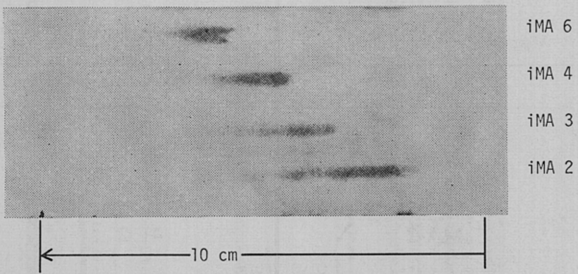

Figure 2. Chromatogram obtained for fractions of PMMA with different molecular weight under a precipitation condition.

When methanol is added to the developer, methanol molecules occupy the adsorption sites on the substrate otherwise for macromolecules. This makes macromolecules mobile so that the R_f becomes higher. In region II, the macromolecules are still soluble in the developer mixture, but methanol molecules occupy all the adsorption sites. As the result the macromolecules are forced to migrate up to the solvent front. However, in the region of $v_2 > 0.6$ (region III), the R_f begins to decrease with further increase of v_2, presumably because the precipitation of macromolecules takes place. A separate experiment showed that when methanol was added at 25° to a 0.8% chloroform solution of this polymer, incipient turbidity appeared first at $v_2 = 0.7$, followed by precipitation of all solutes in the proximity of $v_2 = 0.75$.

The above observation implies that for the chromatographic development of macromolecules, an adsorption–desorption mechanism is responsible in regions I and II, while precipitation is predominantly responsible in region III. Thus we compared the tlc characteristics in regions I and III with respect to the molecular weight dependences of R_f. For this purpose, four fractions of isotactic PMMA having the same tacticity ($i = 1.0$ and $h = s = 0$) but different molecular weight were developed with a chloroform–methanol mixture of $v_2 = 0.05$ on chromatoplate of activated silica gel. Molecular weights of the fractions are listed in Table I. The chromatogram thus obtained indicates practically no molecular weight dependence. In contrast to the development occurring in region I, the chromatogram taken with the mixture having $v_2 = 0.71$ exhibited strong dependency (see Figure 2). These results suggest that the molecular weight dependency of R_f is correlated with polymer precipitation.

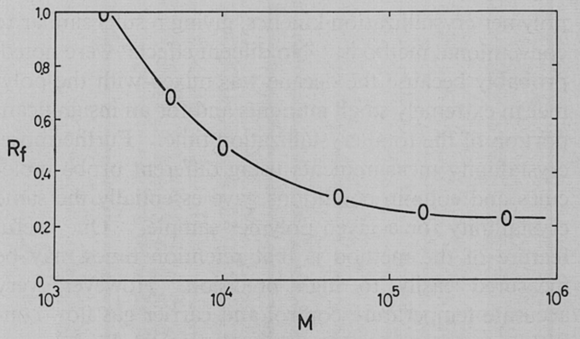

Figure 3. Relation between R_f and logarithm of molecular weight observed by adsorption chromatography for polystyrene fractions.

Another tlc experiment was carried out on six fractions of polystyrene (Pressure Chemical Co., Pittsburgh) with a mixture of cyclohexane (50 ml) and butanone (2 ml) as the initial developer (see Table I). Before the experiment we established that these polymer samples were easily soluble in this mixture at 25° so that no precipitation would take place throughout this tlc experiment. A concentration gradient development was employed: 5 ml of butanone was added to the initial developer at a speed synchronized with the elevation of solvent front. Figure 3 shows the result. It is seen that the molecular weight dependence vanishes rapidly in a range of molecular weights higher than 10^5. This result suggests that the possibility of polymer fractionation based purely on adsorption chromatography is limited to ranges of lower molecular weights. Such a finding is, of course, not new.[8]

In summary, we point out that a complete and effective fractionation of polymers by tlc cannot be achieved so far as the separation mechanism is dominated only by adsorption and desorption processes. It turns out that to separate macromolecules by molecular weight, developers should be chosen so as to give rise to precipitation of macromolecules. This statement differs somewhat from the explanation given recently by Otocka and Hellman for a similar observation.[9]

(8) See, *e.g.*, K. Bürger, *Z. Anal. Chem.*, **196**, 251, 259 (1963); K. Konishi and S. Yamaguchi, *Anal. Chem.*, **38**, 1755 (1966).

