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End Groups in Acrylic Copolymers. 1. Identification of End Groups by Carbon-13 NMR

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ABSTRACT: The end groups of acrylate copolymers prepared by free-radical polymerization have been identified by ^{13}C NMR in a number of different copolymer preparations. In order to increase the relative abundance of end groups and to facilitate spectral assignments, we have used two different procedures to isolate a low M_n copolymer component: size exclusion chromatography and fractional extraction. Integration of quantitative NMR spectra was used to measure the relative concentration of the different classes of end groups.

Introduction

The initial event in the photooxidation of acrylic–melamine coatings in the outdoors is the absorption of sunlight to form free radicals.[1] Since neither the acrylate ester nor the melamine cross-linker components of these coatings absorb sunlight, their photolysis does not contribute directly to photoinitiation. Rather, photoinitiation in unweathered coatings is attributed to the presence of trace chromophoric components: inadvertent impurities, initiator fragments, end groups, and oxidation products introduced either during synthesis or subsequent cure.[1] Such chromophores have not been identified in acrylic–melamine coatings largely due to the chemical complexity of coating formulations. A typical acrylic–melamine automotive enamel may be formulated with 10 or more components, each with its own set of trace chromophores. The task of identifying trace components in such mixtures is, therefore, a formidable one, even for modern spectroscopic techniques.

In addition, it is generally believed that painstaking identification of specific chromophores in polymers is futile since photooxidation will cause changes in chromophore composition. Overall durability, consequently, may not be strongly related to the initial composition. These conclusions are based on photooxidation studies in polyolefins,[2-4] where considerable research has identified chromophoric impurities present prior to weathering and their subsequent photochemistry. In polyolefins, the presence of small amounts of chromophoric impurities triggers free-radical oxidation. During an initial induction period, characterized by low free-radical initiation rates and long kinetic chain lengths, free-radical oxidation leads to the buildup of oxidation products such as hydroperoxides. At some point, these oxidation products dominate the oxidation and autoxidation begins. The length of the induction period prior to autoxidation has been found to be nearly independent of the concentration of initial chromophore. The greatest gain in the weatherability of the polyolefins has come through the use of hindered amine light stabilizers,[5] HALS, and ultraviolet (UV) light absorber additives.[6] These additives can increase weatherability of polyolefins by a factor of 10 or more by delaying the onset of the autocatalytic oxidation phase.

The study of photooxidation in cross-linked coatings such as acrylic–melamines has been less extensive than that in polyolefins.[7-13] Nevertheless, sufficient data exist to conclude that oxidation behavior in these coatings is quite different from that of the polyolefins. Rather than exhibiting an induction period followed by autoxidation, acrylic–melamine coatings photooxidize at near constant rate throughout their usable life as evidenced by a constant increase in carbonyl functionality,[13] constant rate of weight loss,[14,15] and constant rate of oxygen uptake.[16] The addition of light stabilizers provides a relatively modest improvement in weatherability compared to that of the polyolefins.[5]

In previous work on developing rapid tests of coating weatherability, a clear, positive relationship has been established between the photoinitiation rate of free radicals measured in coatings during the first few hours of exposure and their long-term weatherability.[2] Coatings with low initial photoinitiation rates are invariably more durable than coatings with high initial photoinitiation rates. Thus, it would appear that specific information about the origin and nature of chromophoric centers present prior to weathering could lead to improvements in performance. Recent work has shown that the photoinitiation rate is strongly correlated to acrylic copolymer molecular weight and polymerization conditions.[17] These results suggest that the chromophores responsible for photoinitiation in acrylic–melamine coatings may be end groups on the copolymer chain.[17]

The present two-part work initiates a study of synthesis-derived chromophores in acrylic–melamine coatings and their relation to weatherability. In part 1, a ^{13}C NMR procedure is presented that is used to identify and quantify end groups in acrylic copolymers. The procedure involves fractionating the copolymer into low and high molecular weight components. This facilitates the identification of end groups, since the contribution of end groups increases with decreasing molecular weight. Carbon-13 NMR spectra of the components for different acrylic copolymers

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Table I
The Copolymers

copolymer	solv	initiator(s)	M_n	M_n (light)[a]
Q	IBIN[b]	CHPO,[c] AIBN[d]	1690	420
I	MAK[e]	CHPO, TBPB[f]	1610	720
L	xylene	CHPO, AIBN	1990	1080
M	MAK	AIBN	1960	760
N	xylene	AIBN	3170	1610

[a] Resulting from fractional extraction, M_n from analytical SEC (see footnote, Table II). [b] Isobutyl isobutyrate. [c] Cumene hydroperoxide. [d] Azobis(isobutyronitrile). [e] Methyl amyl ketone. [f] *tert*-Butylperbenzoate.

