

## Resonance Raman spectroscopic study of an iodine-doped pseudo-interpenetrating polymer network of natural rubber–poly(carbonate urethane)

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(Received 23 July 1995; revised 12 January 1996)

The resonance Raman (r.R.) spectra of two highly conducting, but distinct, iodine-doped rubber samples, natural rubber (NR) and pseudo-interpenetrating polymer (PIPn) (NR with crosslinked polyurethane) have been investigated. Both systems with excessive iodine exhibit nearly indistinguishable r.R. spectra, with well-resolved iodine modes in the low-frequency region,  $< 1000 \text{ cm}^{-1}$ , and a nearly featureless spectrum in the region of the polymer modes,  $> 1000 \text{ cm}^{-1}$ . When the excess iodine is washed, the r.R. spectrum in the low-frequency range remains unchanged, but the high-frequency region becomes distinct. NR exhibits enhanced polymer backbone modes, but the PIPNs retain featureless spectra. These findings suggest that energy transfer from iodine to the polymer backbone in the case of NR is evident, but no such path exists in the PIPn samples, i.e. different energy transfer paths are operational. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: pseudo-interpenetrating polymer; iodine doped; resonance Raman)

### Introduction

We recently reported the d.c. electrical conductivity studies of iodine-doped (ID) samples of linear natural rubber (NR)<sup>†</sup>, of crosslinked poly(carbonate–urethane) (PCU)<sup>1</sup> and a pseudo-interpenetrating polymer network of linear natural rubber in crosslinked poly(carbonate–urethane) (PIPn)<sup>†,1,2</sup>. The electrical conductivity of the ID saturated samples in general is about eight orders of magnitude greater than the undoped samples. The conductivities of NR and of the PIPNs are essentially the same,  $1.41 \times 10^{-4} \text{ S cm}^{-1}$  of PIPN50 and  $1.40 \times 10^{-5} \text{ S cm}^{-1}$  of NR, but about an order of magnitude greater than that of PCU,  $2.66 \times 10^{-5} \text{ S cm}^{-1}$ . All three systems, PIPN50, NR and PCU are, however, distinct in their iodine saturation capability, 10.3, 5.0 and 2.5 molal respectively. The PIPNs and NR are also different in the dependence of the conductance profiles on the degree of iodine saturation as well the temperature. The conductivity of ID-NR decreases monotonically with temperature lowering, but that of the ID-PIPNs does not, in particular below  $115^\circ \text{C}$ . The distinction between these two polymer networks is also evident from preliminary studies of their AC conductivity<sup>3</sup>.

The distinct conductivity profiles of the PIPNs and of the base polymers, linear natural rubber and PCU, raise questions regarding the operational nature of the charge-migration mechanism. The PIPNs, NR and PCU are structurally different. Does it mean that different electron transfer mechanisms are operational or can the conductivity differences be accounted for on the basis

of structural differences? Resonance Raman (r.R.) spectroscopy is unique in providing structural information not only of the excitation absorbing chromophore, adsorbed/absorbed iodine in this case, but also of the macromolecular structures which are electronically coupled to the chromophore. This stems from the fact that the vibrational emissions of only those molecular modes which are electronically coupled to the excitation absorbing chromophore are enhanced. r.R. studies of ID polymers thus far reported<sup>4–13</sup> clearly show that the r.R. spectrum consists not only of the iodine vibrations, the bands in the low frequency region,  $< 1000 \text{ cm}^{-1}$ , but that it also contains enhanced emissions of the polymer backbone, the bands at higher frequencies. The enhancement of the backbone vibrations is indicative of electronic coupling between the iodine moieties and the polymer backbone structures. This supports the feasibility of the proposal that the high conductivity of ID-NR is because of the participation of the polymer backbone involving conjugated polymer structures<sup>11–13</sup>. In contrast, we reported that the conductivity profiles of the ID-PIPNs are consistent with an entirely different model, an independent charge carrier hopping along single chains connected only at entanglement points with one another<sup>2</sup>. In this communication we provide evidence indicating that the energy transfer mechanism, such as the electronic transition-coupling, between iodine and the polymer backbone in iodine-doped PIPN50 is indeed non-operational. This supports the suggestion that the charge migration mechanism in ID-PIPn is different from the mechanism operational in ID-NR, and that it must either be essentially along the linear NR chains, as proposed earlier<sup>2</sup>, or the hopping of the charge carriers from one iodine cluster to another.

