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End Groups in Acrylic Copolymers. 2. Mechanisms of Incorporation of End Groups and Relationship to Photoinitiation Rates

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ABSTRACT: The mechanisms of incorporation of previously identified end groups during polymerization of acrylic copolymers are discussed. These end groups include vinyl ester groups (formed by disproportionation termination), 2-cyano-2-propyl groups (from azobis(isobutyronitrile) initiator), phenylcarboxy end groups (from *tert*-butyl perbenzoate initiator), and aliphatic ketone (from 2-heptanone solvent), aromatic ketone, cumyloxy, and phenoxy end groups (from cumene hydroperoxide). The composition of copolymer end groups is related to the free radical photoinitiation rate of acrylic–melamine coatings prepared from these copolymers. The concentration of ketone end groups correlates well with the observed photoinitiation rate.

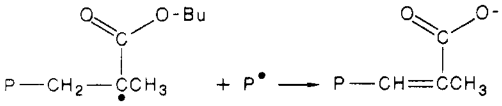
Introduction

In the previous paper[1] (referred to as part 1), an NMR procedure was developed to identify end groups in acrylic copolymers and determine their concentrations. The technique was applied to a series of acrylic copolymers that were polymerized by using different initiators and synthesis solvents. A wide variety of end groups were identified. In this paper (part 2), mechanisms are proposed to account for the incorporation of the different end groups observed. End-group compositions of the copolymers are compared to the rates of formation (photoinitiation) of free radicals on controlled exposure to ultraviolet (UV) light in acrylic–melamine coatings made from these copolymers. The photoinitiation rates have been measured[2] by using a nitroxide doping technique described in detail elsewhere.[3,4] A direct correlation has been found between photoinitiation rates and the long-term weatherability of coatings.[5] The end groups responsible for high photoinitiation rates in some coatings are identified.

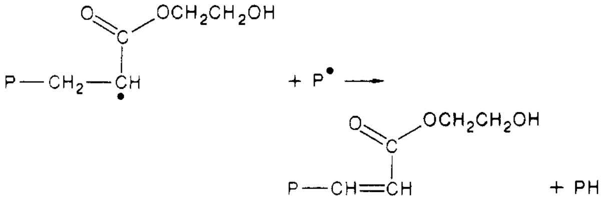
Results and Discussion

Mechanisms of End-Group Incorporation. The solution ^{13}C NMR spectra of light[1] acrylic copolymers I and N from part 1 are reproduced in Figure 1. The end groups that have been identified are shown. These two copolymers have been selected to illustrate the influence of synthesis conditions on end-group structure and concentration. They represent the extremes in the series studied. Other members of the series provide intermediate examples. All of the end groups identified are present in either copolymer I or N. The two spectra represent only the nonvolatile components of the complete copolymer synthesis mixture. Unreacted monomer, noncovalently bonded initiator fragments, and synthesis solvent have been mostly removed. For example, acetophenone is found among the volatiles removed from copolymer I but does not appear in the spectrum shown. The spectroscopic techniques used to obtain spectra, sample preparation, and the assignment of peaks is covered in part 1.[1]

The spectra of copolymers N and I are dominated by ester carbonyl carbon peaks in the 170–180 ppm region, characteristic of acrylate copolymers. Other peaks in these spectra provide direct information about the nature of copolymer end groups. For example, the second largest feature common to both copolymers is a series of three doublets centered at 166.5, 136.5, and 127.6 ppm. These peaks can be assigned to vinyl ester carbonyl carbon, 166.5 ppm, and corresponding vinyl carbons. The formation of these moieties is attributed to disproportionation termination of two copolymer radicals during synthesis.[6] Two kinds of vinyl ester end group are expected, accounting for the doublets, in accordance with the two major acrylate monomers used, acrylate and methacrylate, whose disproportionation is shown in reactions 1 and 2. Reactions 1 and 2 show that every vinyl ester end group must be accompanied by the formation of a corresponding aliphatic end group. This end group is not recognizable in the NMR spectra, using the analysis techniques described in part 1, since it has no unique carbons in the region of study to distinguish it from the other copolymer groups. Vinyl ester end groups appear in all the copolymers studied independent of initiator or synthesis solvent since disproportionation is a termination reaction.