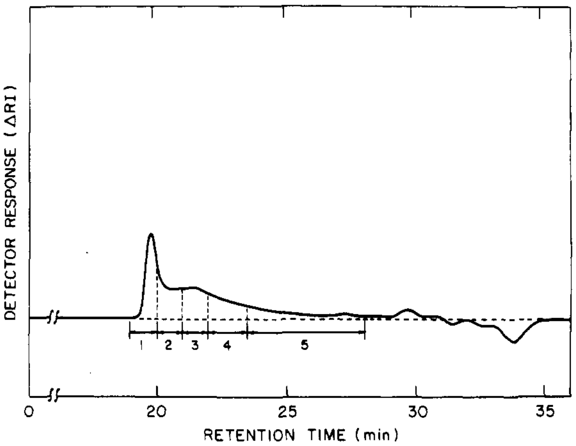

Figure 1. Retention time ranges of the five fractions collected by preparative SEC fractionation.

are analyzed and the concentration of specific end groups determined. In part 2 of this work,[18] the concentration and types of end groups are related to the polymerization conditions (e.g., initiator type and synthesis solvent) and to the photoinitiation rate of coatings made from these polymers.

Experimental Section

Preparation of Acrylic Copolymers. Acrylate copolymers were synthesized by standard free-radical solution polymerization techniques.[19] The monomer composition in the feed was held constant at hydroxyethyl acrylate (HEA, 40%), butyl methacrylate (BMA, 58%), and acrylic acid (AA, 2%). Initiators and synthesis solvents were varied as shown in Table I. Four of the copolymers studied here, labeled I, L, M, and N, correspond to similarly labeled Cymel 325 (American Cyanamid) cross-linked coatings discussed in ref 12 and 17. Copolymer Q was prepared for the present study. The solids level of the solution copolymers ranged from 60–70%.

Preparative SEC Fractionation. Size-exclusion chromatographic (SEC) fractionation of copolymer Q was achieved by the use of a preparative 10 μm gel column (100-Å pore type, 300 cm × 25 mm i.d.; Polymer Laboratories, MA) in conjunction with a Waters 150C ALC/GPC liquid chromatograph (Milford, MA). Tetrahydrofuran (THF) was used as the eluting solvent with a flow rate of 3.0 mL/min at 30 °C.

The fractionation was performed by a programmed multiple injection (20 × 500 μL; ca. 75 mg of the copolymer per injection) and fraction collection with an injection cycle of 36 min. The range of retention times corresponding to each of five collected fractions are illustrated in Figure 1. The total combined volume of each fraction was reduced to ca. 5 mL under a nitrogen flow, and the concentrated copolymer fractions were then freeze-dried in vacuo. The five fractions and the parent copolymer Q were characterized for average molecular weights and molecular size distribution by the analytical SEC procedure described below. The M_n and M_w data are given in Table II.

Fractional Extraction. Forty grams of the copolymer/solvent mix was dissolved in an equal volume of refluxing methanol. Distilled water was added until the refluxing solution became turbid. The turbid solution was allowed to cool and the clear methanol/water upper layer decanted. Methanol and water were then removed by warming the decanted layer to 100 °C under a nitrogen stream. The residue was baked at 130 °C for 30 min to remove remaining volatiles. This procedure yielded about 1.5 g of each of the copolymers or approximately 5–7% by weight of the initial solid content of the parent copolymer/solvent mixtures. Analytical SEC (described below) of the residual copolymers, referred to in the following as light copolymer, revealed a shift in M_n to lower values by 1000 to as much as 1500 amu over the series of copolymers examined, as shown in the fourth and fifth columns of Table I. The copolymer remaining in the lower layer is referred to as heavy copolymer.

Table II
SEC Characterization of Bulk and Fractionated Copolymer Q[a]

sample ID	M_w	M_n	M_w/M_n
Q	5230	1690	3.23
fraction 1	13 335	8765	1.52
fraction 2	11 700	7520	1.56
fraction 3	6655	4160	1.60
fraction 4	3145	2115	1.49
fraction 5	1065	690	1.54

[a] Average molecular weights are calculated on the basis of a SEC calibration curve obtained from poly(methyl methacrylate) standards.

