Detection of Cross-Link Formation by 2 + 2 Photocycloaddition in Poly(vinyl cinnamate) by ^{13}C Solid-State NMR

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Polymers for nonlinear optics (NLO) must be prepared with a macroscopic orientation of chromophores in order to yield second harmonic generation (SHG) for frequency doubling applications. Oriented materials are usually obtained by poling the material above T_g in the presence of an intense electric field and then quenching the material to prevent randomization of chromophore orientation. In practice, slow motion below T_g leads to loss of SHG properties over time, and this problem has had a pervasive influence on research directions in NLO polymers.

One of the more common strategies to stabilize SHG properties is to cross-link the material prior to removing the poling field. Poly(vinyl cinnamate) (PVCN) is one of the more important polymers used in NLO research. It is frequently used as a host polymer into which suitable dyes are introduced, especially those with limited solubilities in other polymers. During the poling process, the polymer may be irradiated with UV light to yield a material with superior SHG retention and reduced solubility.[1-3] This is frequently assumed to be due to photo-cross-linking reactions between cinnamoyl groups in different chains or alternatively between cinnamoyl groups and NLO dye molecules with suitable structures. The mechanism of this cross-linking is proposed to be 2 + 2 cycloaddition of the olefinic groups to yield four-membered-ring cross-link sites.[4] Although this mechanism is appealing in that it is consistent with well-characterized reactions in solution, experimental evidence for this important reaction in NLO polymers has been lacking and its acceptance has not been universal. We demonstrate here that UV irradiation of pure PVCN films results in a partially insoluble material and that careful comparison of ^{13}C solid-state NMR spectra of irradiated films and nonirradiated controls reveals that irradiation caused a reduction in the olefinic carbon content and an increase in the intensity in a region consistent with the proposed cross-link mechanism.

PVCN was obtained from Aldrich and used without further purification. The polymer films were cast from methylene chloride solutions and air-dried. Nominal thickness of the films was measured by a micrometer and estimated at 20 μm. UV radiation at 254 nm was supplied by a Spectroline XX-15F lamp (Fisher Scientific). Three different films were irradiated for 24, 72, and 144 h. A fourth film was cast as a control and not irradiated. The entire films, typically weighing 200 mg, were removed from the plates and loaded into a 7.5-mm zirconia rotor for magic angle spinning (MAS). T_g for pure PVCN is 357 K; thus, spectra were conveniently obtained at room temperature. ^{13}C solid-state NMR spectra were obtained at 50 MHz on a home-built 4.7 T instrument. Cross polarization[5] experiments (contact time 1.5 ms, pulse delay 10 s) exhibited reasonable quantitation and substantially greater sensitivity than single pulse experiments, as expected for a polymer below T_g. A total of 1200 scans provided excellent signal to noise. Assignment of the ^{13}C MAS spectrum of the PVCN control (Figure 1) was based on solution spectra and on observation of the expected response to interrupted decoupling. Figure 1 reports the assignments and numbering scheme used in this paper. Most significant are the very well-resolved signal due uniquely to the olefinic carbon C_7 and the well-resolved signal from the olefinic carbon C_8.

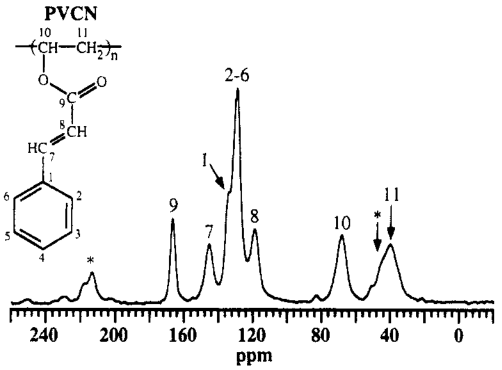

Figure 1. ^{13}C CP/MAS spectrum of the poly(vinyl cinnamate) (PVCN) control film. The assignments and the structure are shown. Asterisks denote spinning sidebands.