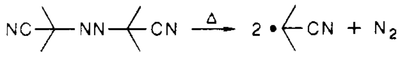


$$P{-}CH_2{-}\dot{C}(C(=O)O{-}Bu)CH_3 + P^\bullet \longrightarrow P{-}CH{=}C(C(=O)O{-}Bu)CH_3 + PH \quad (1)$$



$$P{-}CH_2{-}\dot{C}H(C(=O)OCH_2CH_2OH) + P^\bullet \longrightarrow P{-}CH{=}CH(C(=O)OCH_2CH_2OH) + PH \quad (2)$$

With exception to the ubiquitous vinyl ester end groups, end-group composition reflects the nature of initiator(s) and synthesis solvents. Copolymer N was synthesized in xylene with azobis(isobutyronitrile) (AIBN) as sole initiator. The cyano carbon of the 2-cyano-2-propyl end group is clearly visible in the NMR spectrum of copolymer N as the doublet at 124.4 and 123.6 ppm. With use of thermolysis of AIBN as an example,[6] demonstrated in reaction 3, initiator fragments become covalently bonded to the copolymer by chain initiation (reaction 4) or termination of copolymer radicals (reaction 5). Again, the two signals are due to the two types of adjacent species. The sharp resonance at 120.9 ppm is attributed to the nonvolatilized 2-cyano-2-propyl radical dimer. The spectrum of copolymer N is most notable, in comparison to that of copolymer I, for the complete absence of ketone carbonyl carbon peaks in the 200–220 ppm region. The significance of this is discussed below.



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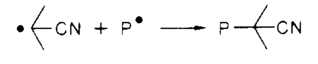


(5)

Copolymer I was synthesized in 2-heptanone (MAK) with cumene hydroperoxide (CHPO) and *tert*-butyl per-

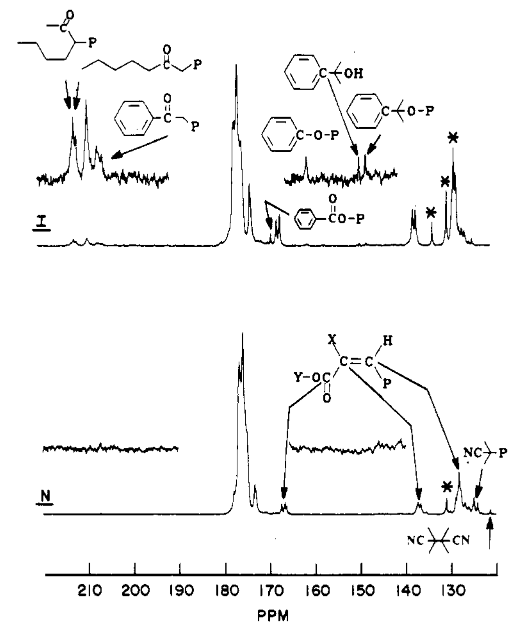
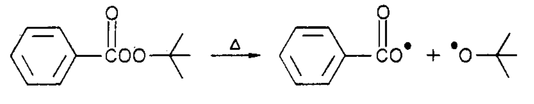
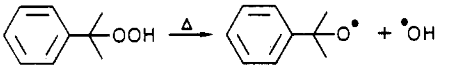


Figure 1. ^{13}C NMR spectra, 75 MHz, of light fractions of copolymers I and N. See part 1 for experimental details.

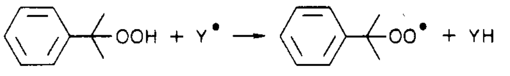
benzoate (TBPB) as coinitiators. A number of initiator-based end groups are identified in this spectrum. The phenylcarboxy end group, carbonyl carbon resonance at 168.6 ppm, results from the thermolysis of TBPB,[6] demonstrated in reaction 6.


(6)

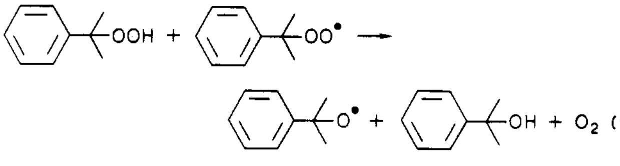
Peaks due to the corresponding *tert*-butoxy end group are hidden in the aliphatic carbon region. The simple thermolysis of CHPO[6] is expected to result in the formation of cumyloxy and hydroxyl end groups (reaction 7).


