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Vibrational Spectroscopic Characterization of Ethylene-co-vinyl Cinnamate Copolymers Before and After UV Exposure

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SUMMARY: Vibrational spectroscopic studies of a series of ethylene-co-vinyl cinnamate (EVCIN) copolymers, before and after exposure to UV radiation, are reported. The purpose of these studies is to determine whether or not significant reaction (photo-crosslinking) of the cinnamate groups in EVCIN copolymers occurs upon UV exposure in the solid state as the concentration (fraction) of cinnamate groups is systematically reduced. By increasing the ethylene concentration in the EVCIN copolymers the cinnamate groups are "diluted" and progressively spaced apart in the copolymer. Somewhat surprisingly, we find that an EVCIN copolymer containing only 5 mole % vinyl cinnamate still undergoes a facile crosslinking in the solid state upon UV exposure.

Introduction

In a recent publication we presented the results of a preliminary infrared characterization study of a commercial poly(vinyl cinnamate) (PVCIN) and its blends with poly(4-vinyl phenol) (PVPh), before and after photo-crosslinking the PVCIN by exposure to UV radiation[1]. PVCIN undergoes crosslinking by the photoaddition of a UV excited cinnamoyl group to an unexcited cinnamoyl group[2,3], as depicted below in Scheme I. The commercial PVCIN used in these prior studies was not "pure" and, in fact, it would have been better described as a copolymer of vinyl cinnamate (VCIN) and vinyl alcohol (VOH), since it contained a significant concentration of the latter segments (≈ 20%). This complicated the interpretation of the infrared spectra, but we were able to demonstrate that quantitative analysis of the fraction of unsaturated (–C=C–) double bonds and "free" (non-hydrogen

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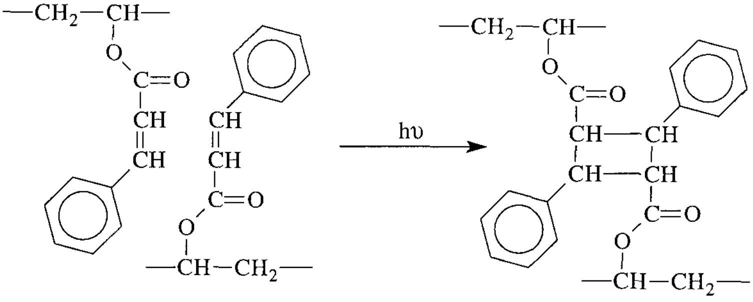
bonded) and hydrogen bonded unsaturated (–CO-C=C–) and saturated (–CO–C–C–) acetoxy carbonyl groups was feasible in these blends as a function of UV exposure time.



Scheme I

In recent work we have focused our attention on chain connectivity and its effect on the free energy of mixing and phase behavior of (co)polymer blends4-9). Of particular interest have been concepts that we have termed intramolecular screening4-6) and functional group accessibility7-9)—factors that limit the number of potentially favorable (to mixing) intermolecular interactions that are formed between complementary functional groups in polymer blends. Crosslinking one or both of the (co)polymers in a polymer blend is another factor that is expected to affect the formation of intermolecular interactions, and (co)polymers containing cinnamate groups afford the opportunity to systematically vary the degree of crosslinking though exposure to different time periods of UV radiation. The principal question that we address in this communication is a natural corollary of the functional group accessibility problem mentioned above and is as follows: "How far apart can we space the cinnamate groups in a copolymer chain and still obtain a significant reaction (photo-crosslinking) of the cinnamate groups upon UV exposure in the solid state?" For these studies we decided to carefully prepare and characterize a number of EVCIN copolymers of known VCIN concentrations and use, principally, infrared spectroscopy to quantitatively determine the rate of crosslinking as a function of UV exposure. The results of the study are described below.

Experimental

Poly(vinyl alcohol) (PVOH) with a reported molecular weight of 89-98K g/mole and containing > 99% vinyl alcohol (VOH) segments was purchased from Aldrich Chemical.

Ethylene-co-vinyl alcohol (EVOH) copolymers containing 58, 45, 18 and 10 mole % VOH (denoted EVOH{58}, EVOH{45}, etc.) were purchased from Polysciences, Inc., and an ethylene-co-vinyl acetate (EVA) copolymer containing 5 mole % vinyl acetate (VAc) (denoted EVA{5}) was purchased from Scientific Polymer Products, Inc. Conversion to PVCIN and the EVCIN copolymers of differing VCIN content was achieved using slight variations of the methodology described by Minsk et al.[2a)]

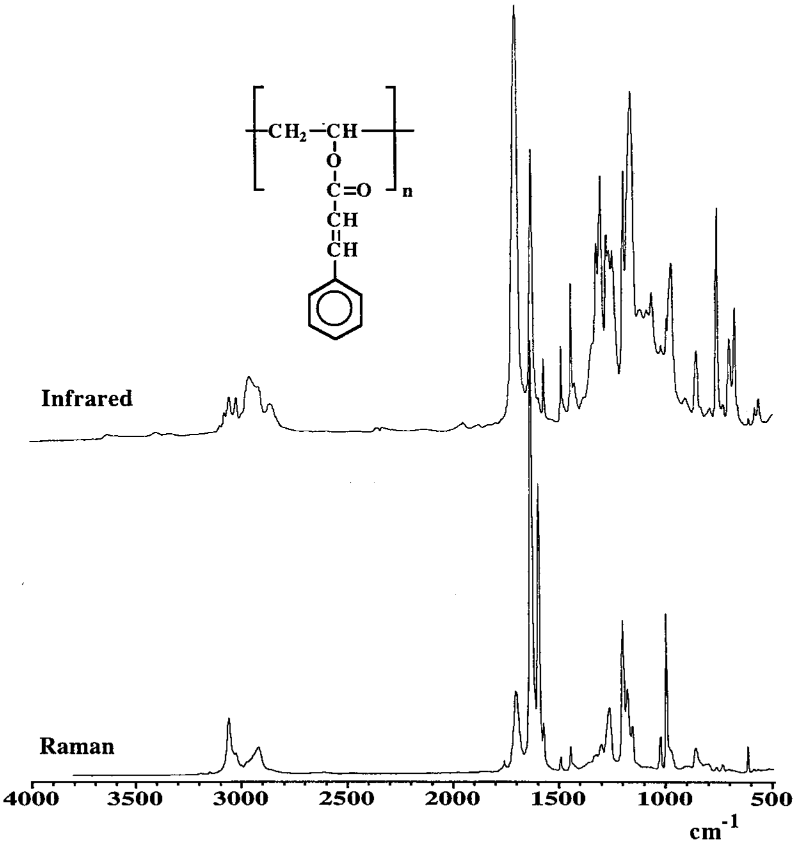


Fig. 1: Infrared and Raman spectra of poly(vinyl cinnamate) in the region from 500-4000 cm^{-1}.