Analytical SEC. A μ-Styragel column set, consisting of five columns in series with permeability limits of 100, 500, 10^3, 10^4, and 10^5 Å, was used for the analysis in conjunction with a Waters 150C ALC/GPC liquid chromatograph. The elution was conducted at 30 °C with THF flowing at 1.5 mL/min. The column set was calibrated with a series of poly(methyl methacrylate) standards (M_{peak} = 29 857, 55 858, 82 856, and 93 000; Scientific Polymer Products, Inc., Ontario, NY).

Preparation of Samples for Carbon-13 NMR. One gram of the copolymer was combined with sufficient $CDCl_3$ to give a total volume of 4 mL in a 10-mm NMR tube. Chromium acetylacetonate, $Cr(AcAc)_3$, was added to each sample to the level of ca. 0.01 M.

Acquisition of NMR Spectra. Solution-state ^{13}C NMR spectra were acquired at 75.4 MHz on a Bruker MSL300 spectrometer. The parent copolymer/solvent mixture Q as well as the heavy copolymers were each signal-averaged for 72 h (260 000 traces). Spectra of the fractions and light copolymers were acquired with 12–20 h of averaging (43 000–72 000 traces). Quadrature detection was employed by using standard single-pulse phase cycling (CYCLOPS)[20-22] and broad-band decoupling with a 30° pulse and a 1-s recycle delay.[23] The sample temperature was maintained at 25 °C. Standard Fourier transformation and phasing routines were applied.[24] The signals from the end groups were expected to be small compared to other spectral features. Since accurate comparisons between spectra were necessary, care was taken to adopt the same spectral phasing for each spectrum. The size of the digitizer allows for a dynamic range of greater than 4000. As shown below, end-group concentrations produce signals no less than 0.02% of the more intense features in the spectrum. The $Cr(AcAc)_3$ was added to all the samples[23] to equalize as much as possible the T_1s of the different types of carbons.

Results

The ^{13}C NMR spectrum of the parent solution copolymer Q is illustrated in parts A and B of Figure 2. Figure 2B illustrates the dynamic range typical of the spectra of the copolymers. In this report, no analysis is made of the spectral range below 100 ppm due to its complexity. The spectral range above 100 ppm, shown expanded in Figure 3, contains a wealth of features. To organize the following discussion, this spectrum is separated into five distinct spectral regions identified in Figure 3 by brackets: A, 220–188 ppm, ketonic; B, 180–163 ppm, ester; C, 162–141 ppm, substituted aromatic; D, 140–125 ppm, vinyl; and E, 125–115 ppm, cyano. The vinyl region, D, includes all vinylic as well as protonated aromatic carbons.

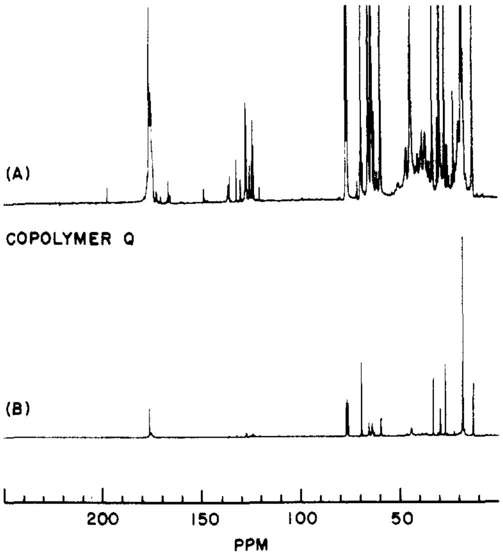

Figure 2. Carbon-13 NMR spectrum at 75.4 MHz of parent copolymer/solvent mixture Q. Spectrum A is a 32X vertical intensity expansion of B.

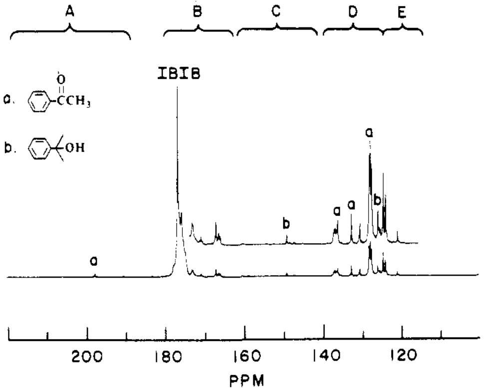

Figure 3. Carbon-13 NMR spectrum of parent copolymer/solvent mixture Q. Expansion of region above 100 ppm.

