Macromolecules **2002,** *35,* 1289−1298

Functional Group Accessibility in Hydrogen-Bonded Polymer Blends. 4. Cross-Linking Effects

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Received October 15, 2001

ABSTRACT: Infrared spectroscopy is a fine tool with which to experimentally explore the effect of chain connectivity and functional group accessibility in hydrogen-bonded polymer blends. Such factors directly affect the fraction of intermolecular hydrogen-bonded groups that are formed and effectively reduce the hydrogen-bonding contribution to the free energy of mixing vis-à-vis analogous low-molar-mass analogues. In this study we report the results obtained from blends of copolymers containing vinyl cinnamate (VCIN) with copolymers containing 4-vinylphenol. The VCIN segment undergoes facile photocross-linking upon exposure to UV radiation, permitting the effect of cross-linking on functional group accessibility and phase behavior to be studied.

Introduction

In previous publications we have shown how we have used infrared spectroscopy to experimentally explore functional group accessibility and steric shielding in hydrogen-bonded polymer blends.[1−4] Such factors directly affect the fraction of intermolecular hydrogen-bonded groups that are formed in polymer solutions and blends and effectively reduce the hydrogen-bonding contribution to the free energy of mixing vis-à-vis analogous low-molar-mass analogues.[5,6] Accordingly, it has been necessary to modify our original theoretical equations that described the free energy of mixing[5] in order to take into account intramolecular screening and “spacing” effects.[6−8] One unanticipated advantage of this work is that we can now use standard self- and inter-association equilibrium constant values more easily obtained from appropriate model low-molar-mass compounds to calculate the free energy of mixing contribution from hydrogen bonding in polymer blends.[8]

Related to this, we have been investigating vinyl cinnamate (VCIN) (co)polymers and their blends with (co)polymers containing 4-vinylphenol as a potential systems that could be used to study the effect of cross-linking on functional group accessibility and phase behavior.[9−11] The VCIN segment undergoes facile photocross-linking upon exposure to UV radiation (see Scheme 1) as we have discussed previously.[9]

Ideally, what we require is a miscible (single phase) blend system where we can “count” the number of intermolecular interactions present and at the same time measure the extent of cross-linking. After an initial encouraging infrared characterization of poly(vinyl cinnamate) (PVCIN) and blends with poly(4-vinylphenol) (PVPh), before and after UV exposure,[9] we turned our attention to the synthesis and characterization of a series of ethylene-*co*-vinyl cinnamate copolymers (EVCIN) prepared from parent ethylene-*co*-vinyl alcohol copolymers (EVOH).[10] The goal of these EVCIN studies was to determine whether significant reaction (photocross-linking) of the cinnamate groups in EVCIN copolymers occurs upon UV exposure in the solid state as the concentration (fraction) of cinnamate groups was 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 found that an EVCIN copolymer containing only 5 mol % vinyl cinnamate still undergoes a facile cross-linking in the solid state upon UV exposure.

Next we studied blends of an EVCIN copolymer containing 18 mol % VCIN (denoted EVCIN{18}) with a dimethylbutadiene-*co*-vinylphenol copolymer containing 18 mol % VPh (denoted DMBVPh{18}).[11] This is a miscible (single phase) polymer blend system exhibiting a single glass transition temperature between −5 and 39 °C (depending upon blend composition), which facilitates the attainment of equilibrium conditions. A series of infrared spectra were recorded as a function of UV exposure time under a standard set of conditions. While it was a relatively straightforward task to measure the fraction of VCIN groups that had undergone photoreaction, obtaining a measurement of the fraction of hydrogen-bonded carbonyl bands as a function UV exposure was complicated by the fact that there were four overlapping carbonyl bands contributing to the band envelope in the carbonyl stretching region (see Scheme 2): two “free” C═O bands attributed to the unsaturated and saturated ester carbonyl stretching vibrations at ≈1712 and 1735 cm^{-1}, respectively, and two corresponding hydrogen bonded C═O bands at ≈1690 and 1712 cm^{-1}. Using digital subtraction or difference spectroscopy and a rather convoluted argument, we were able to infer that about 20% of the VCIN groups had reacted in an 80:20 blend of DMBVPh{18} with EVCIN{18} and that the semiinterpenetrating network appeared to remain a single phase.

However, we did not consider the results obtained from the study of this blend to be definitive, and it occurred to us that if we could essentially completely cross-link the EVCIN copolymer, we would be left with only saturated carbonyl groups; this would greatly simplify the interpretation of the infrared spectrum of the blend (only two C═O bands, a “free” carbonyl band at ≈1738 cm^{-1} and a hydrogen-bonded carbonyl band at ≈1712 cm^{-1}). In this paper we present the results of

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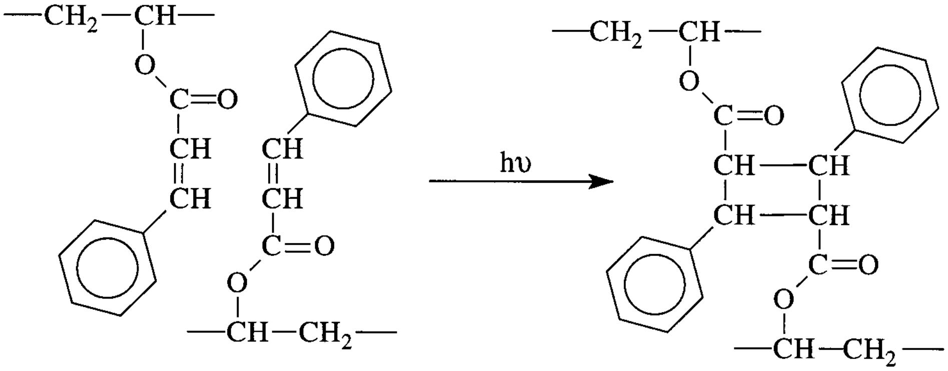
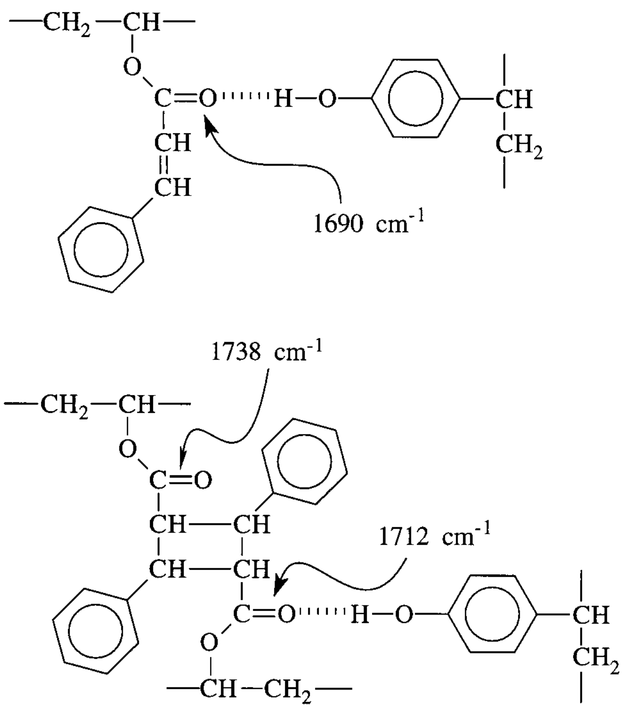
10.1021/ma011793s CCC: $22.00

Scheme 1



Scheme 2



such a study. As we will see, we did not succeed in solving our spectroscopic problems using blends of EVCIN copolymers, but the results pointed the way, and we did finally obtain some measure of success using copolymers of vinyl acetate and vinyl cinnamate (VAVCIN).