In the case of PVCIN, the parent PVOH was suspended in pyridine; cinnamoyl chloride (Aldrich Chemical) was added and the mixture was allowed to react over 4h at 50°C. Following multiple dissolutions, reprecipitations and washings, the PVCIN was dried under vacuum in the absence of light. Figure 1 (top) shows the infrared spectrum of the PVCIN sample, and it is immediately apparent that essentially complete conversion of the PVOH to PVCIN was achieved, as evidenced by the lack of any significant absorbance in the hydroxyl stretching region (3400-3800 cm^{-1}). This is in marked contrast to the spectrum of the commercial sample of PVCIN used in our previous study1). EVCIN{58} and EVCIN{45} copolymers were prepared in a similar fashion, except that the parent EVOH polymers were initially dissolved directly in pyridine prior to the addition of cinnamoyl chloride.

Infrared spectroscopic characterization of the parent EVOH{18} and EVOH{10} copolymers revealed that they were not "pure" (i.e., completely hydrolysed), and there was a significant concentration of VAc segments remaining10). Accordingly, for the preparation of the EVCIN{18} and EVCIN{10} copolymers it was first necessary to hydrolyse the remaining VAc groups in the parent EVOH{18} and EVOH{10} copolymers. This was achieved using the methodology described in ref. 10. Infrared spectroscopy was employed to verify essentially complete conversion to the alcohol by monitoring the absorbance of the VAc carbonyl group. Similarly, the EVCIN{5} copolymer was prepared by initially hydrolyzing the EVA{5} copolymer to the corresponding EVOH{5} before transforming it to the cinnamate.

Samples of PVCIN and the EVCIN copolymers for infrared spectroscopic characterization were prepared by casting thin films on KBr windows from 2% solutions in tetrahydrofuran (THF). After the majority of the solvent had evaporated, the films were placed under vacuum at 50°C for at least 3 hours to completely remove residual solvent. No absorptions attributable to the solvent were observed in the infrared spectra of the samples. After checking that the samples were sufficiently thin to be within the absorption range where the Beer-Lambert law is obeyed, the KBr window containing the film was permanently mounted in a metal infrared sample holder. Photo-crosslinking was performed by placing the holder containing the sample into an evacuated glass chamber under a broad range UV radiation source (Dymax, Light Welder PC-2) at a distance of 18 cm from the lamp (the intensity of the source was measured at 18.6 $\mathrm{mW/cm^2}$ using a Dymax model 306 UV powermeter. The samples did heat up during UV exposure, but the temperature rise was only in the range of 20-27°C (depending on exposure time), and this was not considered problematic.

Infrared spectroscopic measurements were recorded on a Digilab model FTS-45 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal averaged. Raman spectra were performed on a Bio-Rad Fourier transform Raman spectrometer equipped with a Nd:YAG laser and liquid nitrogen-cooled germanium detector. The laser produced a continuous source of radiation at 1064 nm, and the power at the sample was approximately 400 mW. Raman spectra were collected at a resolution of 4 cm^{-1}, and 1000 scans were signal averaged.

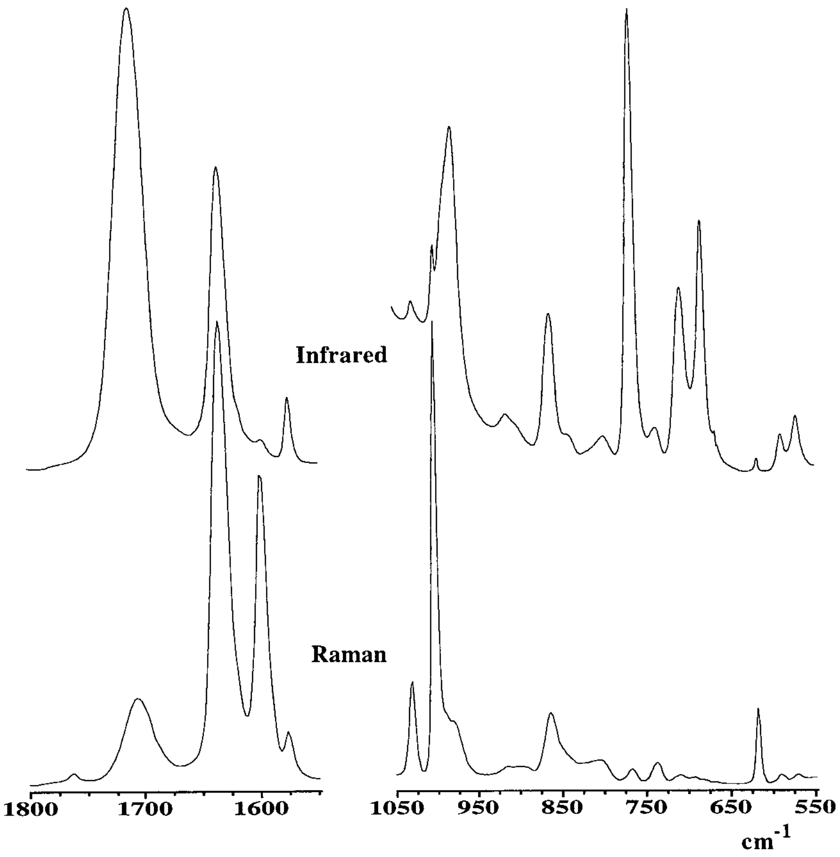


Fig. 2: Scale expanded infrared and Raman spectra of poly(vinyl cinnamate) in the regions from 550-1050 and 1550-1800 cm^{-1}.

Results and Discussion

In our previous infrared studies of the commercial (impure) sample of PVCIN[1] we focused our attention almost exclusively on the region from 1600-1800 cm^{-1}, where the –C=O and –C=C– stretching modes absorb, and made only superficial mention of the other major characteristic bands that are present in the PVCIN infrared spectrum. While we again do not intend to dwell on the precise assignments of the normal modes of PVCIN, as this is not the major purpose of our present work, we have prepared "pure" samples of PVCIN and several EVCIN copolymers and found that other regions of the spectrum can be useful for quantitative analysis of the degree of photo-crosslinking. Thus, it is appropriate to consider both the infrared and Raman spectra of VCIN containing polymers in a little more detail.