One of the initial objectives of these experiments was to follow the chemistry of the initiator cumene hydroperoxide (CHPO). Copolymer Q was prepared for this purpose. Since CHPO was the only aromatic species added (see Table I), any resonances in regions C and D should reflect end groups of the copolymer derived from CHPO. The spectrum in this region, however, as illustrated in Figure 3, is quite complex and could not be interpreted solely on the basis of this hypothesis. Some of sharper resonances in the spectrum are from either the isobutyl isobutyrate (IBIB), acetophenone, or 2-phenyl-2-propanol (cumenol). The latter two species are degradation products of CHPO.[18] Their resonances have been indicated in Figure 3. Other sharp lines may indicate the presence of unconsumed acrylic monomers. The sharp resonance at 167 ppm, for example, is close to those for the vinyl ester carbonyl carbon of the acrylic monomers (BMA, 166.9 ppm; HEA, 166.0 ppm; AA, 171.7 ppm). It is important to note that these sharp line resonances are all due to low molecular weight volatile species that would be removed from the coating during cure and thus should not affect the photoinitiation rate. The broader features between 167 and 165 ppm (two peaks) are also from vinyl ester carbonyl carbons. Their extra line width differentiates them from the monomers, however. The presence of these broader vinyl ester carbonyl resonances and of the narrower monomer line implies that part of the intensity in the vinyl carbon region, D, is from the vinyl carbons associated with the vinyl ester carbonyls. Due to these complications, it is not possible to determine the nature of the CHPO-derived end groups solely from the spectrum of the unprocessed parent copolymer Q shown in Figure 3.

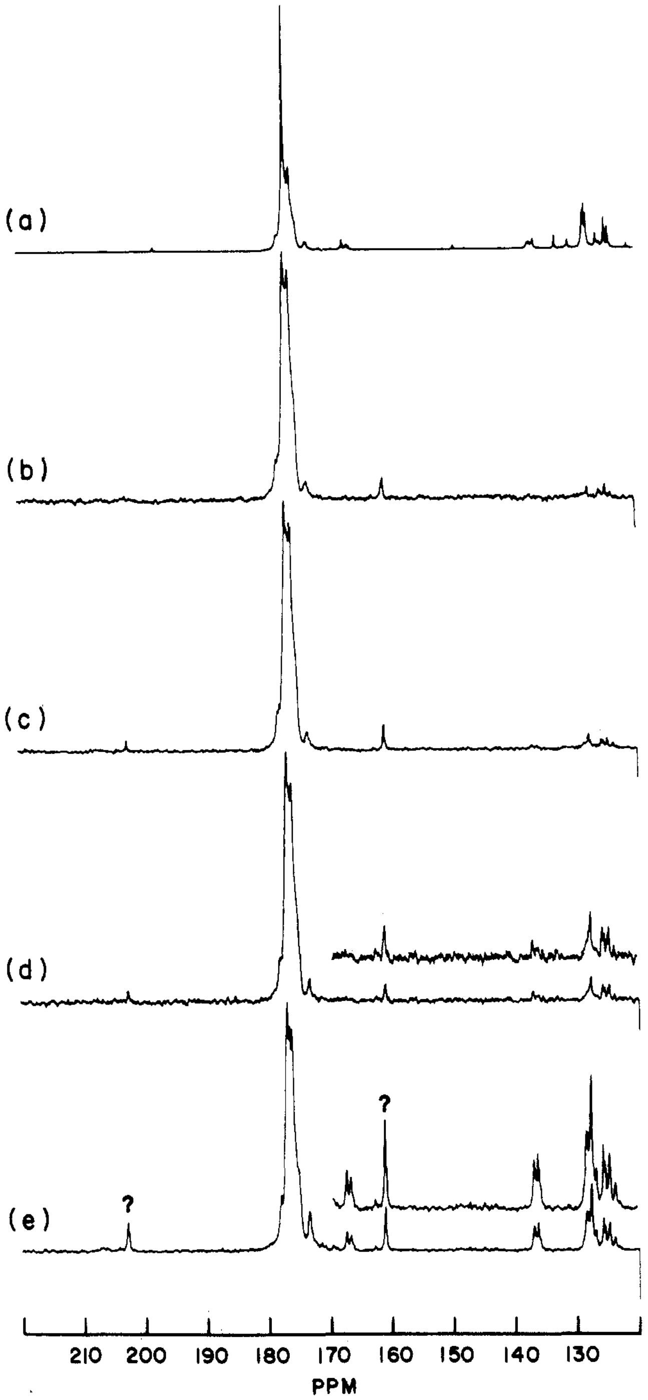

Figure 4. Carbon-13 NMR spectra of the preparative SEC fractions.

