Castor-Acrylated Monomer ^{1}H- and ^{13}C-Nuclear Magnetic Resonance Spectral Assignments

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ABSTRACT: Castor-acrylated monomer (CAM) NMR spectral assignments were made utilizing one- and two-dimensional NMR techniques. The unique structure of CAM resulted in several novel chemical environments which were observed in the NMR spectra. Previously published vegetable oil and fatty acid ester NMR peak assignments were insufficient for complete identification of NMR peaks. Definitive peak assignments, particularly in the alkyl and alkene regions, are required for evaluation of CAM as a specialty comonomer in the synthesis of latex polymers for use as waterborne-coating binders. The NMR peak assignments for CAM will allow the subsequent evaluation of the copolymerizability of CAM as well as the determination as to whether unsaturation is preserved during latex polymer synthesis. ^{1}H- and ^{13}C-NMR spectra of CAM are provided with supporting evidence for the peak assignments and discussion of their relevance. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1850–1854, 2001

Key words: acrylic specialty monomer; castor oil; emulsion polymerization; low VOC coatings; NMR

INTRODUCTION

Castor-acrylated monomer (CAM) has been proposed as a comonomer for emulsion polymerization to produce latex polymers for waterborne coatings, possessing characteristics of both conventional latexes and oil-modified polyesters.[1] Environmental friendliness and ease of handling and cleanup of conventional latexes are desirable properties for combination with the performance properties derived from vegetable oil polymer modification. Incorporation of vegetable oil-derived monomers in a latex polymer provides unsaturation for ambient autooxidative crosslinking after application to the substrate. Latex polymers are already high molecular weight materials[2]; thus, even low levels of crosslinking should result in enhanced performance properties.

Previous attempts to incorporate vegetable oil-derived monomers in latex polymers were unsuccessful because the monomers were derived primarily from reactive drying oils. Although beneficial for ambient oxidative crosslinking, the highly reactive unsaturation was detrimental to emulsion copolymer synthesis, resulting in decreased conversion with an increased degree of unsaturation.[3] Vegetable oil-based unsaturation results in allylic hydrogens which serve as chain-transfer sites during free-radical polymerization.[4] Utilizing nondrying oils, with less reactive unsaturation, should reduce the level of chain transfer observed during emulsion copolymer synthesis.

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Castor oil is the oil of choice because of its nondrying characteristics and high concentration of hydroxyl functional fatty acid. Hydroxyl functionality serves as a reactive site for acrylation of the fatty acid methyl ester produced via the transesterification of castor oil with methanol.[1] Utilizing a branched acrylic monomer, rather than a linear analog, may also reduce the reactivity of allylic sites during latex polymer synthesis due to steric effects.

CAM incorporation must be evaluated to ascertain CAM applicability as a latex comonomer. In addition to copolymerizability, the retention of vegetable oil-derived unsaturation during free-radical synthesis must be determined in order to examine the efficiency of CAM for autooxidative functionality incorporation into latex polymers. Greater reactivity of the acrylate group as compared to the isolated double bond should allow for almost selective polymerization through the acrylate group, while the oil-derived unsaturation is preserved during the course of emulsion polymerization.

The most common industrial method for determining the latex polymer structure is gas chromatography (GC). CAM is difficult to analyze by GC due to its high molecular weight (366 g/m) and low volatility. An alternate method is NMR spectroscopy, which has the advantage of providing molecular-level information concerning structure and chemical composition.[6,7] In addition, the method is nondestructive, permitting the recovery of the original test material.

CAM incorporation in a latex polymer can be quantified once NMR peaks unique to CAM ($C_{22}O_3H_{38}$) are determined. Retention of CAM unsaturation during emulsion copolymerization can also be determined by comparing the quantity of unsaturation in the final polymer to the quantity of CAM incorporated. To perform such an analysis, definitive peak assignments in the CAM ^1H and ^{13}C spectra are necessary. CAM incorporation and double-bond retention are critically important in the evaluation of CAM applicability as a latex polymer comonomer.

EXPERIMENTAL

All NMR spectra were acquired on a Bruker AC-300 NMR spectrometer operating at a frequency of 300.13 MHz for proton and 75.468 MHz for carbon and using a standard 5-mm $^1H/^{13}C$ probe. Routine acquisition files were used to acquire ^1H-NMR spectra with 128 scans and a minimum of 15,000 scans for ^{13}C-NMR spectra. NMR samples were prepared with deuterated chloroform containing 0.03% v/v tetramethylsilane, used as an internal reference. ^1H-NMR samples were prepared at 5 wt %, while ^{13}C-NMR samples were prepared at 15 wt %.