In Figure 1 we show the infrared and Raman spectra of PVCIN in the mid-infrared region from 500-4000 cm^{-1}. For expository convenience, in Figure 2 we show scale-expanded regions of the same spectra from 1550-1800 and 550-1050 cm^{-1}—regions that will be of particular significance to the work reported here.

The VCIN segment is complex, but, to a first approximation, may be considered to be composed of a monosubstituted benzene, a disubstituted olefin that is conjugated to both benzene and ester groups, an unsaturated ester and some remaining aliphatic groups (see Scheme I). We would expect to observe characteristic group frequencies in the infrared and Raman spectra of PVCIN representative of these individual moieties, but we would further expect significant perturbations to the frequencies and especially relative intensities of the normal modes arising from the extensive conjugation present.

The normal modes of monosubstituted benzenes have been extensively studied and the reader is referred to the monographs of Colthrup, Daly and Wiberley[11] and Dollish, Fateley and Bentley[12] for details. Suffice it to say that in monosubstituted benzenes relatively intense characteristic infrared bands include the multiple C–H stretching modes between 3000 and 3100 cm^{-1}, the ring breathing modes at $\approx$ 1604 (m), 1585 (w), 1500 (s) and 1452 (s) cm^{-1}, the mixed in-plane C–H bending and C–C stretching modes at $\approx$ 1073 (w) and 1027 (m) cm^{-1}, the out-of-plane C–H wags at $\approx$ 900 (w) and 750 (s) cm^{-1} and the out-of-plane ring bending modes at $\approx$ 697 (vs) and 540 (m) cm^{-1}. Additionally, a distinct pattern of summation bands between 1780 and 2000 cm^{-1} is observed in monosubstituted benzenes[11]. The corresponding characteristic Raman bands of monosubstituted benzenes[11,12] include the C–H stretching modes, the ring breathing modes at $\approx$ 1600 (s), 1580 (m) and 1452 (w) cm^{-1}, the mixed ring stretching and ring bending modes at $\approx$ 1177 (m), 1156 (w), 1027 (m) and 1000 (vs) cm^{-1} and the in-plane ring bending mode at $\approx$ 620 (w) cm^{-1}. The interested reader is referred to the infrared[13] and Raman[14] spectra of atactic polystyrene which exhibit all of these characteristic modes[13,14].

If we now look for these characteristic bands in the spectra of PVCIN (Figures 1 and 2), we find most of them, but the relative intensities of some of the modes are quite different. For example the ring stretching mode at ≈ 1600 cm^{-1} is extremely weak in the infrared, while in the Raman it is a very strong band—much stronger than the usually dominant band at 1000 cm^{-1} observed in polystyrene and the like. Similarly, the relative infrared intensity of the PVCIN out-of-plane C–H wag at ≈ 770 cm^{-1} is much greater than the out-of-plane ring bending mode at ≈ 690 cm^{-1}—a reversal of what is seen in unconjugated monosubstituted benzenes. Note also that the band at ≈ 1200 cm^{-1}, which is most likely a substituent-sensitive ring mode, has strong intensity in both the infrared and Raman. There are other subtleties, but this is sufficient for our purposes here, and we should now move on to the other major bands associated with the olefinic double bond and the ester group.

Unsymmetrical dialkylsubstituted olefins give rise to characteristically weak to medium intensity –CH=CH– stretching modes in the 1630-1670 cm^{-1} region of the infrared spectrum, but very strong dominant bands in the Raman[11,12)]. In the Raman spectrum of PVCIN (Figure 2) the band observed at ≈ 1635 cm^{-1} *is the most intense band in the entire* spectrum, while it still has a relatively strong absorbance in the infrared. This is undoubtedly the predominantly –CH=CH– stretching mode. Other characteristic bands for the –CH=CH– group are the *trans* and *cis* CH wags that occur as medium-to-strong bands in the infrared between 965-980 and 650-730 cm^{-1}, respectively. In PVCIN- the bands observed at ≈ 975 and 705 cm^{-1} may be reasonably assigned to these modes. This brings us to the essentially isolated band of medium intensity observed in the infrared (and weakly in the Raman) spectra of PVCIN at ≈ 865 cm^{-1}. This band will become important in our forthcoming quantitative analysis (see later), but its assignment is far from clear. An infrared band of very weak intensity has been assigned to a substituent-sensitive out-of-plane ring mode of monosubstituted benzenes[11)] at approximately 900 cm^{-1}. Accordingly, it is reasonable to tentatively assign the 865 cm^{-1} band in PVCIN to a mode containing contributions from the out-of-plane ring and –CH=CH– wagging vibrations.

The C=O stretching mode of the PVCIN unsaturated ester appears at ≈ 1710 cm^{-1}. Unsurprisingly, it is the most intense band in the infrared spectrum. In the Raman it occurs at the same frequency and is of medium-weak intensity. The predominantly C–O stretching mode appears as a relatively broad and intense band at ≈ 1170 cm^{-1} in the infrared spectrum. Apart from the aliphatic C–H stretching modes that occur between 2800-3000 cm^{-1}, it is difficult to assign other bands in the spectra of PVCIN to the aliphatic –CH_2–CH– moiety. Any characteristic bands are simply buried under the modes associated with the rest of the PVCIN segment. And this conveniently leads us to the spectra of the EVCIN copolymers.

In Figure 3 we show the infrared spectra of PVCIN and the ethylene copolymers containing 44, 18, 10 and 5 mole % VCIN. It is important to recognize, when comparing these spectra, that each individual spectrum is scale-expanded to the band of maximum absorbance (the C–H stretching band at ≈ 2900 cm^{-1} in the case of EVCIN{5} and EVCIN{10} and the C=O stretching band at ≈ 1710 cm^{-1} for EVCIN{18}, EVCIN{44} and PVCIN).