Comparison of the spectrum of parent Q with those of fractions from the preparative SEC fractionation technique allows for the assignment of many more of the resonances from copolymer Q. Carbon-13 NMR spectra of fractions 2 through 5 are illustrated in parts b through e of Figure 4. Figure 4a reproduces Figure 3. The new resonances at 203 and 161 ppm (indicated by question marks) are impurities apparently introduced during SEC fractionation. Their interpretation will not be attempted, although their presence does indicate a potential problem with the SEC—induced impurities—that could obscure the correlation of resonances. The presence of these impurities

Table III
Integration over End Group Spectra in SEC Fractions of Figure 4b–e

fractn	M_n	integral[a]	fractn	M_n	integral[a]
0	1690		3	4160	12
1	8765		4	2120	10
2	7520	32	5	695	8

[a] Integral over vinyl ester (167–165 ppm) and vinyl region, D, when main-chain ester region set to 100.

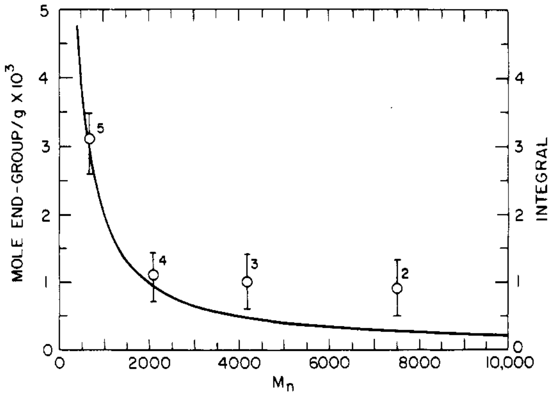

Figure 5. End-group concentration versus M_n for acrylic copolymers (solid line). Points show integral over end-group spectrum of the SEC fractions.

notwithstanding, the fractionation procedure removes the resonances of the monomeric species, as identified in Figure 3, from the spectrum. This allows for greater confidence in assigning the remaining spectral features to parts of the copolymers. Three types of pendant ester groups, derived from BMA, HEA, and AA, are expected in the copolymer. These are represented by the two peaks and high-frequency shoulder between 179 and 175 ppm, seen best in Figure 4b. As M_n is reduced and the relative number of units located next to an end group increases, end group effects will become more important. All of the spectral regions show these effects. Region B, for example, shows additional peaks and changes in relative peak intensities, as seen in Figure 4e. The peak at 172 ppm increases in intensity relative to the pendant ester peaks between 179 and 175 ppm. An increase in relative intensity is also observed for the vinyl ester peaks at 167 and 166.5 ppm. In the vinyl region, D, comparable intensity increases are also observed.

The variation of resonance intensity with molecular weight can be used to differentiate between species incorporated as end groups and other "impurities" that are bound to the polymer (e.g., transesterification of monomers to side chains). End-group concentration is proportional to $1/M_n$. As shown in Figure 5 and reported in Table III, the integrated intensity of the NMR signals over the vinyl ester (167–165 ppm) and vinyl region, D, are roughly proportional to $1/M_n$. It can be concluded that the signals in these regions are due primarily to end groups. Line by line comparison of features in parts b through e of Figure 4 suggests that the composition of end groups is independent of molecular weight; only the total concentration of end groups relative to the main-chain esters changes.

It is clear that significant improvements in signal-to-noise can be achieved by using as low a molecular weight fraction as possible. This can be achieved without using the lengthy SEC technique by use of the simple fractional extraction procedure (see Experimental Section). As shown in columns 4 and 5 of Table I, fractional extraction produces a substantial reduction in M_n. There is also no opportunity for the introduction of impurities and volatile species are removed. Carbon-13 NMR spectra of the five light copolymers are illustrated in Figure 6. They are similar in overall features such as band positions and relative intensities to the spectrum of fraction 5, Figure 4e, which is of comparable M_n (M_n of fraction 5 is 690). The ketonic and substituted aromatic regions, A and C, are shown in vertical expansions above the corresponding full spectrum. New features have appeared in these spectra due to their high signal-to-noise ratio. Resonances that are due to end groups may be determined from comparisons of light to heavy copolymer NMR spectra, as illustrated in Figure 7 for copolymes Q, I, and M. End-group resonances should be present in both light and heavy copolymer fractions with the relative intensity in the light fraction being higher by the ratio of M_n's of the heavy to light fractions. Resonances that are present only in the light copolymer can be attributed to low molecular weight impurities present in the copolymer solution, which have