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Communications to the Editor

Laser Raman Studies of Poly(vinyl chloride)

The first reported Raman spectrum of syndiotactic poly(vinyl chloride) was determined by Koenig and Druesedow in 1969.[1] The observed results in Raman agreed well with previous normal coordinate analysis[2] for infrared assignments. Sensitivity of the PVC sample spectrum in ir and Raman to mechanical and thermal history was demonstrated in the ir by Krimm[3] and by the above workers in the Raman spectrum.

Our work on a thermally treated series of purified Diamond 450 PVC has demonstrated a significant difference between the control spectral pattern and those samples which had been carefully heated and cooled

(1) J. L. Koenig and D. Druesedow, *J. Polym. Sci., Part A-2*, 7, 1075 (1969).

(2) C. G. Opaskar, Ph.D. Thesis, University of Michigan, 1966.

(3) S. Krimm, V. L. Folt, J. S. Shipman, and A. R. Berens, *J. Polym. Sci., Part B*, 2, 1009 (1964).

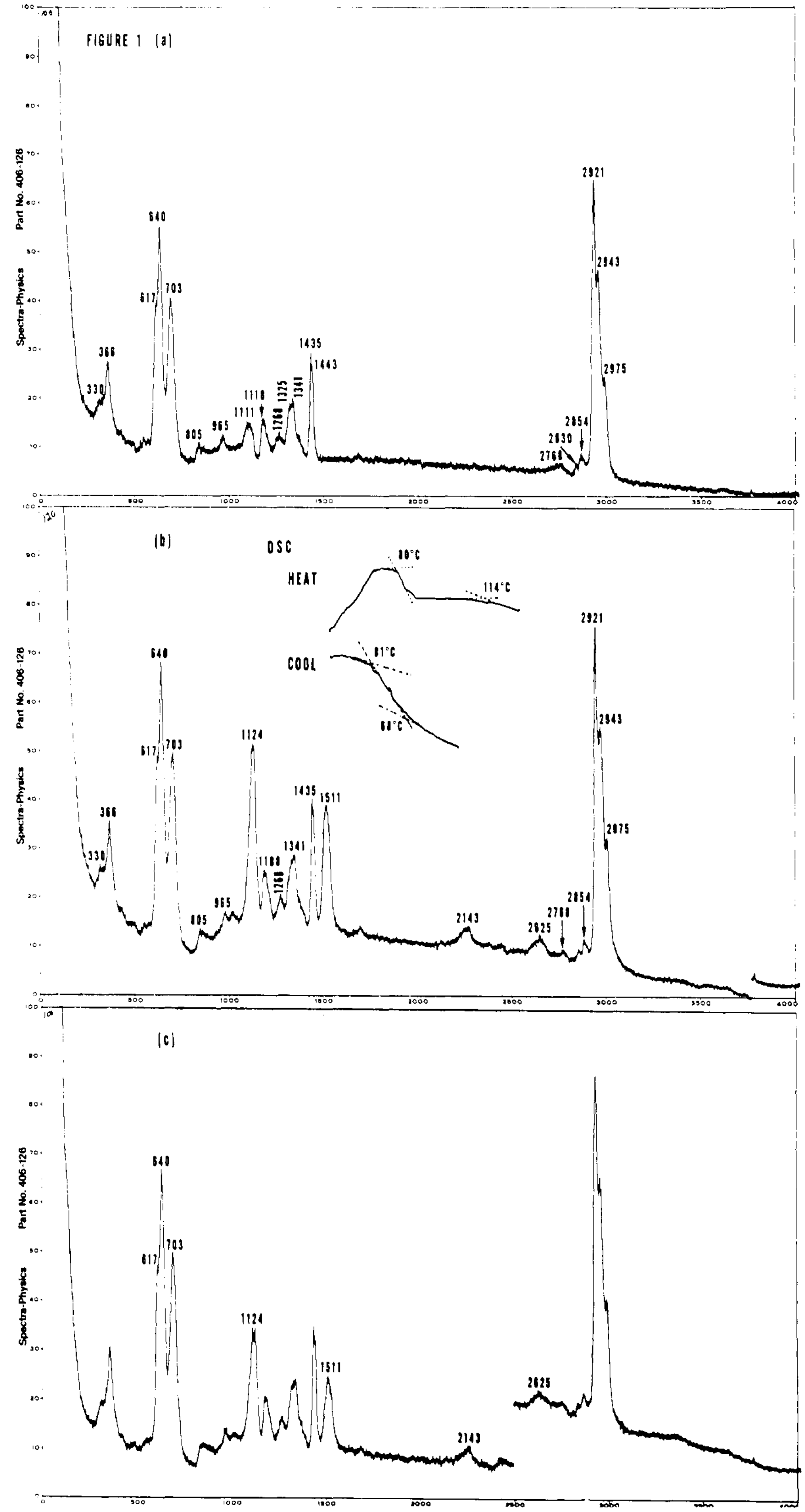

Figure 1. (a) 5°/min to 70°, held 1 min, cooled to room temperature; (b) 5°/min to 130°, held 1 min, cooled to room temperature; (c) 40°/min to 130°, held 1 min, cooled to room temperature.

at varied rates and to varied temperatures. Raman spectroscopy had not been previously used as a sensitive technique for degradation products which may be produced during such treatments, and it was necessary to establish whether the observed differences in band patterns were the results of a decomposition process or of a more subtle structural change in the polymeric system.

Experimental Section

Diamond 450 PVC was obtained from Diamond Shamrock Chemical Co., Cleveland, Ohio. Samples were prepared in sealed aluminum pans and monitored by differential scanning calorimetry (dsc) using a Perkin-Elmer DSC, Model 1. All samples were held at the denoted maximum temperatures for 1 min and cooled as indicated.