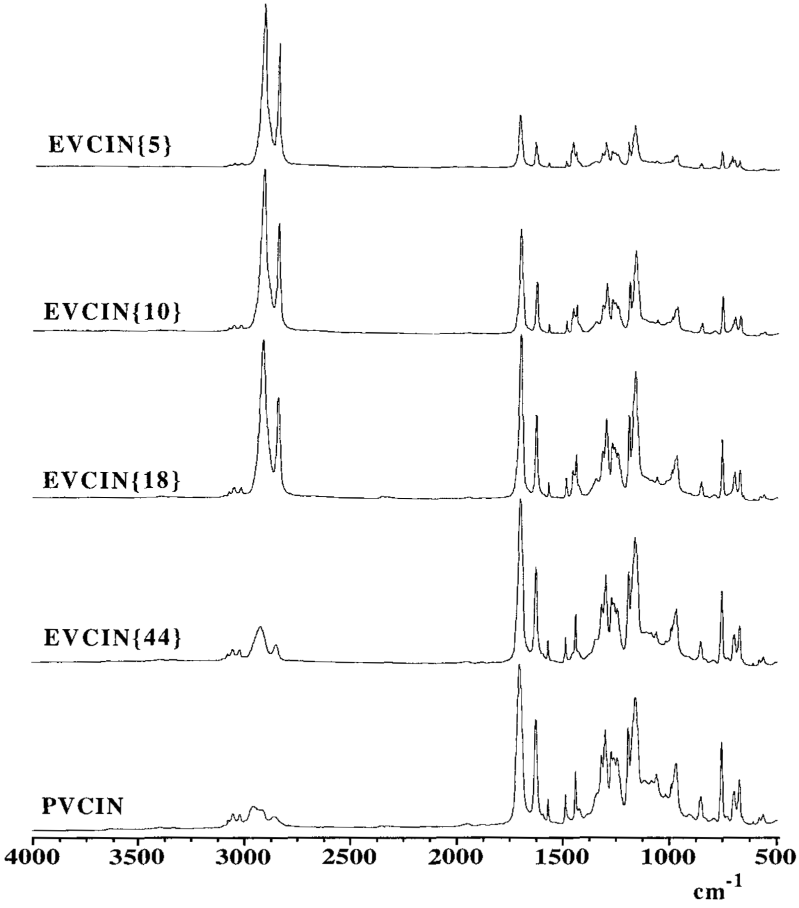


Fig. 3: Scale-expanded infrared spectra of poly(vinyl cinnamate) and ethylene-co-vinyl cinnamate copolymers containing 44, 18, 10 and 5 mole % vinyl cinnamate in the region from 500-4000 cm^{-1}.

First we should note that the spectra are of superb quality (even if we say so ourselves!) and that there is no evidence of any significant absorbance in the O–H stretching region (3200-3800 cm^{-1}), which confirms essentially complete transformation of the VOH to VCIN groups. The ratio of the C–H stretching band at ≈ 2900 cm^{-1} to the C=O stretching band at ≈ 1710 cm^{-1} is a convenient measure of the VCIN concentration in the copolymers. This might be considered a trivial observation to the sophisticated spectroscopist, but there are only subtle differences in the spectra below 2000 cm^{-1}, and one would be hard pressed to distinguish between, say, PVCIN and an EVCIN containing 80 mole % ethylene as illustrated in Figure 4.

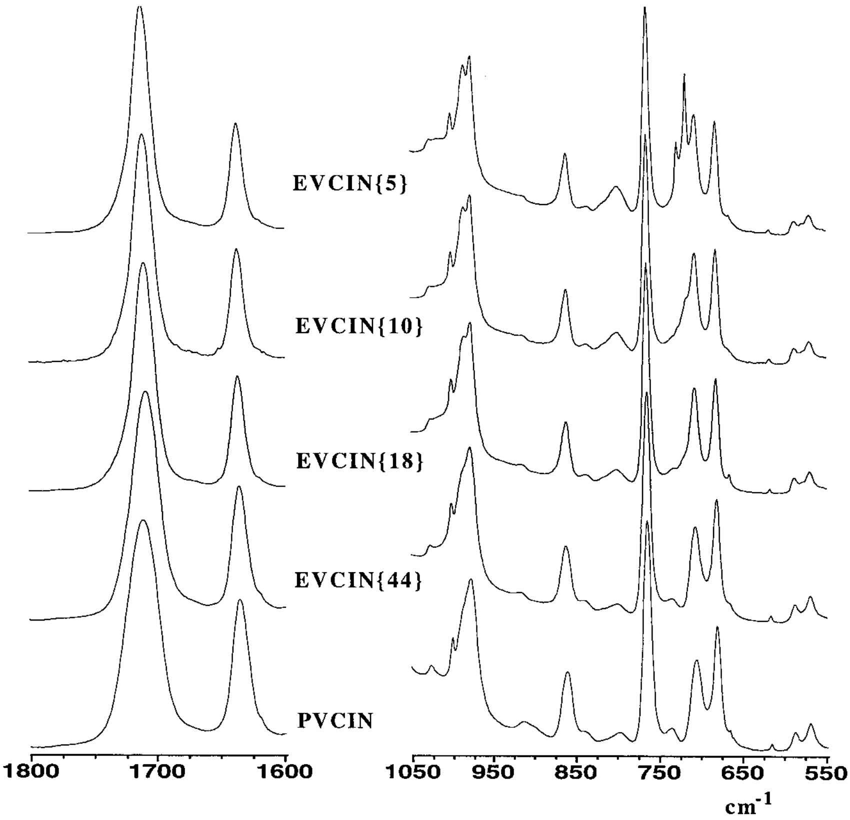
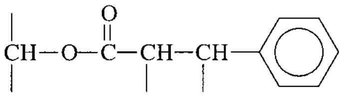


Fig. 4: Scale-expanded infrared spectra of poly(vinyl cinnamate) and ethylene-co-vinyl cinnamate copolymers containing 44, 18, 10 and 5 mole % vinyl cinnamate in the regions from 550-1050 and 1600-1800 cm^{-1}.

Scale-expanded infrared spectra of PVCIN and four of the EVCIN copolymers are presented in the two spectral regions from 550-1050 and 1600-1800 cm^{-1}, as, again, these will be particularly relevant to our forthcoming photo-crosslinking studies. Raman spectra of the EVCIN copolymers were also recorded, but there was, frankly, no additional useful information over that found in the infrared, and we did not pursue this form of spectroscopy further. To reiterate, the infrared spectra are all dominated by modes attributed to the VCIN segment. Only in the case of the EVCIN{5} copolymer (and, with a bit of imagination, maybe EVCIN{10}) does one see the obvious presence of ethylene segments through the classic doublet observed at ≈ 720/730 cm^{-1} attributed to the crystal field splitting of the CH_2 rocking mode13). This indicates that at room temperature EVCIN{5} is semi-crystalline. Once again, we draw the reader's attention to the band at ≈ 860 cm^{-1}, which is reasonably isolated in all the EVCIN copolymer spectra and which we will feature prominently in subsequent quantitative analyses. Finally, we note that the intense carbonyl stretching band at ≈ 1710 cm^{-1} broadens significantly with increasing VCIN content in the (co)polymers. This is entirely consistent with that observed in analogous ethylene-co-vinyl acetate (EVA) copolymers. Such broadening effects have recently been ascribed to transitional dipole coupling which increases as the concentration of carbonyl groups per unit volume increases15).

