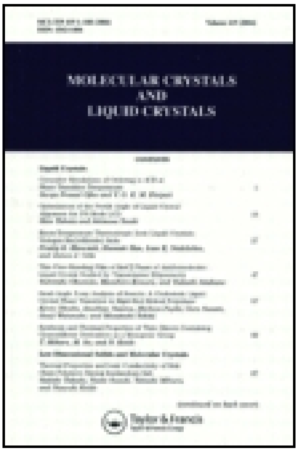

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Optical Studies of Polyphenylenevinylene and Derivatives: Raman and Luminescence Spectroscopy

Frederick H. Long [a] , Duncan McBranch [a] , Thomas W. Hagler [a b] , Jeanne M. Robinson [a] , Basil I. Swanson [a] , K. Pakbaz [c] , Scott Schricker [c] , Alan J. Heeger [c] & F. Wudl [c]

[a] Chemical Sciences and Technology Division Materials Science Laboratory, MS C345, Los Alamos National Lab, Los Alamos, NM, 87545

[b] Materials Division

[c] Institute for Organic Polymers, Department of Physics, UCSB, Santa Barbara, CA, 93106

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OPTICAL STUDIES OF POLYPHENYLENEVINYLENE AND DERIVATIVES:RAMAN AND LUMINESCENCE SPECTROSCOPY

FREDERICK H. LONG, DUNCAN MCBRANCH, THOMAS W.
HAGLER*, JEANNE M. ROBINSON, BASIL I. SWANSON
Chemical Sciences and Technology Division
Materials Science Laboratory,
MS C345, Los Alamos National Lab, Los Alamos,NM
87545 *Materials Division

K. PAKBAZ,SCOTT SCHRICKER,ALAN J. HEEGER,F. WUDL
Institute for Organic Polymers, Department of
Physics,UCSB, Santa Barbara, CA 93106

Abstract We have done Raman and luminescence measurements on a variety of PPV derivatives and oriented polymer blends. Changes in the observed Raman spectra for the polymers studied are consistent with molecular level changes in the polymer structure. Low frequency modes, which may be torsional modes of the polymer, have been observed for the first time. By comparison to site-selective luminescence spectra, it is found that at least two different phonons contribute to the vibrationally resolved luminescence spectra.

INTRODUCTION

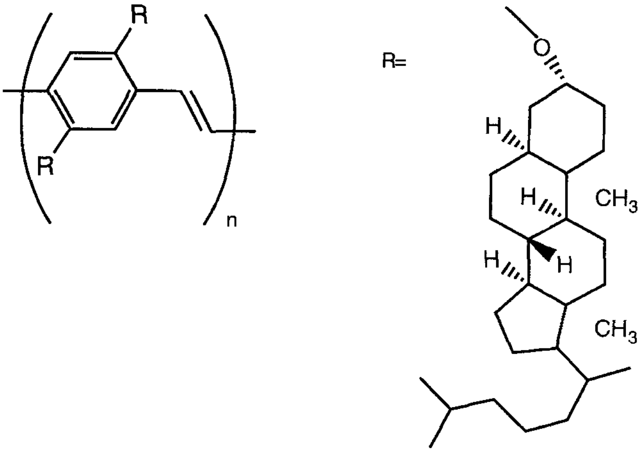
In contrast to most conjugated polymers, PPV has a high luminescence efficiency. Interest in PPV has been driven by the development of polymer LEDs based on PPV and related polymers.[1,2] Since the electroluminescence and photoluminescence spectra are virtually identical, a detailed understanding of the photophysics of PPV is important for the understanding of potential new devices.

PPV derivatives are important because they often show significantly improved processing characteristics.

Not surprisingly, many derivatives of PPV show similar high luminescence quantum efficiencies;futhermore the luminescence spectra of PPV and its derivatives shows significant vibrational structure.[3-5] However,their optical spectra are often shifted by as much as 0.3 eV. It is therefore of considerable interest to understand the vibrational spectroscopy of PPV and its various derivatives. In this paper we report Raman studies of PPV two soluble derivatives including highly-oriented tensile drawn blends in polyethylene.[3] Since PPV has a significant luminescence efficiency, it is difficult to use conventional resonance Raman, because the relatively weak Raman signal is overwhelmed by the fluorescence background[6-8] Using non-resonant excitation, we can minimize the luminescence background and thus observe the Raman spectra down to <300 cm^{-1} for some derivatives of PPV. By combined measurements of the luminescence vibrational structure and the Raman spectra on the same sample, we hope to obtain a detailed picture of the ground and excited state vibrational coupling for this family of important compounds.