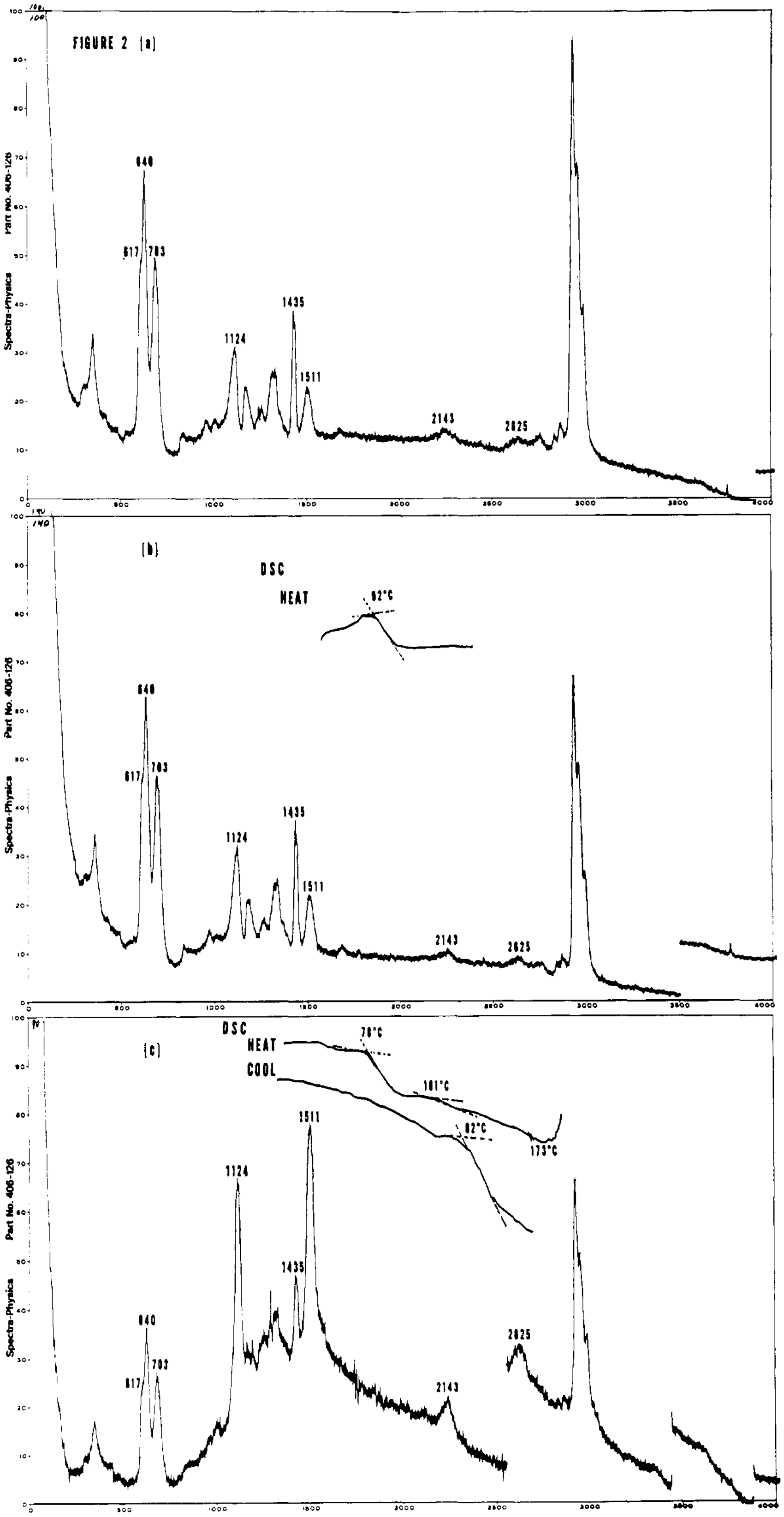

Figure 2. (a) 40°/min to 130°, held 1 min, quenched to room temperature; (b) 80°/min to 130°, held 1 min, quenched to room temperature; (c) 5°/min to 180°, held 1 min, cooled to room temperature.

Raman spectra were obtained in the usual manner on powdered samples taken directly from the DSC pans with a Spectra-Physics Model 700 Raman spectrophotometer using an Argon ion laser at 5145 Å, 150 mW. A sample which was held at 180° for 1 hr and quenched to room temperature displayed such strong fluorescence in the Raman and evidence of degradation that a suitable spectrum was not possible. The presence of an N_2 atmosphere and the use of a gold pan during the thermal treatments gave no improvement. Polarization studies were conducted on samples dissolved in tetrahydrofuran (THF).

Results and Discussion

Figures 1–3 show the Raman spectra obtained at the indicated heating/cooling rates to the denoted maximum