Proton homonuclear correlation (COSY) spectra were acquired using a standard pulse sequence.[8,9] The ^1H 90° pulse length was 14 μs, the dwell time in the F2 domain was 244 μs, and the incremental delay was set to 488 μs, thereby making the sweep width in both F1 and F2 6.8275 ppm. A 45° mixing pulse was used to minimize the diagonal peaks. A total of 16 scans with 192 increments were accumulated with a recycle delay of 3 s. The number of data points acquired in the F2 domain was 2048 per scan, and four preequilibrium scans were used for each acquisition. The total experimental time was 3.7 h. Spectra were processed using a shifted sine-bell for apodization and magnitude calculation in the F1 dimension, giving a 2-D matrix with only positive values. Prior to the application of Fourier transformation, the F1 domain was zero-filled to 2048 points. Postprocessing included symmetrization of spectra to reduce artifacts.

Heteronuclear correlation (HETCORR) ^1H–^{13}C experiments were obtained using the standard pulse sequence.[10] The ^{13}C 90° and 180° pulse lengths were 6 and 12 μs; the ^1H 90° length, 34 μs; the fixed polarization delay, 4 ms; and the delay to permit antiphase ^{13}C magnetization to refocus, 2 ms. The incremental delay was set to 244 μs and the dwell time in the F2 dimension was 100 μs, making the sweep widths in F1 and F2 6.8275 and 66.2499 ppm, respectively. A total of 64 scans with 256 increments were accumulated with a recycle delay of 2.5 s. The number of data points acquired in the F2 dimension was 2048, and four preequilibrium scans were used for each acquisition. The total experimental time was 13 h. The data were processed with Gaussian and shifted sine-bell apodization applied to the F2 and F1 domains and the F1 domain zero-filled to 512 points prior to Fourier transformation. Data processing also included magnitude calculation of the F1 data, yielding a 2-D data set with only positive values.

RESULTS AND DISCUSSION

CAM ^1H-NMR Peak Assignments

The relative number of protons in each environment, determined by normalized peak integra-

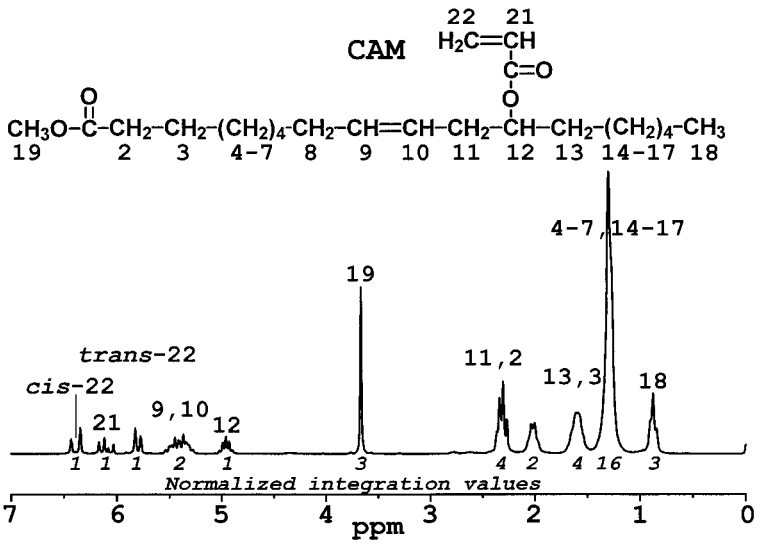

Figure 1 CAM ^{1}H-NMR spectrum.

tion, is displayed below each peak and was used to assist in the ^{1}H-NMR peak assignment (Fig. 1). Of particular interest is the assignment of the olefinic sites. The CAM acrylic olefinic peaks exhibit the typical acrylate peak pattern and are downfield relative to the oil-derived unsaturation. The C9 proton of the oil-derived unsaturation is assigned downfield relative to C10, based on pre-