Experimental Section

The two 2,3-dimethylbutadiene-*co*-4-vinylphenol (DMBVPh) copolymers used in this study containing 18 and 33 mol % 4-vinylphenol (VPh), denoted DMBVPh{18} and DMBVPh{33}, respectively, have been described in previous blend studies.[2,3] Poly(vinyl acetate) (PVA), with a reported molecular weight of 100 000 and T_g of 22 °C, was purchased from Polysciences, Inc. An ethylene-*co*-vinyl cinnamate (EVCIN) copolymer containing 18 mol % vinyl cinnamate (VCIN), denoted EVCIN{18}, was produced from the parent ethylene-*co*-vinyl alcohol (EVOH{18}) by reaction with cinnamoyl chloride, as described in a previous communication.[10] The same procedure was used to prepare the corresponding ethylene-*co*-vinyl hydrocinnamate (EVHCIN{18}) copolymer using hydrocinnamoyl chloride.

Cinnamoyl chloride, hydrocinnamoyl chloride, tetrahydrofuran (THF), methanol, potassium hydroxide, and pyridine were purchased from Aldrich Chemical Co. Vinyl acetate-*co*-vinyl cinnamate (VAVCIN) copolymers containing 4, 10, 17, and 30 mol % VCIN, denoted VAVCIN{4}, VAVCIN{10}, VAVCIN{17}, and VAVCIN{30}, respectively, were prepared from PVA in two steps. Partial hydrolysis of a fraction of the vinyl acetate (VA) groups to vinyl alcohol (VOH) groups was effected by reacting with methanol/KOH, forming a copolymer of vinyl acetate-*co*-vinyl alcohol (VAVOH). All the VOH groups were then subsequently converted to vinyl cinnamate (VCIN) groups by reaction with cinnamoyl chloride, producing the desired VAVCIN copolymer. A similar procedure using the same parent VAVOH copolymers was used to prepare analogous vinyl acetate-*co*-vinyl hydrocinnamate (VAVHCIN) copolymers of the same molar concentration. The interested reader is referred to the theses of Hu[12] and Gamble[13] for experimental details of the transformation of PVA to the various VAVCIN and VAVHCIN copolymers, the determination of copolymer composition by NMR spectroscopy, and infrared characterization.

Polymer samples for infrared analyses were prepared by casting thin films on KBr windows from 1% solution in THF. After most of the solvent had evaporated the sample was placed in a vacuum oven at 70 °C overnight to remove residual solvent. After checking that the sample was sufficiently thin to be within the absorption range where the Beer–Lambert Law is obeyed, the KBr window containing the film was mounted in a metal infrared sample holder. In a typical photo-cross-linking reaction the sample was exposed 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 being in the range of 5–10 mW/cm^2).[9–11] In experiments where essentially fully cross-linked samples were produced the distance of the sample from lamp was shortened to 5 cm. The samples were irradiated in air at ambient temperature for specific time periods and then transferred to the infrared spectrometer for analysis. Infrared spectroscopic measurements were recorded on Digilab model FTS-45 FTIR spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans was signal averaged. Thermal analysis was conducted on a Seiko differential scanning calorimeter (DSC). A heating rate of 20 °C/min was used in all T_g measurement, and T_g was recorded at a midpoint of heat capacity change.

Results and Discussion

Ethylene-*co*-Vinyl Cinnamate (EVCIN). We commence by showing in Figure 1 the region of the infrared spectrum of EVCIN{18} from 1600 to 1800 cm^{-1} where we observe the C=O and C=C stretching modes [denoted $\upsilon_F^{C=O(U)}$ and $\upsilon^{C=C}$, respectively, where U refers to an unsaturated ester (i.e., –O–C(O)–C=C–) and F refers to a "free" carbonyl group (i.e., non-hydrogen-bonded)]. As EVCIN{18} is exposed to UV radiation, the intensity of the $\upsilon^{C=C}$ band at 1638 cm^{-1} and the $\upsilon_F^{C=O(U)}$ band at 1710 cm^{-1} decrease. Concurrently, a new band appears at 1737 cm^{-1} and increases in intensity as a function of UV exposure. This band is attributed to the C=O stretching mode of the saturated ester formed

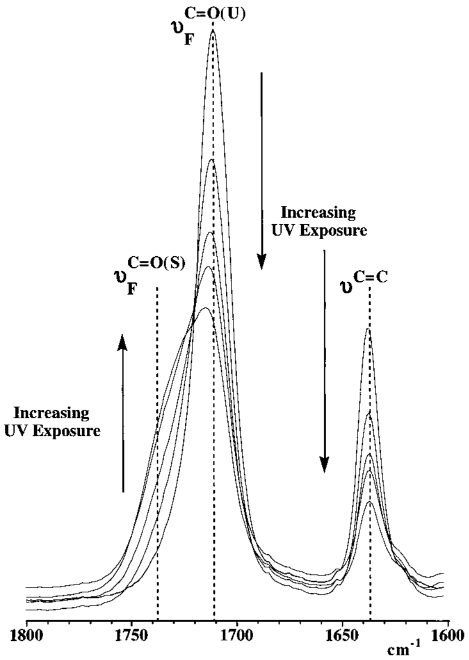


Figure 1. Infrared spectra of EVCIN{18} recorded as a function of increasing UV exposure at room temperature in the carbonyl stretching region (1600–1800 cm^{-1}).

(Scheme 1) during photo-cross-linking [denoted $\upsilon_F^{C=O(S)}$, where S a saturated ester (i.e., $-O-C(O)-C-C-$)]. We intimated in the Introduction that we thought that if we started with a miscible EVCIN–DMBVPh blend and then fully photo-cross-linked the EVCIN copolymer, the fraction of hydrogen-bonded carbonyl groups in the resultant semiinterpenetrating network should be easier to determine using infrared spectroscopy. This is because only the $\upsilon_F^{C=O(S)}$ band and its hydrogen-bonded counterpart, $\upsilon_{HB}^{C=O(S)}$ (where the subscript HB refers to hydrogen bonded), would be present.[10,11]

We therefore performed a series of experiments designed to fully cross-link EVCIN{18} samples by varying the intensity of the UV radiation and time of exposure. Figure 2 (bottom) shows the infrared spectrum of pure EVCIN{18}, while that at the top illustrates the changes that typically occur after prolonged exposure to UV radiation. Note that there is no significant absorption at 1638 cm^{-1} ($\upsilon^{C=C}$), which implies that we have successfully photoreacted all (or, at least, essentially all) of the VCIN groups. However, this is counterbalanced by a large increase in the breadth of the $\upsilon_F^{C=O(S)}$ saturated ester band, which unfortunately negates any perceived advantage we thought we might have by fully cross-linking. We have discussed the causes of broadening in acetoxy-type carbonyl stretching modes elsewhere.[14] Germane to this work is the fact that in ethylene-*co*-vinyl acetate (EVA) copolymers the breadth of the carbonyl band decreases (and changes shape) with increasing ethylene content, as the VA groups are spaced further apart. In any event, the unsaturated C=O band of pure EVCIN{18}, which has an inherently relatively narrow carbonyl stretching mode, transforms into a very broad saturated C=O band upon cross-linking. Some of this band broadening is presumably due to transition dipole coupling[14] caused by the close proximity of the two saturated ester carbonyl groups that occurs when forming the four-membered ring structure (cross-link) (see Scheme 1).