### Experimental

Preparation and purification of the base polymers, linear natural rubber with *cis*-polyisoprene structure,

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† NR: linear natural rubber with *cis*-polyisoprene structure prepared from *Brazilian Manihot glaziovii*<sup>14</sup>. PCU: Poly(carbonate urethane) which was prepared by the biuret triisocyanate reaction with hydroxyl terminated poly(1,6-hexane diol carbonate). PIPn: A pseudo-interpenetrating polymer of linear natural rubber in crosslinked PCU, where nn reflects the weight percent of the crosslinked PCU.

and of the PIPNs, are detailed in earlier publications<sup>1,2</sup>. The PIPN used for these studies, PIPN50 (50% NR + 50% crosslinked PCU), is a single-phased elastomer exhibiting one glass transition temperature ( $T_g = -56.2^\circ\text{C}$ ), and no resolvable electron microscope structure to at least 80 Å. These thin films with a thickness of about 0.2 mm were exposed to iodine vapour under ambient conditions for 3–5 days, and then cut into coin-sized (20 mm in diameter) specimens for further use. The doped solid specimens were dark, opaque and possessed a metallic luster. Acetone washing (see Results) was performed by holding the membrane in a stream of acetone until no visually discernible iodine colour was noted in the wash.

r.R. spectral measurements were conducted using essentially the same setup as described earlier (an on-line setup consisting of a Spectral Physics Argon Laser, a Spex double monochromator with Spex illuminator and an electronically cooled photon counter with Parr photon-counter electronics)<sup>15,16</sup>. The membrane samples were mounted on a rotating sample holder, 3600 rpm, and aligned to provide off-centre circular illumination. The spectra measurements, in the main, were made using the following conditions: ambient temperature,  $20 \pm 1^\circ\text{C}$ ; 4880 Å line; 10 mW power; 0.25 Å wavelength increment; 0.2–5 s integration time. Processing of the spectrum, i.e. wavelength correction, background elimination, noise reduction, if required, and determination of peak positions, was performed on an IBM-based microcomputer with software developed in the laboratory<sup>15,16</sup>. Indene,  $\text{CCl}_4$  and  $\text{CHCl}_3$  were all used for reference peaks for wavelength correction.

Illumination of the iodine-saturated samples using the continuous mode and power as low as 10 mW, resulted in visually observable dissociation of iodine. Thus the measurements were conducted using a chopped mode, 50% on/off cycling, of the incident beam. Under these conditions, no detectable dissociation of iodine occurs, and the spectra were reproducible at as high as 25 mW incident beam power.

### Results and discussion

Consistent with the earlier report, the r.R. spectrum of each of these polymers with high concentrations is dominated by the iodine modes, bands in the low frequency region, with barely discernible and diffused bands in the region containing the polymer modes,  $> 1000 \text{ cm}^{-1}$  (Figure 1, curves 1 and 3 from the bottom)<sup>9</sup>. However, we found that if higher laser power is used, 25 mW or higher, with continuous exposure, the spectrum of iodine-saturated NR changes with time, and the spectrum after prolonged exposure,  $\frac{1}{2}$ –1 h, was similar, but not identical, to the one shown at the bottom of Figure 1 – with well-discerned polymer modes in addition to the iodine modes. In the case of iodine-saturated PIPN50, comparatively minor spectral changes were noticed during measurements with higher laser power, and these were localized primarily in the low-frequency region.

An r.R. spectrum with well-defined details in the low-frequency region, and with either broad or diffused humps in the high-frequency region, similar to those of saturated NR and PIPN shown in Figure 1, has also been reported for  $\beta$ -carotene with high iodine content<sup>9</sup>. We