(7)

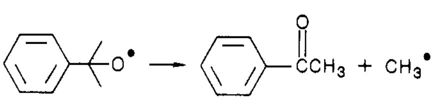
The substituted aromatic carbon of the cumyloxy end group is visible at 147.5 ppm. It is unlikely that CHPO is decomposed entirely by simple thermolysis in this system. The CHPO is added continuously with comonomer over the course of the 8-h synthesis in an amount equal to 2.5% by weight solids. Its half-life at the synthesis temperature is long—$t_{1/2,\mathrm{benzene}}$ = 29 h at 145 °C[7] compared to minutes for AIBN and TBPB. In other words, if decomposition were limited to thermolysis alone, residual CHPO would be present upon completion of the synthesis. None is observed, however. Its absence may be due both to solvent assisted decomposition[8] and/or chain-transfer reaction between CHP and polymer radicals. Chain transfer is demonstrated in reaction 8 and is envisioned as one means by which CHPO could act to reduce the M_n of high solids acrylate copolymers.


(8)

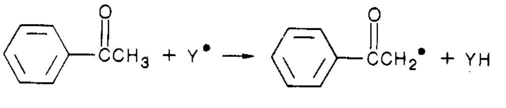
The transfer constant for this reaction, however, is reported to be small at 60 °C, 0.33, in the polymerization of methyl methacrylate.[9] Chain transfer would result in the formation of cumylperoxy radicals. Cumylperoxy end groups are not observed. This may be due to the instability of cumylperoxy end groups at the synthesis temperature. The half-life of dicumyl peroxide is reported to be 28 min at 145 °C in benzene.[7] Reaction between cumylperoxy radical and CHPO, reaction 8, may occur in view of the large amount of CHPO used.[10]


(9)

Reaction 9 leads to the formation of cumyl alcohol and cumyloxy radicals. Both the cumyloxy end group and cumyl alcohol are observed. The decomposition of cumyloxy radicals, reaction 10, accounts for the presence of acetophenone in the volatiles from copolymer I.[8]

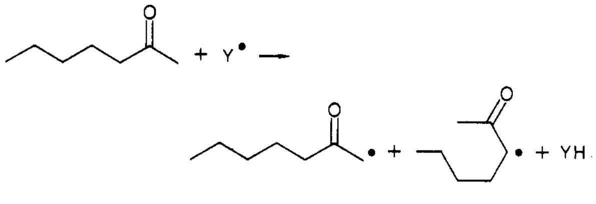

(10)

Hydrogen atom abstraction from acetophenone to yield phenacylmethyl radical, reaction 11, can account for the presence of aromatic ketone end groups believed to be the origin of the NMR signal at 207 ppm.


(11)

The transfer constant for acetophenone in the polymerization of methyl acrylate at 50 °C is reported to be <2.5.[9] The presence of phenoxy end groups, found at 160.4 ppm, suggests that CHPO is not decomposed entirely by a free radical path. The acid-catalyzed decomposition of CHPO yields phenol and acetone.[8] Phenol is a likely source of the phenoxy end group. The transfer constant for phenol at 50 °C in the polymerization of methyl acrylate is reported to be <2.[9]

By analogy to reaction 11, the abstraction of α-keto hydrogen from MAK solvent can account for the aliphatic ketone end group visible at, 212 ppm, as shown in reaction 12.


(12)

The transfer constant for 2-butanone is reported to be 3.2 at 80 °C in the polymerization of methyl acrylate, but considerably less, 0.7, at the same temperature in the polymerization of methyl methacrylate.[9] There is little reason to doubt that xylene and IBIB are also incorporated as end groups during polymerization in these solvents, although evidence for the end groups based on these solvents is likely to be obscured in the present study. Chain transfer with IBIB could be quite high relative to the other solvents studied. A transfer constant of 0.9 is reported for methyl isobutyrate at 80 °C in the polymerization of methyl methacrylate.[9]

It is clear from the discussion above that both synthesis solvent and initiator play a key role in determining the nature of end groups introduced during the free radical polymerization of acrylate copolymers. The concentration of the different end groups has been determined relative to the ester carbonyl group by integration of the NMR signals. These data were given in Table IV of part 1 for the different light copolymers. Using these data and the number-average copolymer molecular weight data of Table I of part 1, it is possible to calculate the expected number of end groups and the relative contribution of each observed. This distribution of end groups is given in Table I of this paper. The values assume an average monomer molecular weight of 130, consistent with the monomer

Table I
Distribution of End Groups as Percent of Total

copolymer	vinyl ester	PH	2-cyano-2-propyl	ketone	phenoxy	cumyloxy	phenylcarboxy
I[a]	29	29	...	18	2	2	5
N[b]	30	30	24	...	...	...	...
Q[c]	15	15	10	4	2	2	...
L	22	22	25	4	0	2	...
M[e]	31	31	16	5	...	...	...