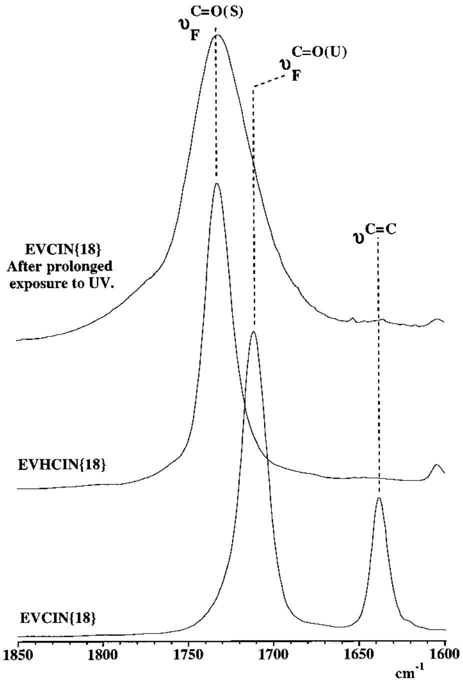
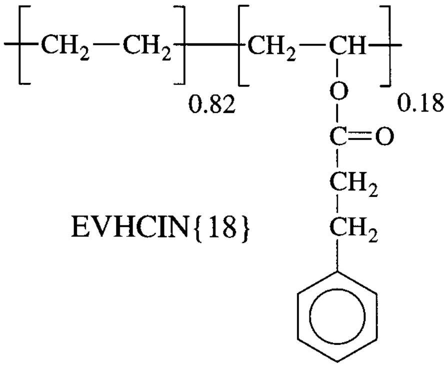


Figure 2. Infrared spectra recorded at room temperature in the carbonyl stretching region (1600–1800 cm^{-1}) of EVCIN{18} (bottom) and EVHCIN{18} (middle) before UV exposure. The top spectrum is that of EVCIN{18} after prolonged UV exposure.

However, it should also be recognized that the structure illustrated in Scheme 1 is simplistic. Egerton et al. have demonstrated that in photoreacted PVCIN at least four possible cyclic stereoisomers are present out of the 11 that can theoretically be formed when two cinnamoyl groups react and that some linear chainlike (possibly from free radical) addition also occurs.[15] A distribution of different structures with saturated ester carbonyl groups having slightly different frequencies will tend to broaden out the composite carbonyl band observed in fully cross-linked EVCIN{18}.

To complete this preliminary study, we synthesized (from the identical EVOH parent used to prepare EVCIN{18}) an ethylene-*co*-vinyl hydrocinnamate copolymer containing 18 mol % vinyl hydrocinnamate (denoted EVHCIN{18}).



EVHCIN{18}

EVHCIN{18} is a fine model for a non-cross-linkable version of EVCIN{18}. The infrared spectrum of the EVHCIN{18} copolymer is shown in the middle of Figure 2. Note that the saturated ester carbonyl band, $\upsilon_F^{C=O(S)}$, is very similar in breadth and shape to that of the unsaturated ester carbonyl band, $\upsilon_F^{C=O(U)}$, of pure

EVCIN{18} (bottom spectrum). This demonstrates that the massive broadening of the carbonyl band after UV exposure is a consequence of the photoreaction.

Vinyl Acetate-*co*-Vinyl Cinnamate (VAVCIN) Copolymers. While we were discovering that the EVCIN copolymers would not be ideal candidates for our studies of functional group accessibility and the effect of cross-linking on hydrogen-bonded polymer blends, we had initiated some VCIN substitution studies of ethylene-*co*-vinyl acetate (EVA) copolymers. By taking a parent EVA copolymer and hydrolyzing a fraction of the vinyl acetate (VA) to vinyl alcohol (VOH) groups, we prepared a series of ethylene-*co*-vinyl acetate-*co*-vinyl alcohol (EVAVOH) terpolymers. Subsequent reaction with cinnamoyl chloride produced the analogous ethylene-*co*-vinyl acetate-*co*-vinyl cinnamate terpolymers (EVAVCIN). We will not dwell on the infrared characterization and experimental cross-linking studies that were performed on these EVAVCIN copolymers and their miscible blends with specific DMBVPh copolymers, but the interested reader can obtain further details from the thesis of Gamble.[13] For our purposes here, the EVAVCIN copolymer studies pointed the way to a possible solution of the problem of band broadening of the carbonyl stretching mode, $\upsilon_F^{C=O(S)}$, that we observed when we attempted to fully cross-link the EVCIN copolymers.

For reasons we will make apparent it was concluded that we should be focusing our attention on vinyl acetate-*co*-vinyl cinnamate (VAVCIN) copolymers and their blends with DMBVPh copolymers. VAVCIN copolymers can be readily produced from a parent poly(vinyl acetate) (PVA) by hydrolyzing a fraction of the vinyl acetate (VA) to vinyl alcohol (VOH) groups and then reacting with cinnamoyl chloride. It might seem, at first glance, that compared to EVCIN copolymers, the presence of the additional carbonyl groups resulting from the incorporation of VA units into the polymer chain must complicate the interpretation of the carbonyl stretching region of the infrared spectrum of VAVCIN copolymers and their blends. However, this is not so. In comparison to EVA and EVCIN, the carbonyl stretching band of PVA is inherently relatively broad ($w_{1/2} \approx$ 23 cm^{-1})—a direct consequence of the higher concentration of dipolar interactions per unit volume.[14] Fortunately, we can use this band broadening phenomenon to our advantage. Figure 3 shows room temperature infrared spectra in the region from 1550 to 1850 cm^{-1} of PVA and three VA copolymers containing 4, 10, and 30 mol % VCIN, denoted VAVCIN{4}, VAVCIN{10}, and VAVCIN{30}, respectively. The band denoted $\upsilon_F^{C=O(VA)}$ at 1737 cm^{-1} is assigned to the carbonyl stretching vibration of the VA segment. Note that the $\upsilon_F^{C=O(U)}$ and $\upsilon^{C=C}$ modes of the VCIN segments are plainly observed at 1712 and 1637 cm^{-1}, respectively.