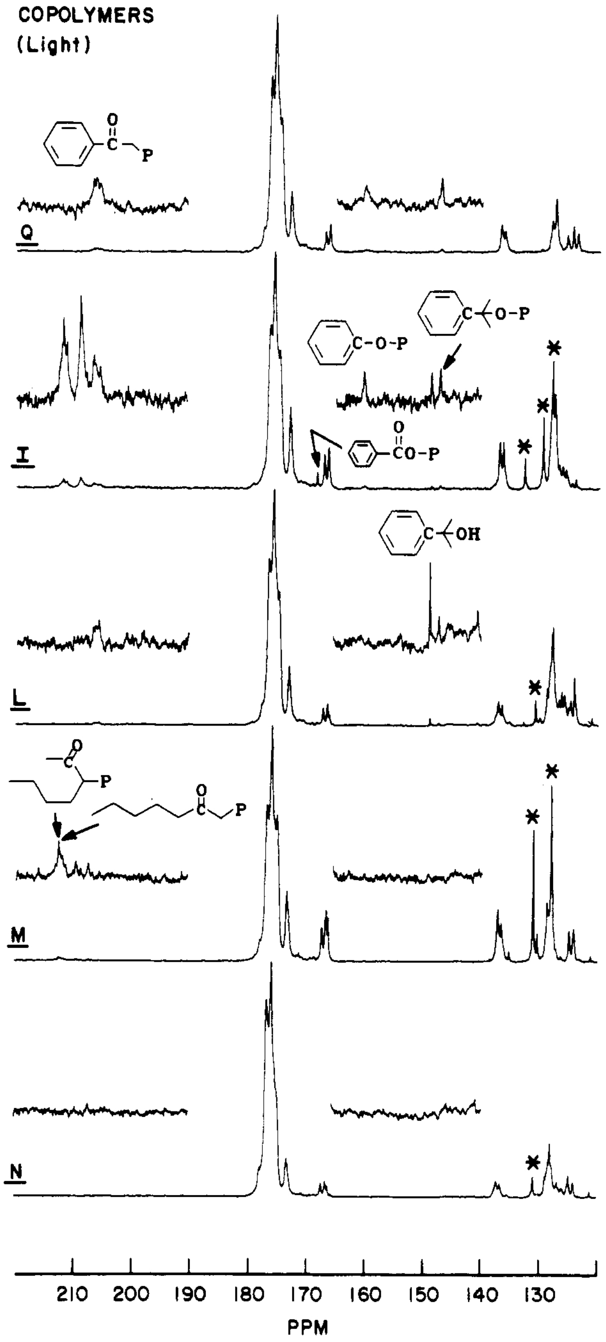

Figure 6. Carbon-13 NMR spectra of the light copolymers from fractional separation.