EXPERIMENTAL

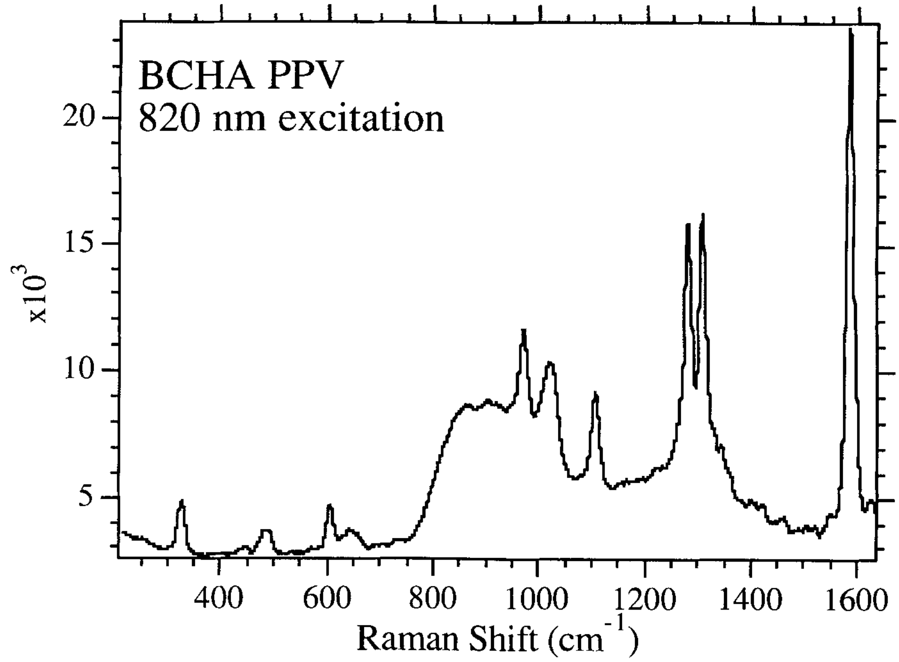
The samples were loaded in a dry box, and care was taken to keep them in an oxygen free environment, less than 10 ppm. The tensile drawn blends were a 1% mix of the luminescent polymer and polyethylene.[3] The two derivatives of PPV studied were MEH-PPV and BCHA-PPV, the structure of BCHA-PPV is shown in figure 1.



The chemical structure of BCHA-PPV.

RESULTS AND DISCUSSION

In Figure 2, the Raman spectra of a spin cast film of BCHA PPV is shown. The laser wavelength was approximately 820 nm. This is 0.7 eV below the absorption maximum of the film. Therefore, the luminescence background was relatively small. Several different spin cast films were examined. The line positions were reproducible; however, the relative amplitude of the low frequency Raman active modes was dependent upon sample morphology.



Full Raman spectra of BCHA PPV taken at 820 nm excitation. The sample is a spin cast film at 10 K.

In Table one, the principal Raman frequencies from this study are listed and compared to previous theoretical predictions for crystalline PPV. It is well-known that the Raman spectra of conjugated polymers are sensitive to the modes that strongly couple to the π electrons; therefore we do not expect to see sides chain vibrational modes in the Raman specta.[9] The spectra observed are similar; however MEH and BCHA PPV exhibit significant differences from pristine PPV. We feel that this can be attributed to the presence of the oxygen on the phenyl group in both cases. Besides an obvious increase in mass over a hydrogen atom, the electrophylic oxygen perturbs the electron distribution on the phenyl ring. The presence of the oxygen leads to an enhancement of the modes near 1300 cm^{-1} in the soluble derivatives.

PPV CAST FILMS			ORIENTED BLENDS		THEORY[9]
BCHA	MEH-PPV	PPV	MEH	BCHA	PPV
1626	1627	1628		1628	1629
1588	1582	1584	1577	1582	1588
1548	1550	1548			1550
1311	1312	1328	1311	1305	1330
					1304
1284	1286		1284	1277	1282
1108	1117	1171	1111	1104	1174
1024	1024				
971	967		966	972?	968
710	710				692
608	603		*1412		620
471	471		*1294		328
440	440		*1131		
	423		*1064		
	309		* denotes PE mode		

Table of principal Raman lines compared to available Raman for pure PPV and theory.PE=polyethylene

We found that Raman data taken with 720 nm light was very similar to the data taken at 820 nm, except for the expected larger luminescence background. No shifts within the experimental resolution of 1 cm^{-1} were found. This is consistent with the observation that the electron-phonon coupling in PPV and its various derivatives is small. In passing we also note that preliminary results show that oxygen exposure has no significant effect on the Raman spectra of the polymers studied.