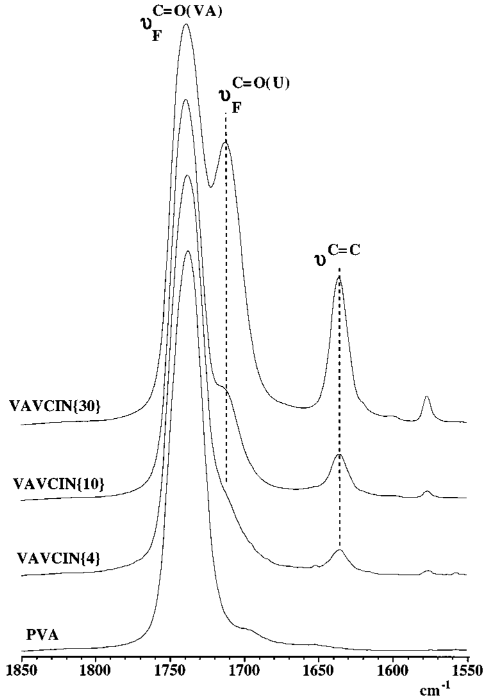
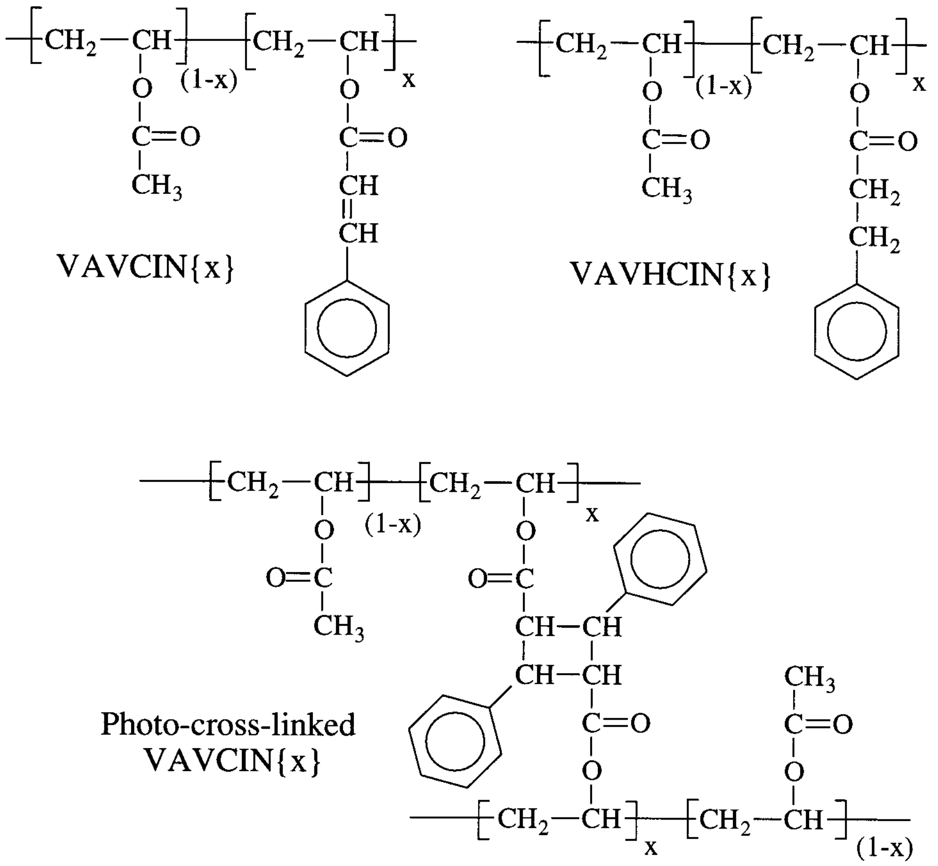


Figure 3. Infrared spectra of PVA, VAVCIN{4}, VAVCIN{10}, and VAVCIN{30} recorded at room temperature in the carbonyl stretching region (1600−1800 cm^{-1}).

We will eventually wish to compare blends of VAVCIN{*x*} copolymers, before and after photo-cross-linking, and for this purpose we will also need to obtain the infrared spectra of the hydrogenated non-cross-linked analogue, VAVHCIN{*x*}, of the fully cross-linked VAVCIN{*x*} (see Scheme 3). Figure 4 compares the room temperature infrared spectra in the region from 1550 to 1850 cm^{-1} of PVA, the VA copolymer containing 10 mol % VCIN (denoted VAVCIN{10}), poly(vinyl hydrocinnamate) (PVHCIN), and the analogous VA copolymer containing 10 mol % VHCIN (VAVHCIN{10}). Note that the frequencies at maximum absorbance of the carbonyl bands of PVA and PVHCIN occur within 2 cm^{-1} of one another. A single carbonyl band is observed in the spectrum of the VAVHCIN{10} copolymer, which is composed of overlapping major and minor components, i.e., $\upsilon_F^{C=O(VA)}$ and $\upsilon_F^{C=O(VHCIN)}$ (the carbonyl stretching mode of the vinyl hydrocinnamate group). In fact, if the spectra of PVA and VAVHCIN{10} copolymer are superimposed upon one another, they appear essentially identical. Finally, for completeness, the spectrum of VAVCIN{10}, with its characteristic $\upsilon_F^{C=O(VA)}$, $\upsilon_F^{C=O(U)}$, and $\upsilon^{C=C}$ modes, is shown at the top of Figure 4. Here again the $\upsilon_F^{C=O(VA)}$ band has the same frequency, broadness, and band shape as that observed in PVA and the VAVHCIN{10} copolymer. Now let us see what happens when we photo-cross-link VAVCIN{10}.

Figure 5 shows the room temperature infrared spectra in the region from 1600 to 1800 cm^{-1} of PVA, VAVHCIN{10}, and an essentially fully photoreacted VAVCIN{10} copolymer. What is important here is that the carbonyl band of the photoreacted VAVCIN{10} copolymer has not broadened significantly relative to the carbonyl bands of PVA or VAVHCIN{10}. This is in marked contrast to the results obtained with the analogous EVCIN copolymers. Close examination of the spectrum of the UV-exposed VAVCIN{10} copolymer reveals that the photoreaction was not totally complete, and we should point out that a barely perceptible $\upsilon^{C=C}$ absorption is detected, along with a small $\upsilon_F^{C=O(U)}$ absorption, on the low-frequency wing of the composite saturated carbonyl band that is composed of $\upsilon_F^{C=O(VA)}$ (major) and $\upsilon_F^{C=O(S)}$ (minor). However, we believe this will not be a source of major error in our forthcoming quantitative analyses of the fraction of hydrogen-bonded carbonyl groups in blends with DMBVPh copolymers. Finally, in the case of the spectrum of VAVHCIN{10} the carbonyl band contains contributions from both $\upsilon_F^{C=O(VA)}$ (major) and $\upsilon_F^{C=O(VHCIN)}$ (minor).

Scheme 3



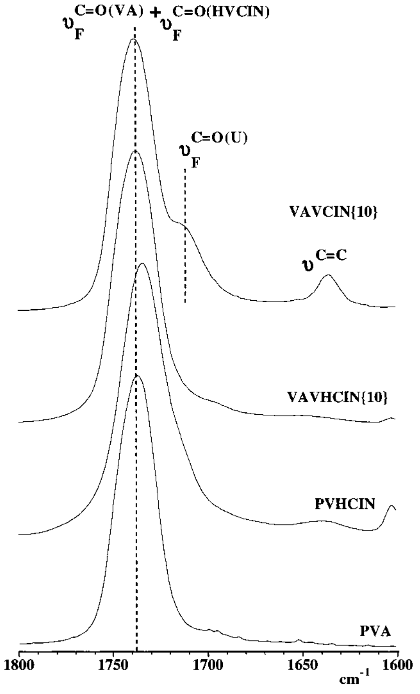


Figure 4. Comparison of the infrared spectra of PVA, PVHCIN, VAVHCIN{10}, and VAVCIN{10} recorded at room temperature in the carbonyl stretching region (1600−1800 cm^{-1}).

VAVCIN{10}−DMBVPh{33} Blends. The above results are encouraging as they indicate that we should be able to initially prepare miscible (single phase) blends of VAVCIN copolymers with DMBVPh copolymers and then essentially fully cross-link the VAVCIN copolymer without significant band broadening of the carbonyl stretching modes. Quantitative analysis of the fraction of hydrogen-bonded carbonyl groups before and after photo-cross-linking can then be used to address such questions as, can we form miscible (single phase) semiinterpenetrating networks, is functional group accessibility a factor in determining the maximum number of intermolecular hydrogen bonds formed, if this is so, how does this affect the hydrogen-bonding contribution to the free energy, and finally, how does the distance between cross-links (or mesh size) affect phase behavior? But before we get to these questions we need to select appropriate miscible VAVCIN blends.