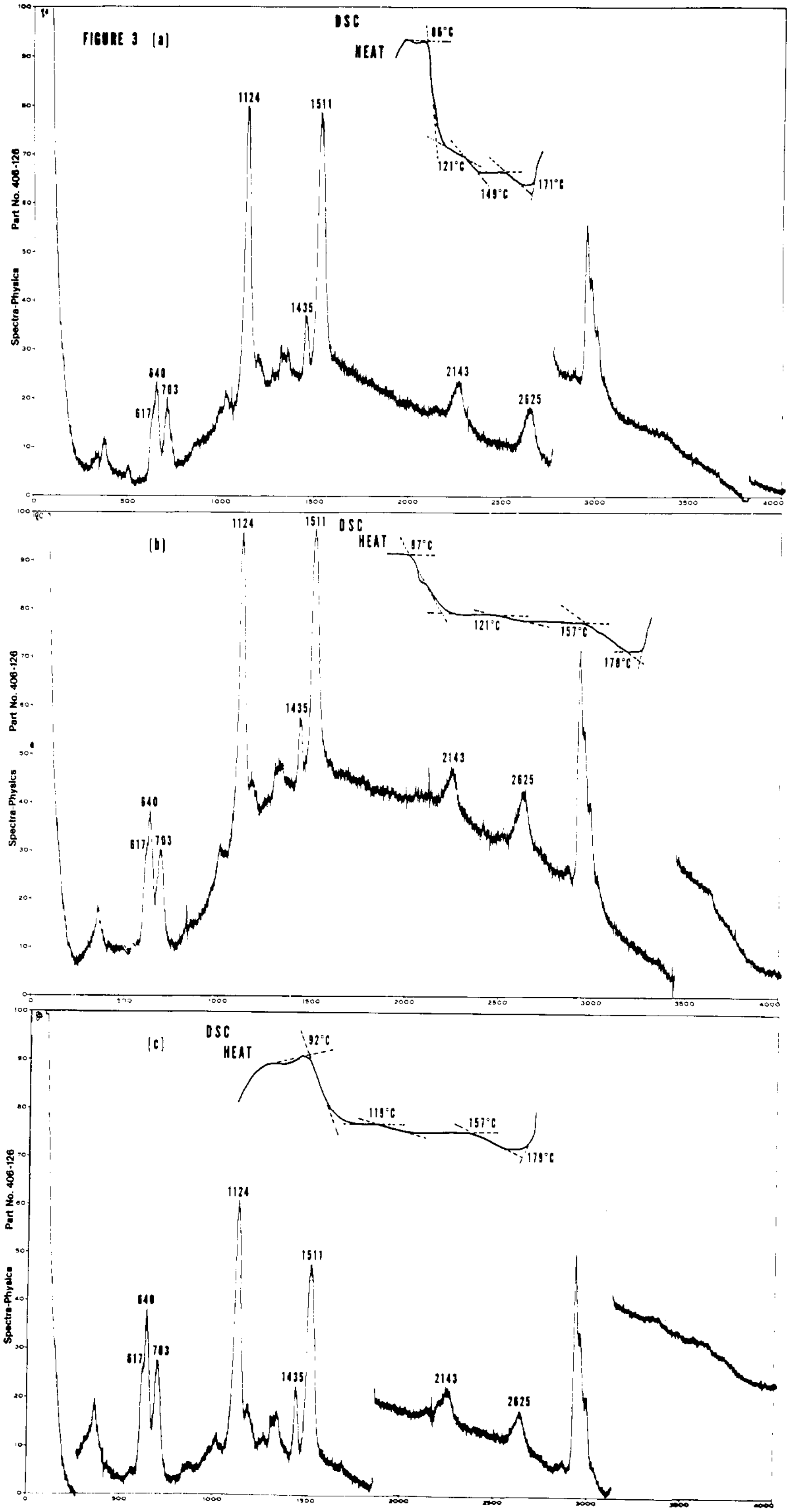

Figure 3. (a) 40°/min to 180°, held 1 min, cooled to room temperature; (b) 80°/min to 180°, held 1 min, cooled to room temperature; (c) 80°/min to 180°, held 1 min, quenched to room temperature.

temperatures. These samples were monitored by dsc during the detailed thermal preparation. The T_g and other minor endotherms are included with the corresponding spectrum for certain of these samples. Differences in the T_g values reflect differences in heating–cooling rates used in the investigations.

It is seen that the PVC control sample exhibited the normal C–Cl stretching vibrations at the 600–700-cm^{-1} region as previously recorded.[1] Upon heating/cooling at 5°/min to the maximum temperature of 180°, these bands decreased to approximately one-half their original intensity and two new major bands at 1124 and 1511 cm^{-1} developed. More rapid heating/cooling rates of 40 and 80°/min to the final 180° temperature gave only slightly varied proportions of the 1124, 1511/615, 700 cm^{-1} peaks. The quenched sample following the 80°/min heating rate and 1 min hold at 180 had a significantly larger proportion of the original 615 and 700 cm^{-1} pair relative to the new "thermal peaks" at 1124 and 1511 cm^{-1} than did the slowly cooled sample. Also, there was significantly less background from decomposition.

The series to 130° maximum temperature also gave definitive variations in the peak intensities in the above spectral regions. The slowest heat/cool rate (5°/min) resulted in the largest amount of "thermal peaks" at 1124 and 1511 cm^{-1}, while the 40 and 80°/min heat/cool rates gave somewhat lesser amounts. The 5, 40, and 80°/min heating rates to 130° maximum temperature all gave lesser amounts of the 1124 and 1511 cm^{-1} pair relative to the heat series to 180° maximum.

The heat/cool series (5, 40, 80°/min) to 70°, a temperature just below the T_g of PVC, gave Raman spectra identical with the untreated control sample spectrum.