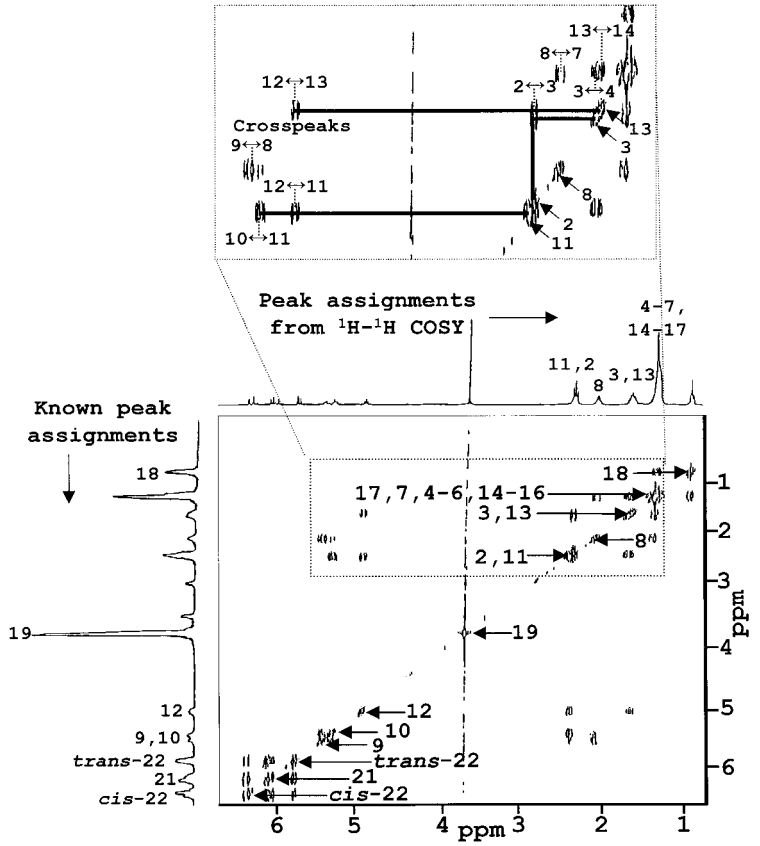

Figure 2 CAM ^{1}H–^{1}H-COSY spectrum.

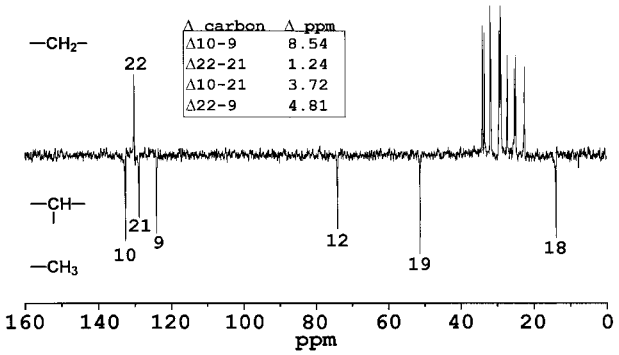

Figure 3 CAM DEPT NMR spectrum.

viously published peak assignments,[11] and confirmed by COSY NMR. The C12, C19, and C18 protons exhibit peaks at the chemical shifts expected based on previously published peak assignments for castor oil.[12]

The remaining peak assignments were conclusively determined via COSY NMR (Fig. 2). Known peak assignments permitted definitive assignment of the remaining peaks by tracing connectivity via the crosspeaks in the COSY spectrum. The advantage of COSY in spreading out the proton spectrum in two dimensions is of unique value in cases where peak overlap is a problem.

Acrylation of the C12 hydroxyl of methyl ricinoleate results in the unique structure of CAM, which, in turn, results in distinct chemical shifts for the C11, C12, and C13 protons. Previously published peak assignments for castor oil suggest that acrylation of the C12 hydroxyl results in a slight upfield shift of the C11 protons, a downfield shift of the C13 protons, and a slight upfield shift of the C12 proton.[12] The chemical shifts of the allylic C11 and C8 protons are especially significant as the sites of autooxidative polymerization in vegetable oil unsaturation.[13] The relative positions of C11 versus C2 protons and C13 versus C3 protons are also critical for correct peak assignment in the alkyl region of the ^{13}C-NMR spectrum.

CAM ^{13}C-NMR Peak Assignments

The CAM DEPT NMR spectrum (Fig. 3) confirms that the peak at 130.1 ppm is due to the methylene carbon in the acrylate double bond, C22. The methine peak at 132.6 ppm is due to C10, since the methylene carbon, C22, is expected to resonate downfield from the methine carbon, C21. The peak at 128.9 ppm is assigned to C21, based on the shielding effect of the ester substituent on

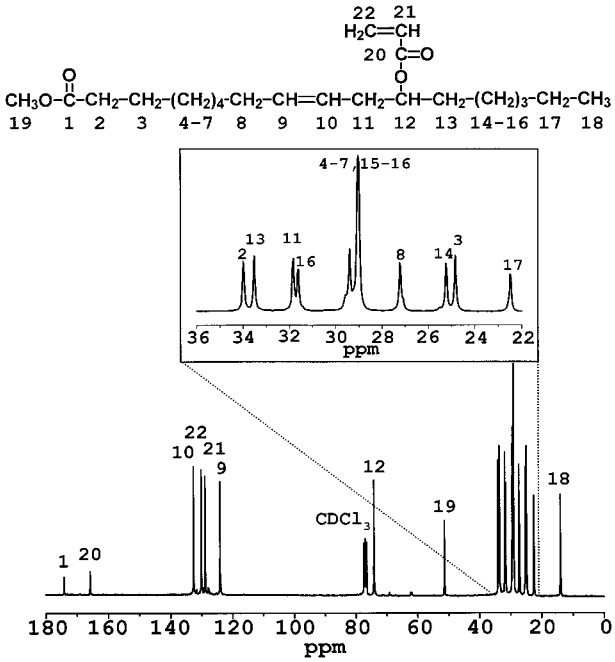

Figure 4 CAM ^{13}C-NMR spectrum.