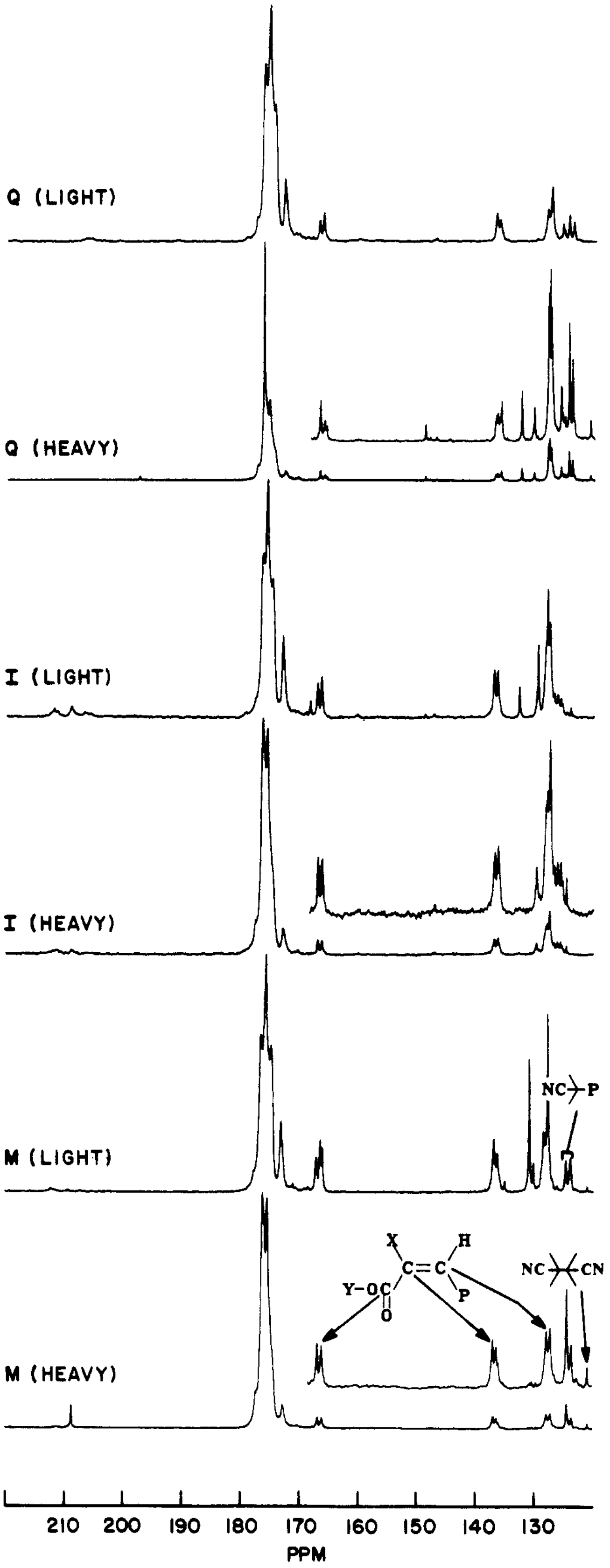

Figure 7. Comparison of ^{13}C NMR spectra of light and heavy copolymers.

not been completely removed by heating, that have tended to migrate into the light fraction. Resonances from such species are indicated by an asterisk, *, in spectra of the light copolymer (Figure 6). All of the other resonances in these spectra (except for the strong main-chain ester resonances and an occasional low intensity residual monomer peak between 167 and 165 ppm) can be attributed to end-group species.

The assignments of the resonances due to end groups on the acrylic copolymer are given in Figures 6 and 7. Resonances were assigned by using chemical shifts and comparisons of spectra from the different copolymers. Reactions leading to incorporation of these end groups are presented in part 2 of this study.[18] The resonances between 125 and 118 ppm are attributed to cyano carbons. These are observed only in copolymers initiated with azobis(isobutyronitrile) (AIBN). Specifically, the resonances at 124.4 and 123.6 ppm are due to cyano carbons from AIBN-derived end groups. The structure of this end group is shown in Figure 7, spectrum M (light). A doublet appears because the first monomer group can be either BMA or HEA. The other carbons in this end group have chemical shifts below 100 ppm and are not identified. The sharp resonance at 120.9 ppm is due to the cyano carbons from the 2-cyano-2-propyl radical dimer (structure in Figure 7, spectrum M (heavy)), a thermal degradation product of AIBN. The resonance frequency of the cyano carbons in AIBN itself is 119.0 ppm, as was verified by spiking heavy copolymer Q with AIBN and observing a new resonance at this frequency. No residual AIBN is observed in any of the copolymers.