We now turn our attention to the changes that occur upon exposure of the VCIN containing (co)polymers to UV radiation. First, it would be pleasing if we could determine which characteristic infrared bands in the spectrum of the saturated ester are formed upon photo-crosslinking (see Scheme I), i.e.:



Spectral subtraction is an appropriate methodology to use, given that the segments are relatively large and minimal coupling between the saturated and unsaturated esters in the (co)polymer chain is anticipated13). Figure 5 shows scale-expanded infrared spectra of PVCIN before (denoted B) and after 10 min of UV exposure (denoted A) [see Experimental Section for details] recorded at room temperature in the region from 500 -1800 cm^{-1}. The most obvious changes are indicated by the vertical dashed lines. The spectrum denoted C is the difference spectrum (B - xA) obtained using a trial-and-error procedure that involves subtracting a specific amount of spectrum A (x = 0.54 in Fig. 5) from spectrum B such that isolated characteristic bands of the VCIN segment (e.g., those at ≈ 1637, 1300, 975, 860, 770, 705 and 690 cm^{-1}) are reduced to the baseline. Assuming that the transformation of the unsaturated to the saturated ester (Scheme I) is the only photo-chemical process occurring upon exposure to UV radiation, it follows that spectrum C should therefore be that of the "pure" saturated ester. The obvious question now arises, "Is the difference spectrum consistent with that expected of a saturated ester of the type shown above?" Indeed it is. The dominant carbonyl stretching mode is now observed at 1735 cm^{-1}, which together with the strong absorption involving the C–O stretching vibration near 1200 cm^{-1}, is characteristic of saturated aliphatic esters.

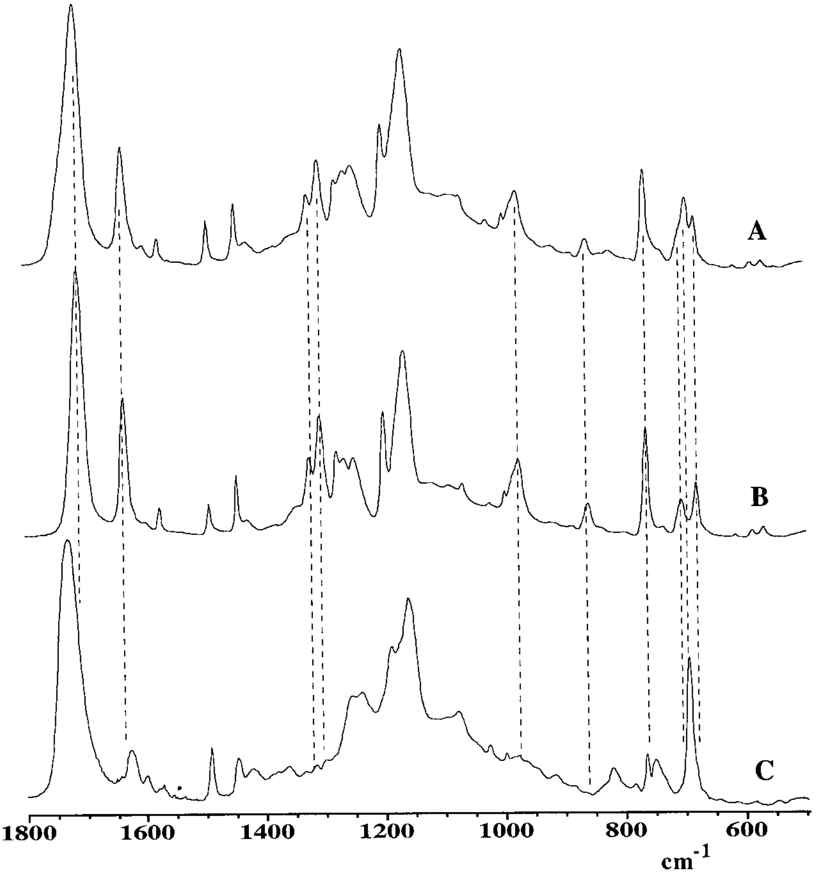


Fig. 5: Scale-expanded infrared spectra of poly(vinyl cinnamate) recorded at room temperature in the region from 500 -1800 cm^{-1}. (A) After 10 min. exposure to UV radiation (B) Before UV exposure and (C) Difference spectrum A - 0.54 B.

Characteristic bands with "normal" intensity relationships, attributed to unconjugated monosubstituted benzene groups, similar to those observed in polystyrene, are also readily identified (e.g., the ring stretching modes at ≈ 1604, 1585, 1500 and 1452 cm^{-1}, the out-of-plane C–H wag at ≈ 750 cm^{-1} and the out-of-plane ring bending mode at ≈ 697 cm^{-1}). The fact that essentially undistorted bands attributed to the carbonyl stretching (1735 cm^{-1}) and out-of-plane ring bending (697 cm^{-1}) modes of the saturated ester have been successfully revealed by spectral subtraction is quite impressive. Spectral subtractions of complex mixtures are rarely perfect, however, and the "clean" elimination of the vast majority of the VCIN bands is probably better than we could have anticipated. Slight changes in band broadness can lead to ambiguities (derivative type bands, etc.) in subtracted spectra ,and this is probably the cause of the slight distortion of the band envelope at ≈ 750 cm^{-1}.

In the Introduction we mentioned that one of the principal motivations for studying EVCIN copolymers was to answer the question, "How far apart can we space the cinnamate groups in a copolymer chain and still obtain a significant reaction (photo-crosslinking) of the cinnamate groups upon UV exposure in the solid state?" It turns out that all the EVCIN copolymers studied, those containing from 100 to 5 mole % VCIN, undergo facile photo-crosslinking reactions upon exposure to UV radiation, albeit at differing rates. We will describe the changes that occur as a function of UV exposure time using as a typical example the copolymer with the lowest concentration of VCIN, EVCIN{5}. We will then describe the methodology used to quantitatively determine the rate of the photo-crosslinking reaction for EVCIN{5} and then use this procedure for the analysis of the other (co)polymers.