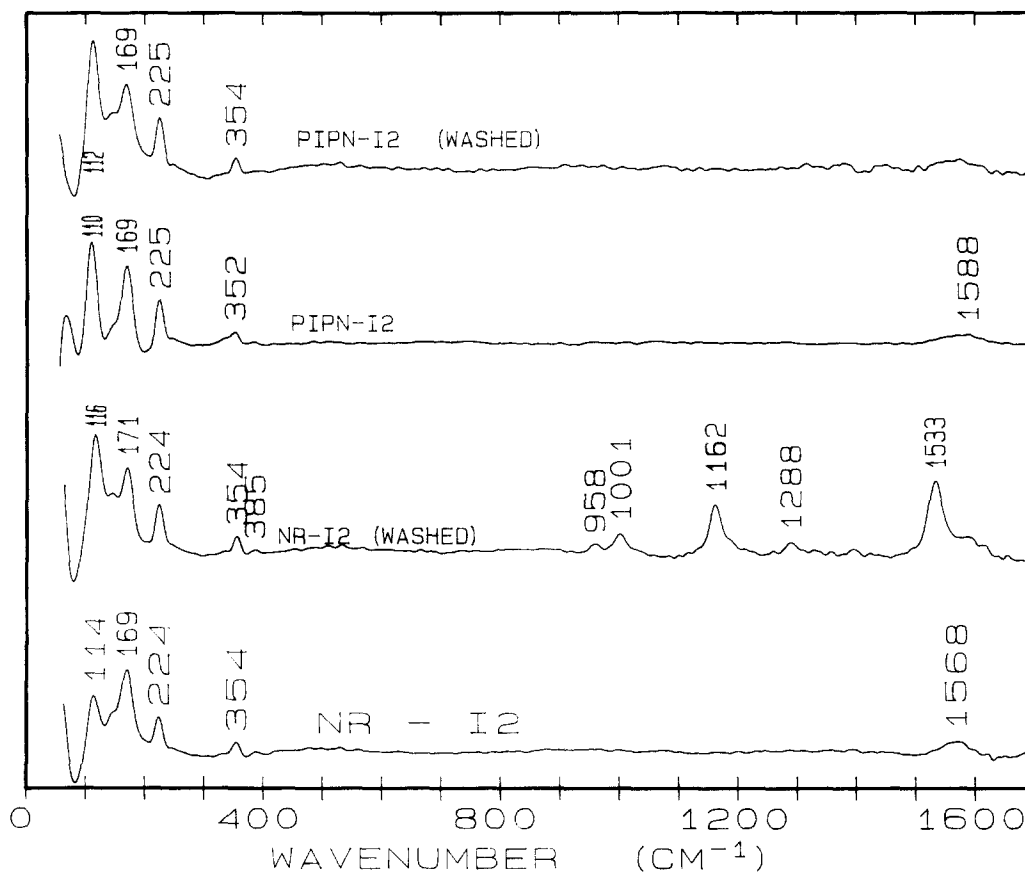


Figure 1 Resonance Raman spectra of iodine-doped, saturated NR and PIPN50. Curves 1 and 3, from bottom, saturated samples as such. Curves 2 and 4 from bottom, after washing surface iodine with acetone

feel that absence of polymer vibration modes in the spectrum of samples with high iodine content was because of the surface-adsorbed iodine. This stems from the following: (a) Visual examination of the samples during the early stages of measurement at high laser power provided clear indication of the continuous stripping of iodine from the membrane; after prolonged exposure the spectral details in the high frequency region did become evident and observable (see previous paragraph). (b) Washing the iodine-saturated NR membrane with acetone yielded reproducible spectra, with details of both the iodine and the polymer backbone modes, with laser power as low as 10 mW and with a 50% exposure cycle (Figure 1, curve 2 from the bottom). It is notable that washing of samples does not alter the spectral characteristics of the system, since the r.R. spectrum of acetone washed iodine-saturated NR (Figure 1) is identical to that reported by Williams and Gerrad<sup>4</sup> for a similar polymer, but without washing and with a lower degree of iodine saturation.

In view of the above considerations, conclusions based on measurements of unwashed ID samples should be taken with caution. The reported r.R. spectra could be that of the surfaced-adsorbed iodine, as is the case for iodine-saturated samples (Figure 1, unwashed samples), or of the surface layer of the membrane only. The following considerations are based on findings from acetone-washed samples, i.e. samples with little or no surface-adsorbed iodine.

Both iodine-doped NR and PIPN50 are indistinguishable in terms of the low-frequency r.R. spectrum (Figure 1). The dominant peak in the region 112–116  $\text{cm}^{-1}$  and smaller peaks at 224–225 and 354  $\text{cm}^{-1}$  are possibly the fundamental and the overtones of  $(\text{I}_3^-)_x$ <sup>4-6</sup>. The small peak at about 162  $\text{cm}^{-1}$  and the shoulder at about 250  $\text{cm}^{-1}$  are at positions reported as the overtones of  $\text{I}_5^-$ <sup>10</sup>. The spectrum lacks any indication of the presence of  $\text{I}_2$  in substantial amounts (>2%) since there is no indication of a peak or shoulder corresponding to the  $\text{I}_2$  fundamental to the 180–210  $\text{cm}^{-1}$  region<sup>7,8</sup>. The iodine in both NR and PIPNs is thus primarily  $(\text{I}_3^-)_x$ , with a small but definite proportion of  $\text{I}_5^-$ , and with little or no  $\text{I}_2$ .