Vinyl ester end groups are observed in all of the copolymers. The ester carbon and both vinyl carbons can be assigned as shown in Figure 7, spectrum M (heavy). The chemical shifts of the ester carbon are 166.9 and 166.1 ppm. The chemical shifts of the vinyl carbons are 136.9, 136.4, 127.9, and 127.4 ppm. Doublets are observed since the vinyl ester can be due either to BMA or HEA. The corresponding resonances in the monomers occur at 166.9 (BMA), 166.0 (HEA), 136.3 (BMA), 130.8 (HEA), 124.5 (BMA), and 127.6 ppm (HEA). A further end group is responsible for a weak resonance, seen only in copolymer I (Figure 6) observed at 168.6 ppm. This resonance is assigned to an aromatic ester carbonyl carbon and is attributed to a phenylcarboxy end group (structure illustrated in Figure 6, spectrum I). The phenylcarboxy end group has been observed in a study of poly(methyl methacrylate) polymers.[25] The carbonyl carbon resonances from this end group were observed to fall between 166.0 and 165.0 ppm depending on the monomer to which the end group was attached. The discrepancy between this value and that observed here may be explained by end group–solvent interactions that shift the resonance or interaction between the copolymer and the solvent $CDCl_3$, whose central line resonance was used as the frequency reference in this work, that shift the solvent resonance. It should be mentioned that shifts between lines from two different copolymer samples that were known to represent equivalent carbons were often of this size. Only the carbonyl carbon of the phenylcarboxy end group can be assigned. The aromatic carbon resonances all fall in the vinyl region where assignments have proven impossible due to the large number of different carbons with nearly identical chemical shifts. Only two aromatic resonances were sufficiently shifted from the vinyl region, D, into the substituted aromatic region, C, to be uniquely assigned. They were the carbon attached to oxygen in a phenoxy end group (resonance at 160.6 ppm, structure illustrated in Figure 6, spectrum I) and the carbon attached to a butyl group in a cumyloxy end group (resonance at 147.5 ppm, Figure 6, spectrum I). Again, the other aromatic carbon resonances fall in the vinyl region and were not assigned.

The final resonances which can be assigned to end groups fall in the ketone region, A. Both aliphatic and

Table IV
Concentration of End Groups

copolymer	est[a]	AIBN[b]	Ket[c]	vin[d]	phox[e]	cumy[f]	phen[g]
Q	100	5	2	8	1	1	na[h]
I	100	na	7	11	1	1	2
L	100	7	1	6	0	0.5	na
M	100	6	2	12	na	na	na
N	100	4	0	5	na	na	na

[a] Main-chain ester, 179–172 ppm. [b] 2-cyano-2-propyl end group, integrated 122.4 and 123.6 ppm peaks. [c] Ketone, 212, 209, and 206 ppm. [d] Vinyl ester, doublet at 136.9 and 136.4 ppm. [e] Phenoxy end group, 160.4 ppm. [f] Cumyloxy, 147.5 ppm. [g] Phenylcarboxy, 168.6 ppm. [h] Initiator of parent initiator not present.

aromatic ketones are observed. Aliphatic ketones are observed only when methyl amyl ketone (MAK) is used as a synthesis solvent (copolymers I and M). MAK is incorporated as an end group in two ways (shown by the structures in Figure 6, spectrum M).[18] The chemical shift of the carbonyl carbon of both species will be almost identical and are at 212 ppm. The other aliphatic ketone resonance (at 209 ppm, seen best in Figure 6, spectrum I) is presumably due to an unknown impurity in the MAK used for the copolymer I synthesis. The aromatic ketone resonance (206 ppm) is only observed in polymers initiated with CHPO (copolymers Q, I, and L). The presumed structure for this end group is given in Figure 6, spectrum Q. Only the carbonyl carbons in these end groups are assigned. The remaining resonances in the aliphatic ketones occur below 100 ppm while those for the aromatic ketone occur in the vinyl region.

The relative concentrations of the different end groups observed in these copolymers can be determined by an NMR integration procedure. The pendant ester resonances of the acrylic copolymers between 179 and 172 ppm were integrated and assigned a value of 100. Since there is one pendant ester group for each monomeric unit included in the copolymer, integration over the various end-group resonances gives their concentration as number of end groups per 100 incorporated monomers. The results of this procedure are given in Table IV. The integration was only over regions of the spectrum above 100 ppm that contained nonoverlapping resonances (and at least one such resonance exists for each identified end group). Throughout this procedure, care was taken to ensure where necessary that the integration counted a contribution from only one carbon per end group. Under this condition, the integrals are directly proportional to the concentration of each type of end group.

Conclusion

An NMR method had been developed for identifying end groups in acrylic copolymers. The procedure involves concentrating the end groups by fractional extraction of the lower molecular weight components of the copolymer. End group associated resonances are flagged because their intensities increase as $1/M_n$. End groups of acrylate copolymers prepared by free-radical polymerization have been identified in a number of different copolymer preparations. Integration of resonances in the NMR spectra have been used also to gauge the relative concentration of the different classes of end groups.

In part 2 of this work,[18] reactions that account for the incorporation of the different end groups are presented. The effect of end groups on the photoinitiation rate and weatherability of coatings made from these polymers is discussed.

Registry No. (HEA)(BMA)(AA) (copolymer), 72259-85-9; CHPO, 80-15-9; TBPB, 614-45-9; AIBN, 78-67-1.

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