Figure 6 shows absolute absorbance infrared spectra in the region from 1600-1800 cm^{-1} for an unexposed sample of EVCIN{5} and the *same* sample that had been exposed to UV radiation for 5, 10, 20 and 30 min. [see Experimental Section for details]. The –C=C– stretching mode and the unsaturated ester carbonyl band at 1637 and 1712 cm^{-1} are both observed to decrease uniformly as a function of UV exposure time. At the same time, a new band, attributed to a saturated ester carbonyl stretching mode at ≈ 1735 cm^{-1}, is detected as a shoulder, and its intensity increases systematically with UV exposure time. These observations are consistent with previous trends noted for PVCIN1), but, unlike these previous studies, where we used a curve fitting procedure and employed the relative absorbance of the –C=C– stretching mode to measure the extent of photo-reaction, in this work we use spectral subtraction in the region below 900 cm^{-1}, which appears to be a more convenient methodology.

Figure 7 shows corresponding infrared spectra in the region from 600-900 cm^{-1}. Here, if we display overlapping spectra in absolute absorbance (as in Fig. 6), the figure is very confusing, and it is very difficult to follow the trends. Accordingly, it is more convenient to display the individual spectra in the scale-expanded version. Fortunately, the characteristic doublet assigned to the CH_2 rocking vibration observed at ≈ 720/730 cm^{-1} can be considered an internal standard and used as a guide to follow trends. Note that with increasing exposure to UV radiation the bands at ≈ 865, 770, 705 and 680 cm^{-1} decrease systematically with respect to the 720/730 cm^{-1} CH_2 rocking vibration (denoted by ↓), while those at ≈ 830 and 697 cm^{-1} increase (↑). For completeness, the band at ≈ 800 cm^{-1} does not appear to change (↔).

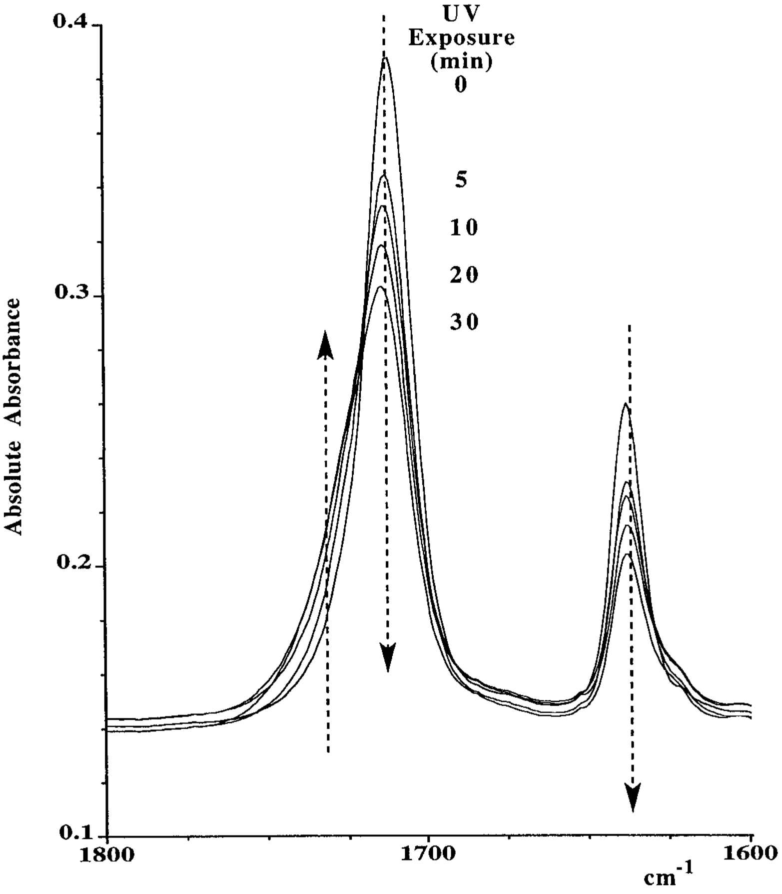


Fig. 6: Absolute absorbance infrared spectra of EVCIN{5} recorded at room temperature in the region from 1600 -1800 cm^{-1} after 0, 5, 10, 20 and 30 min. exposure to UV radiation.

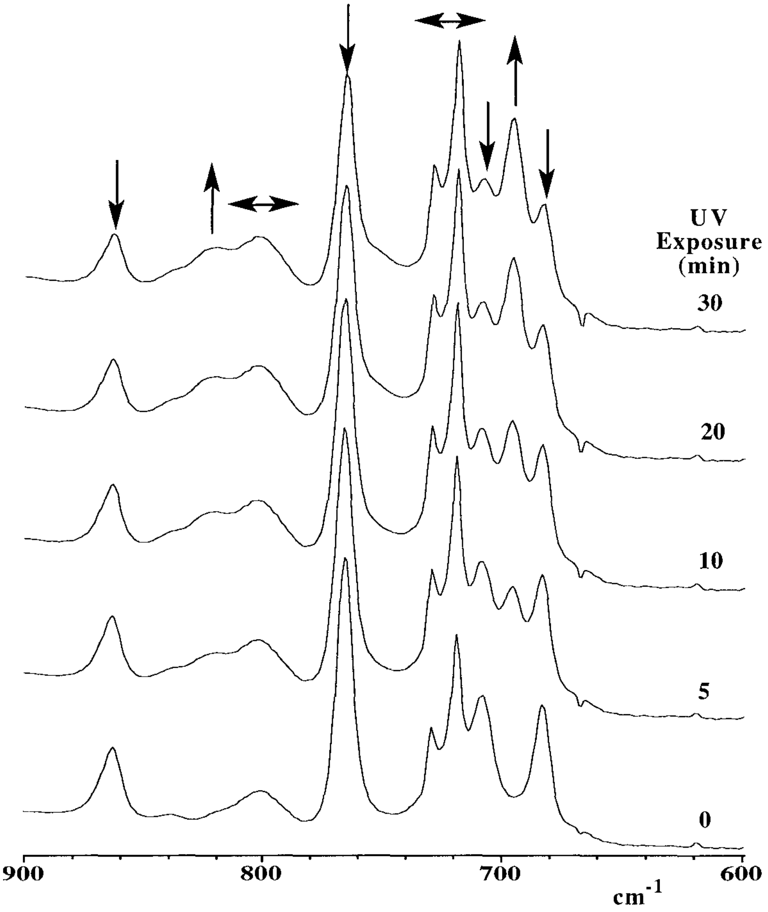


Fig. 7: Scale-expanded infrared spectra of EVCIN{5} recorded at room temperature in the region from 600 -900 cm^{-1} after 0, 5, 10, 20 and 30 min. exposure to UV radiation.

