gases were circulated through a temperature control device (±1K) prior to entry to the cell to insure thermal equilibration. Dielectric response was obtained with an automatic recording system described previously[9,10]. The oxygen content of exposed samples was not measured as the sample size was too small for accurate determination.

In heterogeneous dielectrics, a virtual charge at the interface between media of different permittivities and/or conductivities can cause polarization effects that are manifest as dielectric activity. Mathematical models for these systems have been produced[11,12]; and it has been shown that dielectric activity, represented as dielectric loss, ϵ'', can be written as a sum of terms:

$$\epsilon'' = \epsilon''_{\text{dipolar}} + \epsilon''_{\text{Int}} + \frac{1}{\omega RC} \qquad (1)$$

where $\epsilon''_{\text{dipolar}}$ represents the contribution of dipolar motion to the dielectric loss, ϵ''_{Int} represents the polarization caused by charge build-up at the heterogeneous media interface and $1/\omega RC$ represents a conductivity term for the capacitative sample. (ω is the angular frequency measurement, R is the resistance of the sample and C is the capacitance). Terms for ϵ' (the dielectric constant) corresponding to the dipolar and interfacial effects have also been derived. However, the conductivity term $(1/\omega RC)$ has no ϵ' counterpart. Thus an increase in conduction (lower resistivity) of a system could increase its dielectric loss via the last term in equation (1), or the second term in the case of a heterogeneous system where one of the components becomes more conductive. Polyacetylene should have little, if any, dielectric relaxation due to dipole motion within the polymer[13], and, therefore, any changes in dielectric properties should be due to changes in conductivity. In our experiments, temperature was scanned at a constant frequency and capacitance and tan delta were monitored. Capacitance is directly proportional to ϵ' and tan delta equals ϵ''/ϵ' and is the phase angle between the applied a.c. voltage and the current response of the sample to this voltage[13]. The fibrillar structure of polyacetylene does not permit ascertainment of the true sample size and volume of each sample and, therefore, tan delta which is independent of sample geometry is used in these experiments. Increases in conductivity manifest themselves as changes in tan delta (d.c. conductivity effect) or ϵ' and tan delta (interfacial polarization effect).

The interfacial effect is not unexpected as the polyacetylene morphology is known to be fibrillar in nature[2] and it is felt that conduction occurs along these fibres. Any discontinuity in the fibrillar structure will produce a charge transport barrier, thus creating an effective heterogeneous system consisting of a highly conducting medium in an insulating one (the interfibrillar gas).

The results shown in *Figure 1*, A and *Figure 2* are typical of those observed in these $(\text{–CH=CH})_n$ experiments with high *cis* content samples. It is seen that tan delta remains relatively constant until a specific temperature is reached, at which time it begins to increase rapidly with increasing temperature. In the same temperature régime where the increase in tan.

It is known that elevated temperatures cause thermal conversion from the *cis* to the *trans* form of polyacetylene[1]. It

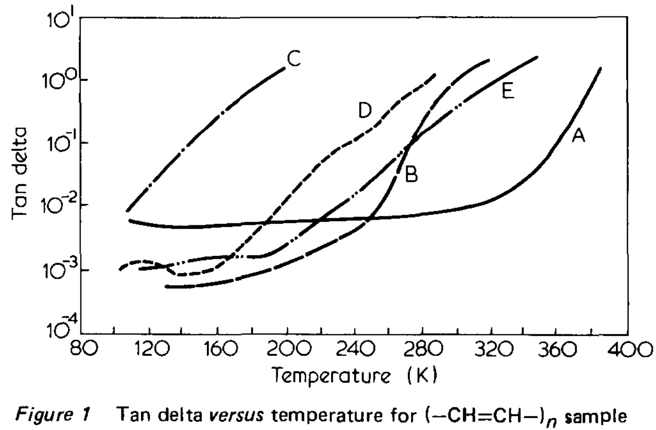

Figure 1 Tan delta *versus* temperature for $(\text{–CH=CH–})_n$ sample of 160 μm thickness. A, ~90% *cis* sample in flowing argon. 5 min air exposure prior to experiment; B, sample A after thermal conversion at 390K (20 min) to ~60% *trans* in flowing argon; C, sample B with flowing oxygen (2 h oxygen exposure (293K)) prior to experiment, 20 h oxygen exposure (293K) after experiment; D, sample C after flowing argon at ~393K for ~12 h, ~90% *trans*; E, sample D after ambient exposure 100 h, then argon for 20 h at 400K, >90% *trans*

0032–3861/80/030250–02$02.00

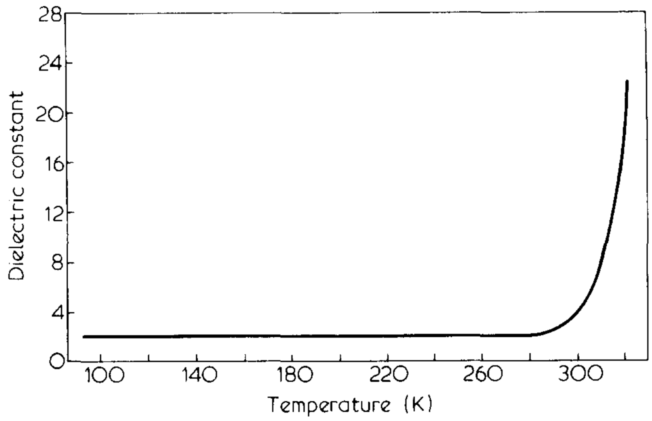

Figure 2 Dielectric constant *versus* temperature for ~90% *cis* (–CH=CH–)$_n$ sample. Flowing argon during thermal cycle. See *Figure 1*, A

has also been shown that the *trans* form exhibits large changes in conductivity in this temperature regime[2]. Since changes in ϵ' and tan delta are taking place and (–CH=CH–)$_n$ exhibits ohmic contacts with gold[7], it must be concluded that the data in these figures represent interfacial polarization effects that are manifestations of increased conductivity of the samples. The increased conductivity is due to thermal activation of the samples as well as continuing *cis–trans* conversion at the elevated temperatures.