We recently described modifications to our original computer program (referred to as “Phase Calculator”) that was written by Dr. J. Graf and was included with our 1991 monograph.[5] Using equilibrium constants obtained from appropriate low molar mass mixtures, it was shown that the hydrogen-bonding contribution to the free energy of mixing of analogous polymer blends could be determined after due accounting for factors attributed to chain connectivity.[6−8] The equations used to calculate the overall free energy of mixing for hydrogen-bonded polymer blends, taking into account these factors, have been described in detail in ref 7. To predict miscibility maps for DMBVPh blends, we further require the molar volume and solubility parameter of the average repeating unit that contains one VPh moiety. This is calculated automatically in the computer program using group contributions.[5] Armed with these values, together with the value for the intermolecular screening parameter, $\gamma = 0.3$,[6,16] and the appropriate molar volume and solubility parameter values for PVA

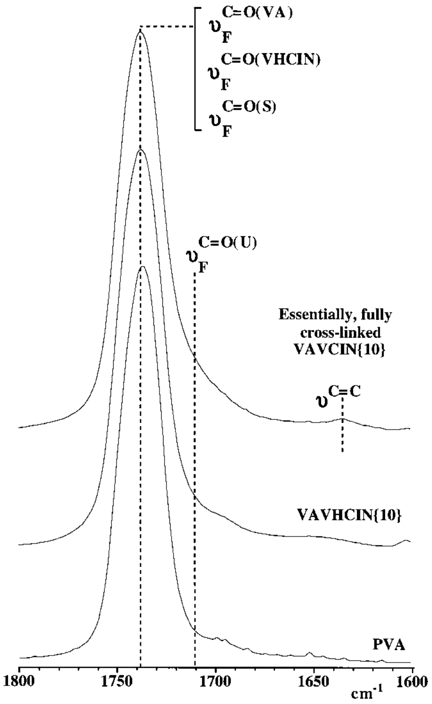


Figure 5. Comparison of the infrared spectra of PVA, VAVHCIN{10}, and an essentially fully cross-linked VAVCIN{10} recorded at room temperature in the carbonyl stretching region (1600−1800 cm^{-1}).

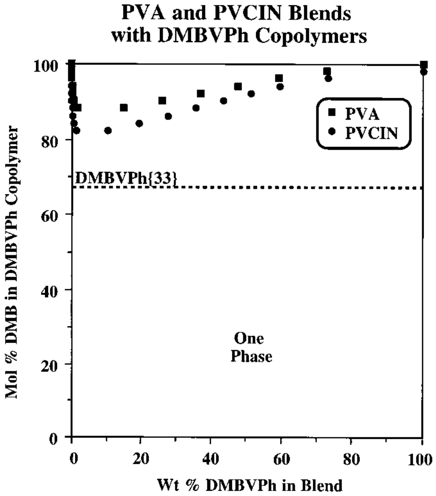


Figure 6. Theoretically predicted miscibility window for DMBVPh{*x*} copolymer blends with PVA and PVCIN at 25 °C.

and PVCIN,[5] we are confident that we can make a sound prediction of the miscibility maps for DMBVPh blends.

Figure 6 shows the result of such a theoretical calculation. The miscibility map at 25 °C for PVA and PVCIN blends with the series of DMBVPh copolymers was calculated at intervals of 2 mol % VPh ranging from pure PVPh to pure poly(dimethylbutadiene) (PDMB). Miscible systems (i.e., those that are single phase across the entire range of blend compositions) are predicted for blends PVA with DMBVPh copolymers containing from 0 to 88 mol % DMB. For PVCIN blends the miscibility window is a little narrower ranging from 0 to 81 mol % DMB (primarily due to the fact that the molar volume of the VCIN segment is somewhat larger than the VA segment, resulting in a small "dilution" effect). However, the most important conclusion for our purposes here is that miscible blend systems of VAVCIN copolymers of any composition are predicted with DMBVPh copolymers containing greater than ≈20 mol % VPh. This is because substituting a VCIN segment for a VA segment in the polymer chain does not significantly reduce the number of ester carbonyl groups per unit volume. Any specific VAVCIN copolymer will have a miscibility gap with DMBVPh copolymers that falls between the limits set by PVA and PVCIN. We chose for our blend studies a DMBVPh copolymer containing 33 mol % VPh (denoted DMBVPh{33}). This represents a compromise. We required a VPh concentration that is high enough to ensure that we are well within the predicted range of miscibility with VAVCIN copolymers (see dotted line in Figure 6). At the same time the VPh concentration should not be too high, because the T_g of the DMBVPh copolymer increases into a temperature range where we potentially may have serious problems (achieving equilibrium conditions, the $\Delta\chi$ effect, thermal and oxidative degradation, etc.) The T_g of DMBVPh{33} is 94 °C, and miscible blends with VAVCIN copolymers fall in a convenient range below this temperature (see later).

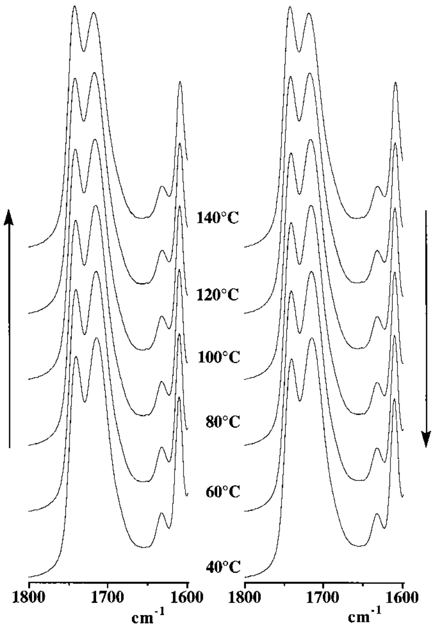


Figure 7. Infrared spectra of an 80:20 wt % blend of DMBVPh{33} and VAVCIN{10} recorded in the carbonyl stretching region (1600−1800 cm^{-1}) at 20 deg intervals in the range of 40−140 °C as the sample is heated and cooled.

Figure 7 shows the infrared spectra in the range from 1600 to 1800 cm^{-1} of an 80:20 DMBVPh{33}:VAVCIN{10} blend recorded at 20 deg intervals as a function of temperature from 40 to 140 °C. On the left are spectra recorded as the sample was heated, and on the right are the corresponding spectra recorded upon cooling. Two obvious, well-resolved, carbonyl bands are observed at ≈1740 and 1715 cm^{-1}. The former is attributed to "free" (non-hydrogen-bonded) VA carbonyl groups, $\upsilon_{\mathrm{F}}^{\mathrm{C=O(VA)}}$. The latter has two components, one major and one minor. The major contribution to the band at 1715 cm^{-1} is associated with hydrogen-bonded VA carbonyl groups, $\upsilon_{\mathrm{HB}}^{\mathrm{C=O(VA)}}$, while the minor component is due to "free" VCIN unsaturated ester carbonyl groups, $\upsilon_{\mathrm{F}}^{\mathrm{C=O(U)}}$. Finally, the hydrogen-bonded VCIN unsaturated ester carbonyl groups, $\upsilon_{\mathrm{HB}}^{\mathrm{C=O(U)}}$, is present at 1690 cm^{-1} (see Scheme 2) as a shoulder on the low-