As mentioned previously, the characteristic band for the VCIN group at ≈ 865 cm^{-1} is reasonably isolated with a well defined baseline and is particularly useful for monitoring the correct amount of the "pure" unexposed spectrum to subtract in difference spectroscopy. This is illustrated in Figure 8, which shows scale expanded infrared spectra of EVCIN{5} recorded before and after 30 min. UV exposure together with the resultant difference spectrum obtained using the 865 cm^{-1} band to determine the correct subtraction parameter.

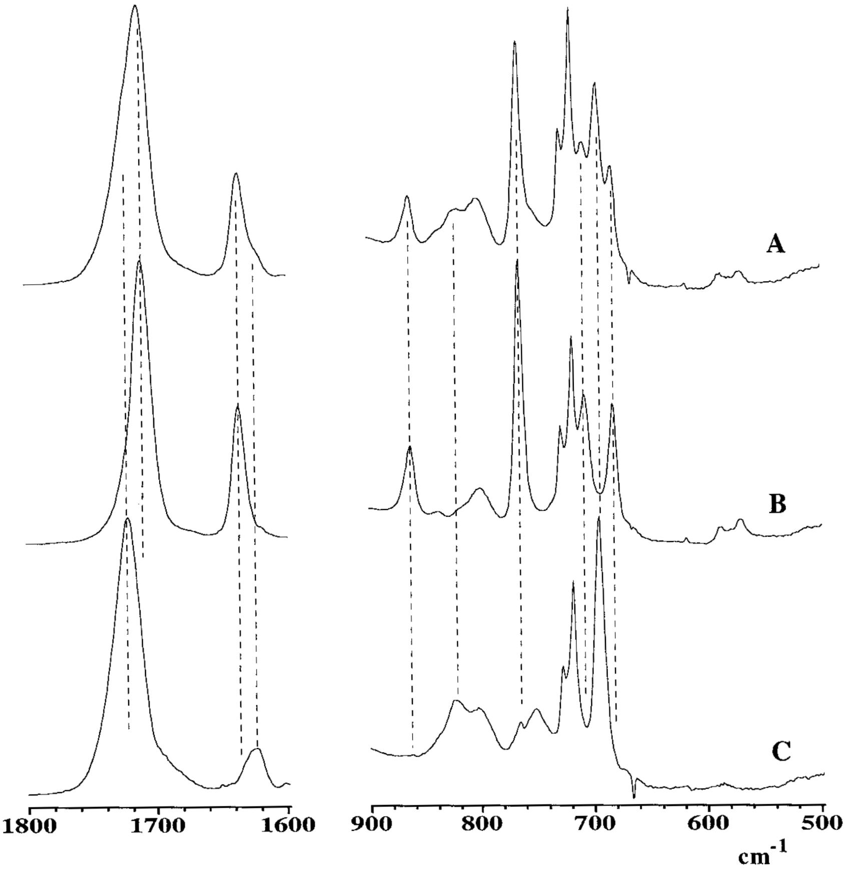


Fig. 8: Scale-expanded infrared spectra of EVCIN{5} recorded at room temperature in the regions from 500-900 and 1600-1800 cm^{-1}. (A) After 30 min. exposure to UV radiation, (B) Before UV exposure, and (C) Difference spectrum A - 0.44 B.

We cannot resist gloating a little about the quality of this difference spectrum. Note the definition and band shape of the saturated ester carbonyl band at 1735 cm^{-1}, which has been extracted from the relatively weak shoulder on the high frequency side of spectrum A. Similarly, the band revealed at ≈ 1630 cm^{-1} in the difference spectrum is the weak shoulder observed on the low frequency side of spectrum A, and we believe that this is probably due to the –C=C– stretching vibration of the *cis*-isomer (isomerization of the –C=C– group during UV exposure is not unexpected). Note also the almost perfect elimination of the VCIN bands at 685 and 705 cm^{-1} and the lack of any significant distortion to the band shape of the out-of-plane ring bending mode of the saturated ester at 697 cm^{-1}.

For the example shown in Fig. 8 a subtraction parameter of 0.44 was determined, and this represents the fraction of VCIN segments that remain in the sample, $f^{C=C}$, after a UV exposure time of 30 min. Obviously, it follows that the fraction of –C=C– groups that have reacted is $(1 - f^{C=C})$. Using the same methodology, we list in Table 1 the subtraction parameter determined for the PVCIN, EVCIN{44}, EVCIN{18}, EVCIN{10} and EVCIN{5} samples for UV exposure times of up to 60 min.

Tab. 1. Subtraction parameters

Time (min)	Subtraction Parameter				
	PVCIN	EVCIN{44}	EVCIN{18}	EVCIN{10}	EVCIN{5}
0	1	1	1	1	1
5	0.65	0.73	0.75	0.71	0.65
10	0.51	0.60	0.62	0.58	0.51
20	0.34	0.45	0.57	0.55	0.46
30	0.22	0.37	0.48	0.50	0.44
40	0.17	0.31	0.44	0.47	0.41
50	0.15	0.23	0.43	0.43	0.37
60	0.13	0.20	0.40	0.39	0.30

Note that the subtraction parameter value for a given VCIN (co)polymer decreases systematically with UV exposure time, as it should, because it represents the fraction of original VCIN (co)polymer remaining in the sample. Figure 9 summarizes these results graphically. At the top is a plot of the fraction of VCIN groups that have reacted $(1 - f^{C=C})$ as a function of UV exposure time. Here we see that for a given UV exposure time the fraction of VCIN groups that have reacted decreases with decreasing concentration (or increasing "dilution") of VCIN segments for the PVCIN, EVCIN{44} and EVCIN{18} (co)polymers. However, the results obtained for the EVCIN{10} copolymer are very similar to those of the EVCIN{18}and, in the case of the EVCIN{5}, significantly above the curve for EVCIN{18} [error in measurement is estimated at ± 0.02]. We will come back to this point shortly.