These series illustrate the time/temperature dependency of the new "thermal peaks." The difference in spectral patterns between a slow or fast quench cooling treatment from a high (180°) or an intermediate final temperature (130°) demonstrated the influence of the time dependency of the changes which are occurring, and that the final temperature to which the polymer system is subjected is not necessarily the controlling parameter for the development of the 1124 and 1511 cm^{-1} pair. A higher final temperature (180°) at the slowest heating rate (5°/min) gave the largest amount of the latter peaks, while the intermediate temperature (130°/min) gave intermediate levels, and the lowest temperature (below T_g, 70°) resulted in no detectable amounts of those bands within the time limits of the investigation.

Conclusion

Previous literature work has shown[1] that Raman peaks at 617, 640, and 703 cm^{-1} are strong and the latter two are polarized in both the Raman and infrared. This fact ruled out the folded syndiotactic form for PVC and confirmed the presence of extended syndiotactic chains. The calculated[1] A_2 modes are at 1499, 1322, 1158, 1046, and 562 cm^{-1}. These bands are forbidden in the infrared for the extended syndiotactic structure with C_{2v} symmetry. Other models for the PVC chain are those for the folded (D_2 symmetry) syndiotactic and the helical (C_3 symmetry) isotactic forms. The helical (C_3 symmetry) form can be eliminated on the basis of the infrared inactivity of the modes. The decision between the assignment of strong A modes for the folded syndiotactic PVC and A_2 modes of the extended syndiotactic may be made on the basis of the dichoric properties for the "thermal peaks." Modes which are only Raman active are polarized for the folded syndiotactic form (A modes), while modes which are Raman active only for the extended form would exhibit depolarized behavior (A_2 modes).[1] With regard to the two thermal peaks, the band at 1124 cm^{-1} is clear of solvent lines when dissolved in THF and clearly exhibits polarized behavior. The band at 1511 cm^{-1} is partially screened by the Raman lines of THF but also appears to be polarized. Therefore, since these thermal peaks are polarized, it is suggested that they could be due to the presence of the folded syndiotactic structure. However, their strong intensities and difference from the calculated (1499 and 1158 cm^{-1}) frequencies make it necessary to consider the alternative possibility.

Work by Rimai, Kilponen, and Gill,[4] reported while our communication was in review, gave precedent to highly sensitive Raman detection of conjugated polyenes. Their excitation profiles of resonance-enhanced Raman spectra were demonstrated for all-*trans*-β-carotene and lycopene. Enhancement made it possible to observe Raman lines at 10^{-7} *M* concentration in solution. Assignments of two strong bands for β-carotene ($\bar{\nu}_1$ = 1158 and $\bar{\nu}_2$ = 1527 cm^{-1}) and lycopene ($\bar{\nu}_1$ = 1158 and $\bar{\nu}_2$ = 1515 cm^{-1}) were made on the basis of previous literature work.[5] The $\bar{\nu}_1$ Raman fundamental was assigned to the single-bond stretching mode, and the $\bar{\nu}_2$ to the double-bond stretching mode of conjugated polyenes. Overtones were noted at *ca.* 2313, 2679, 2163, and 3048 cm^{-1}.

It is concluded that a decomposition process is being monitored during our thermal treatments, rather than a predegradative structural reorientation of the polymer system. This interpretation is reinforced by most recent Raman observations for conjugated polyenes which have bands of interest at *ca.* 1500 and 1100 cm^{-1}.[4] It is well established that such polyenes are major degradative products for PVC systems.[6] The detailed assignments of the strong Raman peaks at 1124 and 1511 cm^{-1}, as well as other noted peaks developed at 2143, 2625, 3017, and 3175 cm^{-1}, are not possible from this initial data, but tentative interpretation from the above discussion implies that strong Raman-active, infrared-inactive bands at 1124 and 1511 cm^{-1}, as well as overtone and combination bands, are originating from degradative polyene structures which are detectable at extremely low concentration levels in thermally treated PVC.

Further temperature series closer to the actual T_g temperature range will be studied for the PVC system, as well as for certain allied structural chemical and physical modifications. It would seem in view of the above data that Raman spectroscopy will be one of the most informative methods to monitor such phenomena.

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