From a combination of theoretical analysis and known Raman spectra we can assign the principal features of these spectra.[8-11] The mode at 1628 cm^{-1} is the vinylene (C=C) stretch mode. The strong line seen at 1586 cm^{-1} can be attributed to a symmetric stretch of the phenyl group. It is interesting to note that it is the 1586 cm^{-1} mode that shifts significantly in the stretch oriented blend. Previous measurements have proven the existence of large conjugation lengths in these materials.3 In heavily doped PPV, where Raman experiments and quantum chemical calculations have established that a quinoid configuration may be the dominant structure, a Raman shift of 20 cm^{-1} in the 1586 cm^{-1} mode is observed.[8] The reduction in the benzene mode frequency is consistent with an increased quinoid character in the ring. In contrast, for the BCHA spin cast film, this mode hardens to 1588 cm^{-1}. This is consistent with a reduced conjugation length associated with more isolated phenyl groups formed by out of plane torsional motions. It is likely that the increased band gap of BCHA-PPV (2.5 eV) with respect to MEH-PPV (2.3 eV) is due to twisting of the phenyl groups out of the vinylene plane.

The mode at 1171 cm^{-1} in pristine PPV is the C-H rocking motion on the phenyl group.[10] This mode appears at 1108 cm^{-1} in BCHA-PPV and 1117 cm^{-1} in MEH-PPV. The observed large reduction in this mode frequency is expected when heavy side chains replace the hydrogens on the benzene. In contrast, the vinylene stretch mode is relatively unaffected by side group substitution. The mode observed in the neighborhood of 600 cm^{-1}, is most likely analogous to the 605.6 cm^{-1} mode observed in benzene, which has been assigned to a pinching carbon ring.[11] Some of the lower frequency modes may be torsional modes.

Several studies have shown that the luminescence of PPV exhibits strong spectral diffusion when the excitation is in the tail region of the absorption.[4] We have found a dramatic example of this in our measurements of stretch oriented PPV polymer blends, figure 3. A detailed discussion of these and other luminescence measurements will be presented in another paper.[5] For the purposes of this paper, the significant result is the splitting of the first and second phonon lines into two distinct components. We believe that this is due to two different high frequency modes that couple strongly to the first excited electronic state. Further work is planned along this direction.

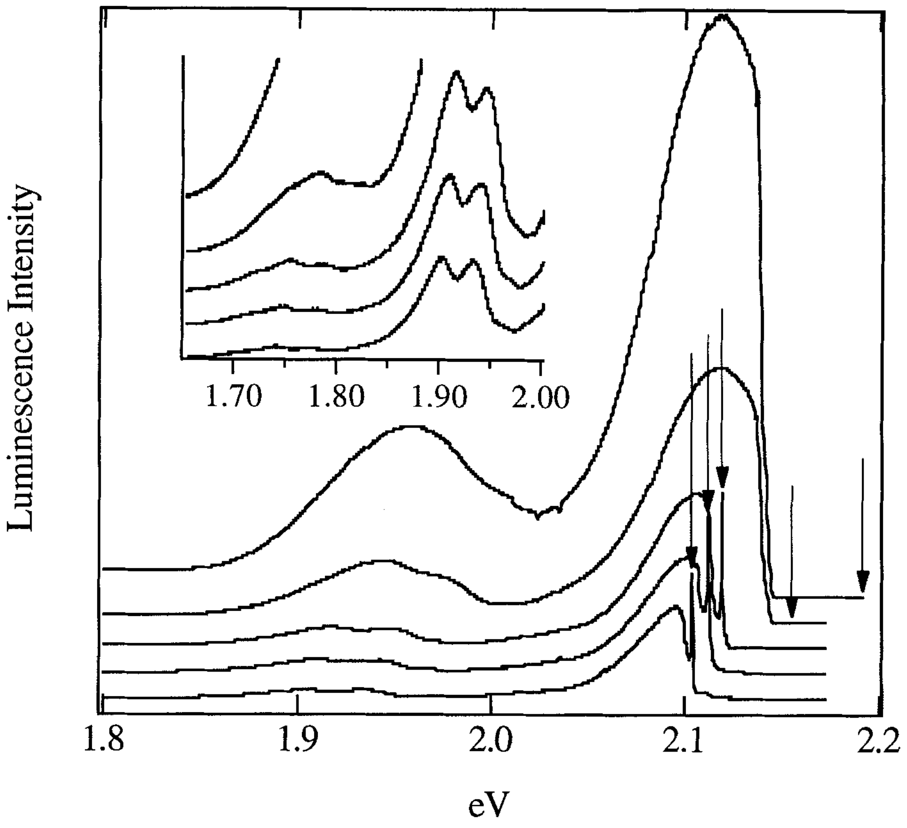


Figure 3: Excitation dependence of the luminescence of a tensile drawn oriented blend of MEH-PPV and polyethylene.

SUMMARY

We have performed Raman and luminescence studies of several PPV derivatives including stretch-oriented blends. By tuning sufficiently far from resonance we have experimentally observed numerous modes below

1000 cm^{-1}. Changes in the observed Raman spectra for the polymers studied are consistent with molecular level changes in the polymer structure. By comparison with site selective fluorescence measurements, we have identified that two different modes are part of luminescence pattern. By combining several different vibrational measurements we hope to fully characterize the vibrational spectroscopy of the PPV family of polymers.

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