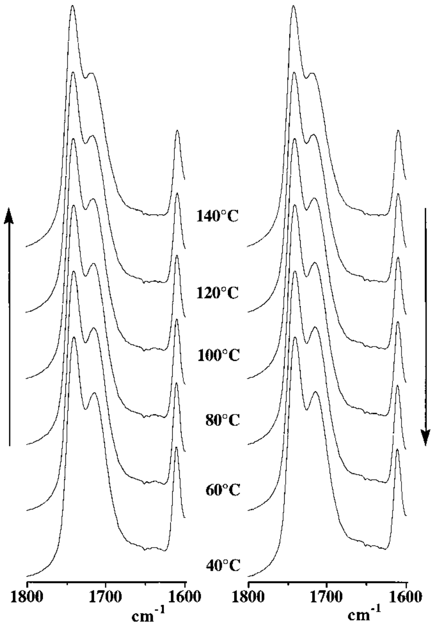


Figure 8. Infrared spectra of an 80:20 wt % blend of DMBVPh{33} and essentially fully cross-linked VAVCIN{10} recorded in the carbonyl stretching region (1600−1800 cm^{-1}) at 20 deg intervals in the range of 40−140 °C as the sample is heated and cooled.

frequency side of the main hydrogen-bonded band. For completeness, note that the VCIN C=C stretching mode, $\upsilon^{\mathrm{C=C}}$, is clearly identified at 1635 cm^{-1} together with the band at 1613 cm^{-1} which is assigned to a ring stretching mode of the VPh group. As the temperature is increased, we see the familiar increase of the "free" band relative to that of the hydrogen-bonded band (but remember this is complicated by the fact that the $\upsilon_{\mathrm{F}}^{\mathrm{C=O(U)}}$ band overlaps the more intense $\upsilon_{\mathrm{HB}}^{\mathrm{C=O(VA)}}$ band). The intensity of the major $\upsilon_{\mathrm{HB}}^{\mathrm{C=O(VA)}}$ band relative to these other modes indicates that the blend is highly mixed at the molecular level and is probably a single phase. However, simple inspection of a significant degree of hydrogen bonding is not proof that we have a single phase. Finally, an important observation, and the reason we show the heating and cooling cycles, is that after heating and subsequent cooling to 40 °C the spectra are essentially identical. This is good evidence that we are working effectively under equilibrium conditions.

Figure 8 shows similar spectra to those just described above (Figure 7), but after the 80:20 DMBVPh{33}: VAVCIN{10} blend had been exposed to UV radiation and the VAVCIN copolymer had been effectively fully photoreacted. Indeed, there is no significant absorbance at 1635 cm^{-1}, which is consistent with essentially complete reaction of the −C=C− groups of the VCIN segments. Compared to Figure 7, the most striking difference in the spectra shown in Figure 8 is the apparent decrease in the ratio of the relative intensities of the hydrogen-bonded to "free" bands. But before we interpret this as a simple decrease in the fraction of hydrogen-bonded carbonyl groups, we must remember that the hydrogen-bonded band in Figure 7 was made up of two components, $\upsilon_{\mathrm{HB}}^{\mathrm{C=O(VA)}}$ and $\upsilon_{\mathrm{F}}^{\mathrm{C=O(U)}}$. Now things change. In the fully photoreacted DMBVPh{33}: VAVCIN{10} blend the "free" band at ≈1735 cm^{-1} is actually a composite of two bands associated with "free" VA carbonyl groups, $\upsilon_{\mathrm{F}}^{\mathrm{C=O(VA)}}$, and "free" saturated VCIN ester groups, $\upsilon_{\mathrm{F}}^{\mathrm{C=O(S)}}$. The hydrogen-bonded band at ≈1711 cm^{-1} is also composed of two bands attributed to hydrogen-bonded carbonyl groups, associated with the VA carbonyl groups, $\upsilon_{\mathrm{HB}}^{\mathrm{C=O(VA)}}$, and the saturated VCIN ester carbonyl groups, $\upsilon_{\mathrm{HB}}^{\mathrm{C=O(S)}}$. The changes observed upon temperature cycling again indicates that we are working under equilibrium conditions.

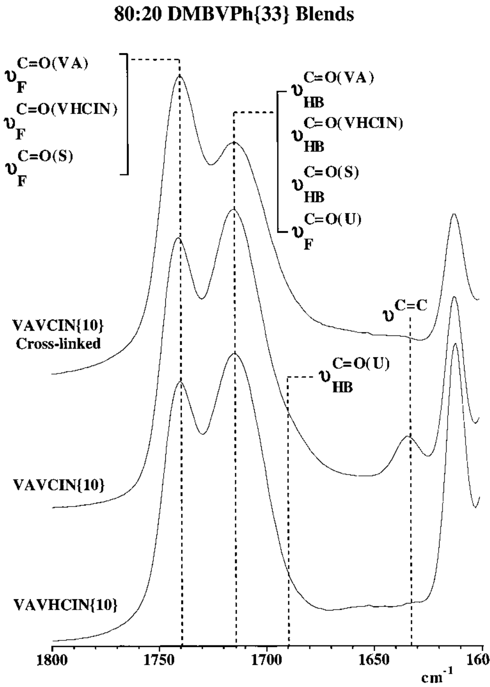


Figure 9. Infrared spectra of an 80:20 wt % blends of DMBVPh{33} with VAVHCIN{10} (bottom), VAVCIN{10} (middle), and the fully cross-linked VAVCIN{10} sample (top) recorded in the carbonyl stretching region (1600−1800 cm^{-1}) at room temperature.

In Figure 9 we compare the room temperature infrared spectra of the 80:20 DMBVPh{33} blends of VAVCIN{10}, the hydrogenated analogue, VAVHCIN{10}, and the fully cross-linked VAVCIN{10} copolymer. For now we ask the reader to accept that DSC analysis of the DMBVPh{33} blends with VAVCIN{10} and VAVHCIN{10} indicates that they are single phase (more on this later). Although we have stressed that the infrared spectra of the two blends cannot be directly compared, the total fraction of hydrogen-bonded carbonyl groups appears by simple inspection to be about the same. However, it is the comparison of the fraction of hydrogen-bonded carbonyl groups in the 80:20 DMBVPh{33} blends of the fully cross-linked VAVCIN{10} and VAVHCIN{10} copolymers that is most important. Here we can, in effect, compare the cross-linked copolymer blend (or semiinterpenetrating network) with an un-cross-linked copolymer blend counterpart that is closely analogous (see Scheme 3). Given that we are dealing with a constant concentration of carbonyl groups in the two blends and assuming that there is no phase separation upon cross-linking (which we will verify later), then the fraction of hydrogen bonds should be identical within the bounds of experimental error, providing that there are no functional group accessibility problems. This is obviously not the case.