The two polymers, however, exhibit distinct spectra in the >1000  $\text{cm}^{-1}$  region of the polymer vibration modes (Figure 1, curves 2 and 4). The spectrum of ID-NR contains strong C–C and C=C stretches at 1162 and 1533  $\text{cm}^{-1}$ , and broad and weaker bands at 960, 1000 and 1288  $\text{cm}^{-1}$  from the polyene vibrations<sup>4</sup>. In contrast, the spectrum of ID-PIP50 is devoid of any details which could be attributed to enhanced polymer vibrations. The barely noticeable, broad and ill-defined band at about 1576  $\text{cm}^{-1}$  could be one of the stretching modes

of the polymer, but it is clearly not enhanced through electronic resonance coupling to the iodine electronic transition. The enhanced polymer modes in ID-NR and the absence of any such occurrence in ID-PIP50, is direct evidence that the energy transfer from iodine to the polymer backbone does occur in the former, resonance-linked enhancement, but not in the ID-PIP50s.

These findings provide evidence that there is no energy transfer from iodine to the polymer in the ID-PIP50s, i.e. no electronic transition-polymer coupling, and that it does occur in ID-NR. Since both of these systems exhibit increased conductivity, the mechanisms of charge migration must be different. A mechanism invoking charge transfer from iodine to the polymer backbone and subsequent migration through the backbone structure<sup>11-13</sup> is a feasible explanation of the enhanced conductivity of ID-NR, but not for the ID-PIP50 systems. For the latter systems, a mechanism such as charge-hopping from one iodine cluster to another, or independent charge-hopping along single polymer chains<sup>2</sup> could provide a rational explanation for their enhanced conductance.

#### Acknowledgement

This work was supported by a National Science Foundation Grant (# DMR9628224) and Donors of the Petroleum Research Foundation of the American Chemical Society.

#### References

- 1 Frisch, H. L. and deBarros, G. G. *J. Polym. Sci., Part A: Polym. Chem.* 1992, **30**, 937
- 2 Frisch, H. L. and Chen, Z. J. *J. Polym. Sci., Part A: Polym. Chem.* 1994, **32**, 1317
- 3 Frisch, H. L., Chen, Z. J. and Chen, X. *Makromol. Chem. Symp.* 1994, **81**, 181
- 4 Williams, K. P. J. and Gerrard, D. L. *Polym. Commun.* 1990, **31**, 290
- 5 Kiefer, W. *Appl. Spectr.* 1974, **28**, 115
- 6 Martinsen, J., Pace, L. J., Phillips, T. E., Hoffman, B. M. and Ibers, J. A. *J. Am. Chem. Soc.* 1982, **104**, 83
- 7 Parrett, F. W. and Taylor, N. J. *J. Inorg. Nucl. Chem.* 1970, **32**, 2458
- 8 Pace, L. J., Martinsen, J., Ulman, A., Hoffman, B. M. and Ibers, J. A. *J. Am. Chem. Soc.* 1983, **105**, 2612
- 9 Harada, I., Furukawa, Y. and Tasumi, M. *J. Chem. Phys.* 1980, **73**, 4746
- 10 Teitelbaum, R. C., Ruby, S. L. and Marks, T. J. *J. Am. Chem. Soc.* 1978, **100**, 3215
- 11 Thakur, M. *Macromolecules* 1988, **21**, 661
- 12 Cholli, A. L. and Thakur, M. *J. Chem. Phys.* 1989, **91**, 7912
- 13 Thakur, M. and Elman, B. S. *J. Chem. Phys.* 1989, **90**, 2042
- 14 deBarros, G. G. and Frisch, H. L. in 'Elastomeric Polymer Networks' (Eds J. E. Mark and B. Erman), Prentice Hall, Englewood Cliffs, NJ, 1992, Ch. 22
- 15 Bullock, P. A. and Myer, Y. P. *Biochemistry* 1978, **17**, 3084
- 16 Myer, Y. P., Srivastava, R. B., Kumar, S. and Raghavendra, K. *J. Protein Chem.* 1983, **2**, 13