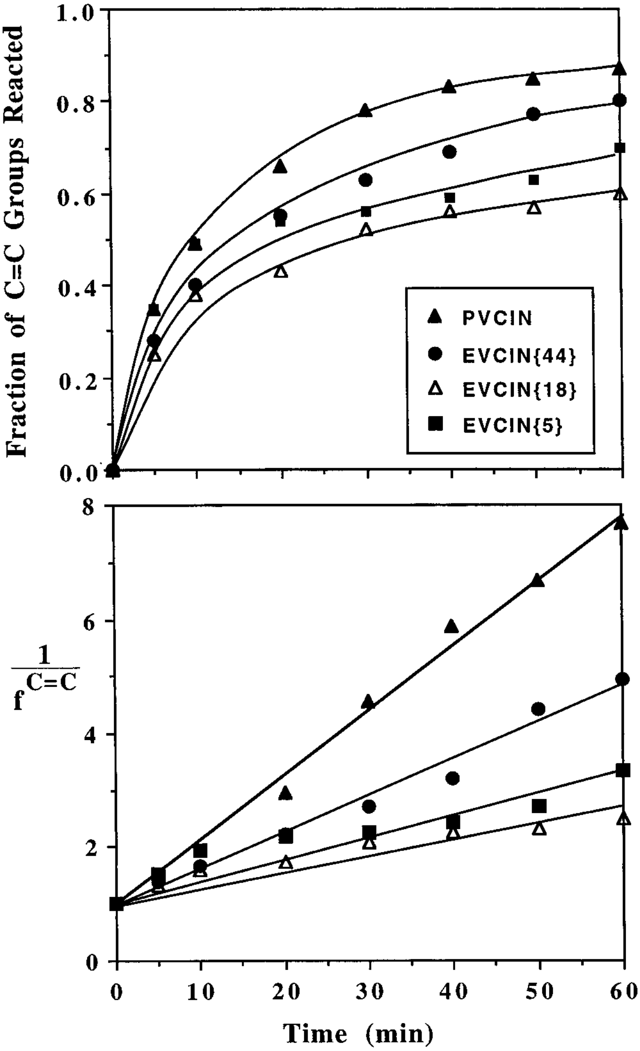


Fig. 9 Top: Graph of the fraction of –C=C– groups that have reacted (1 - $f^{C=C}$) versus UV exposure time for PVCIN and the three EVCIN{44}, EVCIN{18} and EVCIN{5} (co)polymers. Bottom: Plot of $1/f^{C=C}$ as a function of UV exposure time.

At the bottom of Fig. 9 we show a plot of ($1/f^{C=C}$) as a function of UV exposure time. A linear relationship is consistent with the simple kinetic scheme[1] that is depicted by:

$$-\frac{d[C=C]}{dt} = k\,[C=C]^2 \qquad (1)$$

A linear least squares fit of the different sets of data yields slopes of 0.12, 0.065, 0.023, 0.022 and 0.031 min^{-1} for the PVCIN, EVCIN{44}, EVCIN{18} and EVCIN{5} (co)polymers, respectively. On a per mole VCIN basis, [i.e., rate x 100/(mole % VCIN)], the rates of the photo-reaction of the VCIN groups for the PVCIN, EVCIN{44} and EVCIN{18}(co)polymers are comparable (0.12, 0.15 and 0.13 min^{-1}). This implies that under the experimental conditions employed, the rate of the photo-reaction of the VCIN groups is unaffected by chain connectivity and "dilution" by the ethylene segments down to at least 18 mole % VCIN. Surprisingly, on a per mole VCIN basis, the rate of the photo-reaction for the EVCIN{10}and EVCIN{5}copolymers are significantly greater (0.22 and 0.62 min^{-1}, respectively). However, this we believe is an artifact caused by the appreciable crystallization of the ethylene sequences in EVCIN{10}, and especially EVCIN{5}(as evidenced by the presence of the 720/730 cm^{-1} doublet—Fig. 8). Since a fraction of the ethylene segments reside in the crystalline phase, while the VCIN segments almost certainly reside exclusively in the amorphous regions, the effective VCIN concentration in the amorphous phase is greater than the overall nominal VCIN concentrations of 10 and 5 mole %, respectively. More work is necessary to substantiate this hypothesis.

In any event, before we loose sight of the main purpose of this present study, the results displayed in Fig. 9 indicate that about 25% of the available VCIN segments in all the (co)polymers undergo photo-crosslinking reactions after 5 min. of UV exposure under the experimental conditions employed. To illustrate the significance of this result, consider the following argument. Assume that we have an EVCIN{5} copolymer with a molecular weight of, say, 70,000 g/mole. The molecular weight of an average repeat containing one VCIN group for an EVCIN{5} copolymer, is ≈ 700 g/mole, therefore there are approximately 100 VCIN groups in an average chain. If 25% of the VCIN photo-react in 5 min. of UV exposure, this means on average that 25 crosslinks per chain are formed. Even allowing for intramolecular crosslinking and other inefficient, spurious reactions, this is a high degree of crosslinking, and the majority of the sample will reside in a three dimensional network.

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References

1). M. M. Coleman, Yin Hu, M. Sobkowiak, P. C. Painter, *J. Polym. Sci: Polym. Phys.*, **36**, 1579 (1998)

2). (a) L. M. Minsk, J. G. Smith, W. P. Van Deusen, J. F. Wright, *J. Appl. Polym. Sci.*, **2**, 302 (1959). (b) E. M. Robertson, W. P. Van Deusen, L. M. Minsk, *J. Appl. Polym. Sci.*, **2**, 308 (1959).

3). A. Reiser, *Photoreactive polymers*, Wiley Interscience, J. Wiley & Sons, New York (1989).

4). M. M. Coleman, P. C. Painter, *Prog. Polym. Sci.*, **20**, 1 (1995).

5). P. C. Painter, B. Veytsman, S. Kumar, S. Shenoy, J. F. Graf, Y. Xu, M. M. Coleman, *Macromolecules*, **30**, 932 (1997).

6). M. M. Coleman, L. A. Narvett, Y. H. Park, P. C. Painter, *J. Macromol. Sci.—Phys.*, **B37**, 283 (1998).

7). M. M. Coleman, G. J. Pehlert, P. C. Painter, *Macromolecules*, **29**, 6820 (1996).

8). G. J. Pehlert, P. C. Painter, B. Veytsman, M. M. Coleman, *Macromolecules*, **30**, 3671 (1997).

9). M. M. Coleman, P. C. Painter, *J. Macromol. Chem. Phys.*, in press.

10). M. M. Coleman, X. Yang, H. Zhang, P. C. Painter, *J. Macromol. Sci.—Phys.*, **B32**, 295 (1993).

11). N. B. Colthup, L. H. Daley, S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd Edition, Academic Press, Boston, 1990.

12). F. R. Dollish, W. G. Fateley, F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, J. Wiley & Sons, New York, 1974.

13). P. C. Painter, M. M. Coleman, *Fundamentals of Polymer Science*, 2nd Edition, Technomic, Lancaster, PA, 1997

14). P. J. Hendra, J. K. Agbenyega, *The Raman Spectra of Polymers*, John Wiley & Sons, New York, 1993.

15). P. C. Painter, G. J. Pehlert, Yuhong Hu, M. M. Coleman, submitted.