Using established methodology,[5,6] we can curve resolve the spectra of the 80:20 wt % DMBVPh{33} blends of the fully cross-linked VAVCIN{10} and VAVHCIN{10} copolymers as shown in Figure 9. Taking into

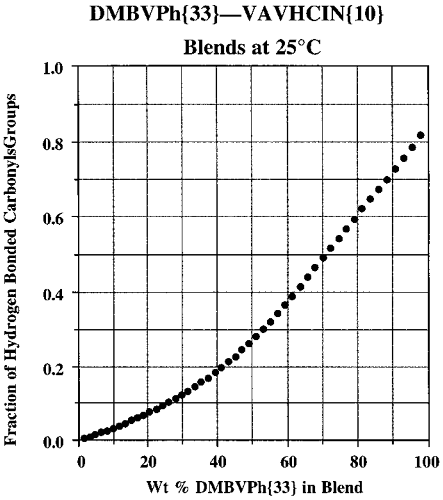


Figure 10. Theoretical plot of the fraction of hydrogen-bonded carbonyl groups present in a miscible blend of DMBVPh{33} with VAVHCIN{10} at 25 °C as a function of blend composition.

account the differences in absorptivity of the "free" and hydrogen-bonded bands ($a_R = 1.5$),[5,6] we obtain values of 0.55 and 0.62 for the fraction of hydrogen-bonded carbonyl groups, respectively. Employing the appropriate values of the molar volumes and standard self-association and interassociation equilibrium constants, we can readily calculate the fraction of hydrogen-bonded carbonyl groups in a single-phase system as a function of blend composition using the modified Phase Calculator program mentioned above.[5−8] Figure 10 shows the results of such a calculation at 25 °C for the DMBVPh{33}−VAVHCIN{10} blend system. For an 80:20 wt % blend approximately 62% of the carbonyl groups are predicted to be hydrogen bonded if the system is single phase. This is precisely what we determine experimentally. We should obtain the same value for the 80:20 wt % blend of DMBVPh{33} with the fully cross-linked VAVCIN{10} system, but we only experimentally determine that 55% of the carbonyl groups are hydrogen bonded. This implies that about 11% of the carbonyl groups become inaccessible in the semiinterpenetrating network. This is an interesting result, as the apparent number of inaccessible carbonyl groups corresponds closely to the concentration of VCIN carbonyl groups segments that are now largely in cross-linked moieties. However, before we get carried away, the question arises, did phase separation cause the reduction of the fraction of hydrogen-bonded carbonyl groups? Or put another way, is the semiinterpenetrating network miscible? This brings us to our thermal characterization studies.

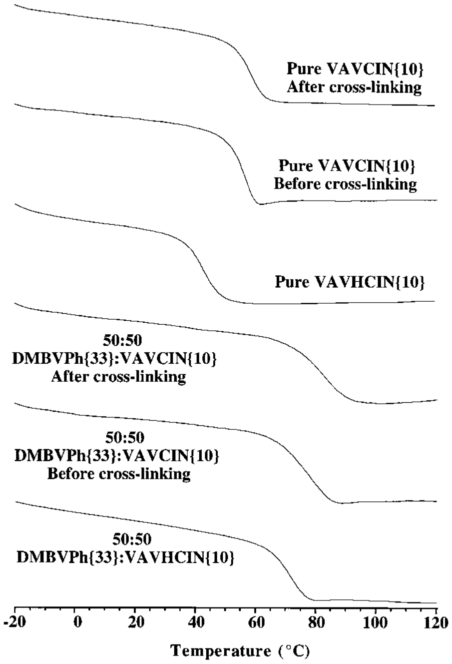


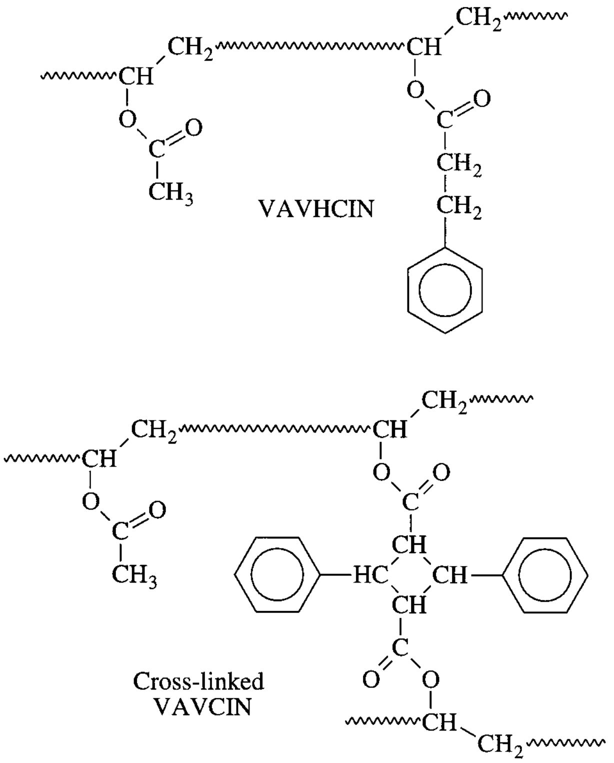
Figure 11. DSC thermograms of pure samples of VAVHCIN{10} and VAVCIN{10} before and after cross-linking (top) and corresponding 50:50 wt % blends with DMBVPh{33} (bottom).

Figure 11 shows a series of DSC thermograms for pure VAVHCIN{10} and VAVCIN{10} before and after cross-linking. The T_g's were determined to be respectively 43, 56, and 61 °C. As expected, the VAVHCIN{10} and VAVCIN{10} random copolymers, which are composed primarily of VA segments, have T_g's that are somewhat elevated from that of pure PVA. Presumably VAVCIN{10}, which contains the −C═C− moiety in the VCIN side group, has a slightly stiffer chain and thus has a T_g slightly higher than VAVHCIN{10}. Upon cross-linking VAVCIN{10}, the T_g increases to 61 °C, as would be expected.[17] However, since we are eliminating the −C═C− double bonds in the photoreaction, it is more appropriate to compare the T_g's of VAVHCIN{10} and the cross-linked VAVCIN{10} materials (ΔT_g = 18 °C), if we are interested in the effect of cross-linking upon T_g. The bottom three thermograms of Figure 11 were obtained from 50:50 wt % DMBVPh{33} blends. Pure DMBVPh{33} has a T_g of 94 °C. All three blends exhibit single T_g's that are intermediate between those of the pure materials. This is good evidence that they are all single phase (at least at the size scale measured by DSC). Again, there is the anticipated marked shift to higher temperature ($T_g \approx$ 88 °C) for the semiinterpenetrating network (the DMBVPh{33} blend with the cross-linked VAVCIN{10}) compared to that of the analogous blend with VAVHCIN{10} ($T_g \approx$ 72 °C).

In summary to this point, the DMBVPh{33}−VAVHCIN{10} blend system was determined to be miscible—the blends are transparent, exhibit a single T_g, and have a fraction of hydrogen-bonded carbonyl groups consistent with a single phase. The fully cross-linked DMBVPh{33}−VAVCIN{10} semiinterpenetrating system was also found to be transparent and have a single T_g consistent with a single phase. However, the infrared analysis of the fraction of hydrogen-bonded carbonyl groups was not consistent with a single phase, *in the absence of additional screening or problems with functional group accessibility.* Would we expect such problems? Consider the schematic diagram shown in Scheme 4.

From simple inspection, it is not hard to imagine that the carbonyl groups associated with the rigid cross-linked VCIN segments are not as accessible as those associated with the VA or VHCIN segments. The carbonyl groups in the cross-link moiety cannot freely rotate and are screened by the close proximity of the phenyl rings and main chain. In fact, they may be essentially inaccessible, as inferred by the infrared spectroscopic data. This would reduce the fraction of hydrogen-bonded carbonyl groups formed and, in turn, reduce the hydrogen bonding or "chemical" contribution to the free energy of mixing.[5−8] However, this favorable,

Scheme 4



albeit reduced, free energy contribution is evidently still enough to overwhelm unfavorable contributions due to "physical" forces (solubility parameter differences), free volume, etc., resulting in a single-phase semiinterpenetrating network.