We now discuss the effect of thermal treatment and atmosphere on the temperature position of the conductivity edge (as defined by the abrupt increase in tan delta with temperature). Thermal conversion to a higher percentage *trans* sample (*Figures 1*, A and *1*, B) shifts the conduction edge to a lower temperature. The *cis* form has a higher tan delta at low temperature than any of the *trans* samples. Exposure of the *trans* film to oxygen (*Figure 1*, C) or air shifts the edge to extremely low temperatures. We have shown previously[7] that O_2 can raise the room temperature conductivity of polyacetylene by at least two orders of magnitude. As would be expected for oxygen doping, the oxygen exposed sample has a conduction edge that is lower than its air counterpart.

The recovery of samples after exposure to oxygen, or air is of major importance. During the initial stages of oxygen exposure, the sensitization process can be reversed with argon flow[7]. In the dielectric experiments, this is accomplished more readily at elevated temperatures; however, the results are more complicated as further *cis–trans* conversion is taking place during the experiments. However, the results in *Figure 1*, (B, C, D, E) indicate that the process is at least partially reversible. The effect is not unlike that observed in a recent e.s.r. study on polyacetylene, where oxygen exposure produced an initial irreversible step in e.s.r. response followed by a second reversible step[16]. Our conductivity studies[7] indicate that there is also a third irreversible process that causes decreases in sample conductivity. Although the oxygen effect is reversible to the extent measured above, the samples were somewhat brittle at the end of experiments.

In conclusion, these experiments corroborate our findings[7] showing oxygen to be a dopant for (–CH=CH–)$_n$: dielectric measurements give enhanced d.c. conductivity and interfacial polarization effects. The dielectric results further indicate that charge transport barriers in the samples (fibril–fibril boundaries or electrode fibre interfaces) cause interfacial polarization effects which lead to anomalously high dielectric constants. These results further indicate that rigorous care must be taken to avoid exposure of (–CH=CH–)$_n$ to oxygen.

ACKNOWLEDGEMENT

The advice and encouragement of Professors MacDiarmid and Heeger (University of Pennsylvania) regarding the synthesis and study of polyacetylene is gratefully acknowledged. Helpful discussions with A. Epstein are also acknowledged. We wish to thank M. Zielinski for typing this manuscript.

REFERENCES

1 Ito, T., Shirakawa, H. and Ikeda, S. *J. Polym. Sci. Polym. Chem. Edn.* 1974, **12**, 11
2 Maricq, M. M., Waugh, J. S., MacDiarmid, A. G., Shirakawa, H. and Heeger, A. J. *J. Am. Chem. Soc.* 1978, **100**, 7729; Chiang C. K. *et al. J. Am. Chem. Soc.* 1978, **100**, 1013; *J. Chem. Phys.* 1978, **69**, 5098 and references therein
3 Hau, S. L., Signorelli, A. J., Pez, G. P. and Baughman, R. H. *J. Chem. Phys.* 1976, **69**, 106
4 Gill, W. D., Clarke, T. C. and Street, G. B. *Bull. Am. Phys. Soc.* 1979, **24**, 327; Seeger, K., Gill, W. G., Clarke, T. C. and Street, G. B. *Solid State Commun.* 1978, **28**, 873
5 Litchtmann, L. S., Fitchen, D. B. and Temkin, H. *Bull. Am. Phys. Soc.* 1979, **24**, 327
6 Berets, D. J. and Smith, D. S. *Trans. for Soc.* 1968, **64**, 823
7 Pochan, J. M., Gibson, H. W. and Bailey, F. C. Submitted to *Polym. Lett.*
8 MacDiarmid, A. G. and Heeger, A. J., University of Pennsylvania, Private communication
9 Pochan, J. M., Hinman, D. F. and Turner, S. R. *J. Appl. Phys.* 1976, **47**, 4245
10 Pochan, J. M., Hinman, D. F., Froix, M. F. and Davidson, T. *Macromolecules*, 1977, **10**, 113
11 Maxwell, J. C. 'Electricity and Magnetism', Clarendon Press, Oxford
12 Van Beek, L. K. H. 'Progress in Dielectrics' (Eds. J. B. Burks and J. Hart) Vol 7, Heywood Press, London 1967, p 69
13 'Anelastic and Dielectric Effects in Polymeric Solids', McCrum, N. G., Read, B. E. and Williams, G., Wiley, New York, 1967
14 Sillars, R. W. *Proc. R. Soc. A* 1939, **169**, 66
15 Chiang, C. K., Fincher Jr., C. R., Park, Y. W., Heeger, A. J. Shirakawa, H., Louis, E. J., Gau, S. C. and MacDiarmid, A. G. *Phys. Rev. Lett.* 1977, **39**, 1098
16 Snow, A., Brant, P., Weber, D. and Yang, N. L. *J. Polym. Sci. Polym. Lett.* 1979, **17**, 263