C22 (ref. 14) as well as the small difference in acrylic double-bond shifts. The peaks at 132.6 and 124.1 ppm are assigned to C10 and C9, respectively. This assignment is based on previous studies[14,15] as well as on the large (~8 ppm) difference in their chemical shifts. These peak assignments were also confirmed by ^{1}H–^{13}C heteronuclear correlation NMR.

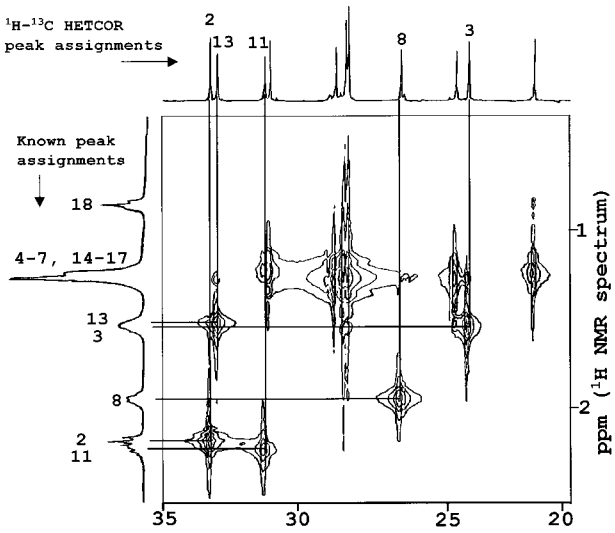

Figure 5 CAM ^{1}H–^{13}C heteronuclear correlation spectrum.

Table I ^{13}C-NMR CAM Alkyl Peak Assignments

^{13}C-NMR Chemical Shift (ppm)	CAM Carbon Assignment
36.8	C11
34.0	C2
33.5	C13
31.6	C16
29.0	C4—C7, C15
27.2	C8
25.2	C14
24.8	C3
22.5	C17

In addition to the olefinic region, the peak assignments for C19, C12, and C18 ^{13}C-NMR peaks are confirmed by the DEPT spectrum. Methyl ester carbons are expected to have a chemical shift around 50 ppm. Thus, the peak at 51.32 ppm is assigned to C12. Esterification of the substituent hydroxyl of C12 in methyl ricinoleate is expected to change its chemical shift from 71.6 ppm to an estimated value of 75.7 ppm, in reasonable agreement with the observed shift at 74.1 ppm. Assignment of C18 to the peak at 14.0 ppm is straightforward from the expected chemical shift.

Principal assignments of peaks in the carbonyl region were made based on the expected chemical shifts.[11,16] Thus, the peak at 174.2 ppm was assigned to C1, and C20 was assigned to the peak at 165.9 ppm due to the shielding effect of the vinyl substituent. Also, the assignment of the peak at 22.5 ppm as C17 is based on its proximity to the C18 peak (Fig. 4).

Assignment of the remaining carbon peaks is ambiguous based solely on previously published literature assignments for the alkyl region of the ^{13}C-NMR spectrum of castor oil.[11] The identification of these sites are critical in order to determine the incorporation of CAM in latex polymers and the autooxidative reactivity of CAM latex polymers. Conclusive peak assignment in the alkyl region was accomplished using CAM ^{1}H–^{13}C heteronuclear correlation NMR (Fig. 5). The ^{1}H chemical shifts of the C13, C3, C8, C2, and C11 protons, determined via COSY NMR spectroscopy, were used to ascertain the positions of C2, C13, C11, C8, and C3 carbon chemical shifts summarized in Table I.

The ^{1}H–^{13}C heteronuclear correlation spectrum shows five ^{13}C shifts (31.6, 29.4, 29.0, 25.2, and 22.5 ppm) for the large ^{1}H peak at 1.3 ppm. From previously published peak assignments and known peak positions, C16 and C14 are assigned to 31.6 and 25.2 ppm, respectively. The remaining sites (C4–C7 and C15) are assigned to the peaks centered at 29.0 ppm.

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