DMBVPh{33} Blends with VAVCIN{4} and VAVCIN{17}. If the above conclusion is correct, that carbonyl groups present in the cross-linked structures formed after photoreaction of the VCIN groups are essentially inaccessible to the phenolic hydroxyl groups in the semiinterpenetrating VAVCIN{10}−DMBVPh{33} network, it follows that the fraction of hydrogen-bonded carbonyl groups should change systematically if the concentration of VCIN in the VAVCIN copolymer is varied. And indeed this is so. Using the same methodology described above for the 80:20 wt % DMBVPh{33} blends of the fully cross-linked VAVCIN{10} and VAVHCIN{10} copolymers, we determined the fraction of hydrogen-bonded carbonyl groups from spectra of analogous 80:20 wt % DMBVPh{33} blends of the essentially fully cross-linked VAVCIN{4} and VAVCIN{17} copolymers ($f_{HB}^{C=O}$ = 0.58 and 0.52, respectively). The results were compared to those obtained from 80:20 wt % DMBVPh{33} blends of the VAVHCIN{4} and VAVHCIN{17} copolymers ($f_{HB}^{C=O}$ = 0.60 and 0.63, respectively). This implies that 3 and 17%, respectively, of the carbonyl groups in the semiinterpenetrating networks are sterically shielded or inaccessible to phenolic hydroxyl groups. Within the error of measurement, this correlates with the original concentration of VCIN in the VAVCIN copolymer. Moreover, thermal analysis indicated that the two semiinterpenetrating networks had single T_g's, strongly suggesting that there was no phase separation. The interested reader is referred to the thesis of Hu for details of the infrared spectra, curve resolving, and DSC thermograms.[12]

EVCIN{18} Blends Revisited. The conclusion that the saturated VCIN carbonyl groups are essentially inaccessible in cross-linked structures formed after photoreaction is an important factor when considering the effect of cross-linking on the phase behavior of hydrogen-bonded polymer blends. To reiterate, the above initially miscible DMBVPh{33}/VAVCIN{x} blends remain miscible after fully cross-linking the VAVCIN{x} copolymer, because there is a sufficient favorable free energy of mixing contribution gained from the formation of hydrogen bonds between the phenolic hydroxyl and VA acetoxy carbonyl groups to offset any unfavorable free energy contributions, primarily from "physical" forces. In contrast, consider the case of an initially miscible DMBVPh/EVCIN blend. If after fully cross-linking the EVCIN copolymer most of the carbonyl groups are now inaccessible to the DMBVPh phenolic groups, the blend may well phase separate because there is now no significant free energy of mixing contribution from hydrogen bonding. This can be qualitatively tested by studying specific EVCIN blends. We deliberately chose a blend of DMBVPh{18} with EVCIN{18} because the solubility parameters of the average repeats of these copolymers are quite close [δ = 8.5 and 9.0 (cal cm^{-3})$^{0.5}$], which infers that only a moderate free energy contribution from the hydrogen bonding of phenolic hydroxyl to VCIN ester carbonyl groups is necessary to overwhelm the unfavorable "physical" contributions.

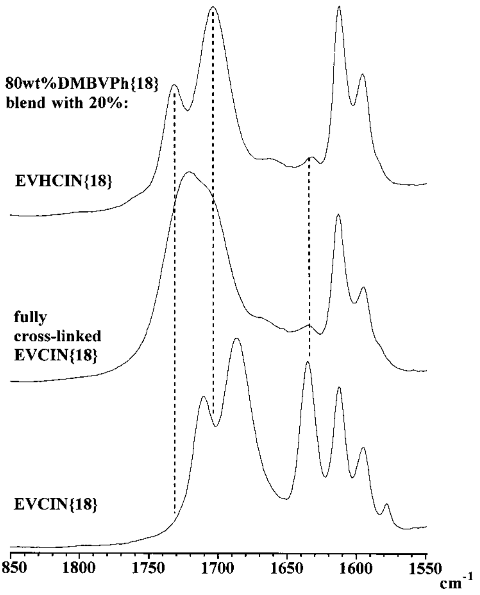


Figure 12. Infrared spectra of an 80:20 wt % blends of DMBVPh{18} with EVCIN{18} (bottom), the fully cross-linked EVCIN{18} sample (middle), and EVHCIN{18} (top), recorded at room temperature in the region from 1550 to 1850 cm^{-1}.

Figure 12 shows the infrared spectra of 80:20 wt % blends of DMBVPh{18} with EVCIN{18} (bottom) and EVHCIN{18} (top) in the range from 1550 to 1850 cm^{-1}. Note that the hydrogen-bonded carbonyl bands in both cases (respectively at 1686 and 1703 cm^{-1}) dominate over their non-hydrogen-bonded counterparts (respectively at 1712 and 1733 cm^{-1}). Using standard curve-fitting methods, the fraction of hydrogen-bonded groups, $f_{HB}^{C=O}$, was determined to be 0.63 ± 0.02, and this corresponds well to that calculated for single-phase materials using the modified Phase Calculator program described above. The blend films are transparent, and thermal analysis of the blends reveals a single T_g consistent with miscible blend systems. The middle

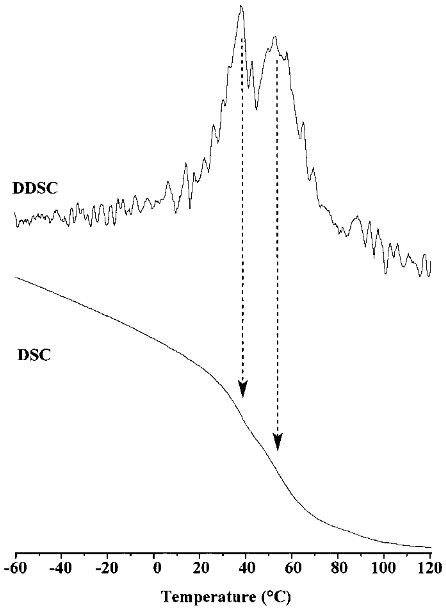


Figure 13. DSC thermogram (bottom) and its derivative (top) recorded from an essentially fully UV photo-cross-linked sample of a 80:20 DMBVPh{18} blend with EVCIN{18}.

spectrum of Figure 12 is that of the DMBVPh{18} blend with EVCIN{18} after essentially complete UV cross-linking. Note that the C═C band at 1635 cm^{-1} is barely detectable and that the spectral envelope between 1550 and 1650 cm^{-1} is now very similar to that observed in the EVHCIN{18} blend spectrum (top). In marked contrast, however, the carbonyl band envelope between 1680 and 1750 cm^{-1} is very different. Now the “free” carbonyl band dominates, and the hydrogen-bonded carbonyl band appears as a shoulder. Band broadening, discussed at the beginning of this work, complicates the measurement of the fraction of hydrogen-bonded groups, $f_{HB}^{C=O}$. However, we can unambiguously state that the relative intensity of the hydrogen-bonded band is far less than would be expected for a single-phase blend, assuming all the carbonyl groups were accessible.

Turning to results of thermal analysis, single T_g’s at 39, −5, and 28 °C are observed for pure DMBVPh{18}, EVCIN{18}, and an 80:20 blend of these copolymers. The latter is consistent with a miscible blend before cross-linking. After extensive exposure to UV radiation the cross-linked 80:20 wt % DMBVPh{18} blend with EVCIN{18} shows evidence of two T_g’s as illustrated in the DSC data (and first derivative of these data) presented in Figure 13. This would appear to substantiate the above hypothesis that if the carbonyl groups in the cross-linked moieties are shielded from the phenolic hydroxyls, the free energy contribution to the free energy of mixing from hydrogen bonding will be greatly reduced. Thus, the contribution from “chemical” forces may not be sufficient to offset the unfavorable free energy contribution from “physical” forces, and phase separation will occur assuming the appropriate kinetics.

Acknowledgment. The authors gratefully acknowledge the financial support of the National Science Foundation, Polymers Program.

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