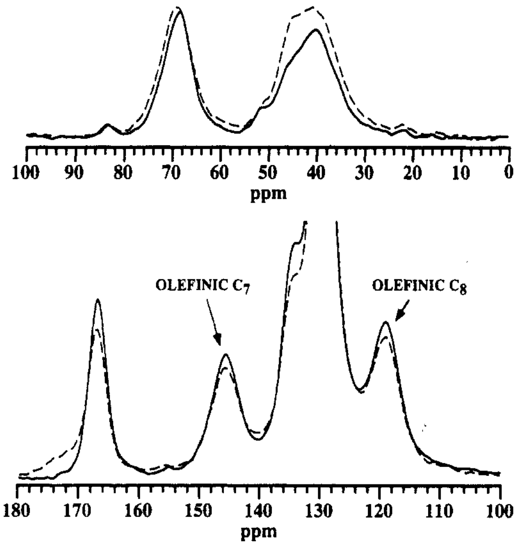

Figure 2. ^{13}C CP/MAS spectra of a UV-irradiated PVCN film (dashed line) and the nonirradiated control (solid line). The effects of photo-cross-linking, including reduction in olefinic carbon signals and formation of additional intensity in the aliphatic region, are apparent.

Figure 2 reports careful comparisons of the control spectrum (solid lines) and the spectrum of the 24-h-irradiated material (dashed lines). Since these spectra were obtained on samples of slightly different mass, they were normalized to have identical intensities for the aromatic signal C_2–C_6, which seemed to be invariant to irradiation. For all of the samples studied, the clearest change upon irradiation was a decrease in the olefinic signals and a corresponding (or slightly greater) increase in the band at 38–48 ppm. Stereochemical considerations indicate that interchain dimerization could produce up to 11 different dimer structures; these can conveniently be divided into products of head-to-tail (1) and head-to-head (2) reactions.[6]

Inspection of Figure 2 shows that the most obvious change upon irradiation is a 15% decrease in the intensities of the olefinic peaks. This intensity was apparently converted into additional signal intensity in the 38–48 ppm region, on top of the resonance for the main chain methylene carbons. We developed a sense of the expected four-membered-ring shifts for structures 1 and 2 by studying reasonable model compounds in spectral data

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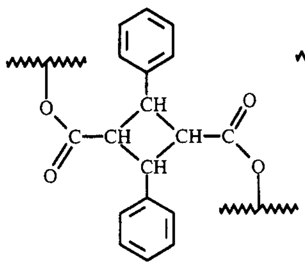

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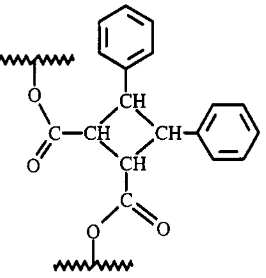

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bases and by using the predictive feature of the SPECINFO database on the STN service, which is called SPECAL. We concluded that the aliphatic carbons formed in the proposed cross-linking reaction should have chemical shifts between 38 and 49 ppm and that the resolution in Figure 2 combined with the complications of stereochemical isomerization would not permit selection between 1 and 2 as the major product. Spectral searching and prediction also indicated that formation of 1 and 2 would be accompanied by a several ppm downfield shift for the carbonyl resonance, and this is very clearly apparent in Figure 2. A smaller predicted change in C_1 can also be inferred from the figure. The only apparent anomaly in Figure 2 is that the increase in the aliphatic signal intensity is slightly larger than the decrease in the olefinic signal intensity, but this observation is easily rationalized if cross-linking the polymer is assumed to improve cross polarization dynamics. Thus, we conclude that the experimental evidence presented here is strongly supportive of the proposed 2 + 2 photo-cross-linking reaction for pure PVCN, but we are unable to determine the detailed stereochemistry of the cross-link site at this time.

Exposing the PVCN films for longer periods of time (72 and 144 h) did not obviously cause any additional cross-linking. The cycloaddition is a rapid reaction that is usually carried out in a few seconds for the very thin films (2 μm or less) typically prepared for SHG studies. The expected penetration depth of the UV radiation into our polymer film was estimated to be 200 nm or less based on the reported molar absorptivity of ethyl cinnamate in solution and the composition and density of the polymer. Thus, one would expect that less than 1% of the cinnamoyl groups would be photo-cross-linked in our thick films, and this must be reconciled with our observation that extended irradiation converted ca. 15% of the chromophores. We propose that as dimerization occurred on the film surface, the resultant bleaching allowed further penetration of the radiation so that a greater effective penetration depth was realized after protracted irradiation.

This study suggests the ability of solid-state NMR to detect and potentially quantify the extent of photo-cross-linking in a PVCN NLO polymer host–guest system. Future NMR studies will be carried out on insoluble fractions concentrated from photo-cross-linked films as well as efforts to observe reactions with suitable dye molecules. We have previously reported NMR experiments characterizing the time scales of chromophore reorientation,[7] and investigating the effects of cross-linking on chromophore dynamics would address a central problem in NLO polymer chemistry.

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References and Notes

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