[a] Copolymer synthesized in MAK with TBPB and CHPO as coinitiators. [b] Copolymer synthesized in xylene with AIBN as initiator. [c] Copolymer synthesized in IBIB with AIBN and CHPO as coinitiators. [d] Copolymer synthesized in xylene with AIBN as a coinitiator. [e] Copolymer synthesized in MAK with AIBN as initiator.

Table II

	photoinitiation rate, mol/g·min × 10^8		ketone end group concn, mol/g × 10^8	
copolymer[a]	initial	sustained[b]	aliphatic	aromatic
N	0.3	0.07	...	...
M	1.0	...	3600	...
L	1.3	...	...	2800
I	5.0	0.8	12000	4000

[a] Copolymers crosslinked in 70/30 ratio with Cymel 325 (American Cyanamid) at 130 °C for 30 min. [b] Photoinitiation rate sustained after 20 h "QUV-like" exposure.

composition used: HEA (58%), BMA (40%), and AA (2%). The calculation also assumes that all vinyl ester end groups arise through disproportionation termination with the generation of a corresponding saturation site, PH, according to reactions 1 and 2. This analysis accounts for 75–85% of the total number of end groups expected with the exception of copolymer Q synthesized in IBIB. Since this analysis depends strongly on the ratio of M_n in the light and unfractionated polymers, the largest error is likely to occur in the case of copolymer Q which has the lowest light fraction M_n. Alternately, the low accounting may be real and attributable to the incorporation of unobservable IBIB-based end groups. Considering that the accounting depends not only on molecular weight ratios of low molecular weight polymer but also on NMR integrations of fairly weak signals, it is noteworthy that the agreement between expected and observed end group concentration is as good as it is. To our knowledge, this is the first natural abundance ^{13}C NMR analysis to account quantitatively for virtually all significant end groups in acrylic polymerization.

Relationship between End Groups and Photoinitiation Rates. The differences in end-group composition are reflected in measurements of photoinitiation rates (listed in Table II) from melamine cross-linked coatings of these copolymers. As discussed in part 1, the rate of photoinitiation of free radicals correlates well with the long-term weatherability of coatings.[5] Two different photoinitiation rates are reported in Table II, an initial rate and a sustained rate. The initial rates are measured in freshly prepared, unweathered coatings. These measurements have been reported earlier and directly reflect the initial composition of the copolymer.[2] The sustained rates are measured after a coating has been weathered for 20 h in a QUV-like weathering chamber. The procedure of nitroxide incorporation necessary to determine the photoinitiation rate of a weathered coating will be described in detail elsewhere.[11] Studies of the photoinitiation rate behavior with exposure time reveal that the photoinitiation rate drops during the first 20 h from its initial value and is then sustained for long (>1000 h) times. Interestingly, the photoinitiation rates of both coatings I and N drop by the same proportion, although the photoinitiation rate of coating N is always lower than that of coating I. The sustained photoinitiation rates in coating I and N are significantly different (0.8 compared to 0.07 × 10^{-8} mol/g·min. According to simple theories of photooxidation, the oxidation rate of coating I should be greater than that for coating N by a factor equal to the square root of the ratio of photoinitiation rates ($\sqrt{}(0.8/0.07) = 3.4$). This difference is larger than improvements typically observed when photostabilizers are added to acrylic–melamine coatings. Despite the variation of photoinitiation rate with time, it is clear that chromophores present initially on the acrylic copolymer have a profound effect on the sustained photoinitiation rate and thus on long-term weatherability. Clearly, an understanding of the manner in which copolymer end groups contribute to photoinitiation is a key to improving the intrinsic photostability of acrylic–melamine coatings.

In theory, end groups may contribute directly to photoinitiation through primary photochemistry, excited-state homolysis, hydrogen atom abstraction or electron transfer, or indirectly through secondary photochemistry energy transfer. Energy transfer in acrylic–melamine coatings has recently been examined by Bauer et al.[12]

The contribution that each end group makes to the measured initial photoinitiation rate can be estimated on the basis of the comparisons of the data in Tables I and II and the known photochemistry of the given groups. In particular, it is possible to eliminate several of the end groups as major contributors to photoinitiation. For example, the 2-cyano-2-propyl and vinyl ester end groups do not absorb light above 280 nm, the cutoff of the light source used. They are not expected to contribute to photoinitiation through primary photochemistry.[13] This conclusion agrees with the very low photoinitiation rate measured for coating N. The vinyl ester end groups can also be eliminated as a major source of photoinitiation on the basis of the low photoinitiation rate of coating N. It is not clear whether the presence of these end groups, or some as yet unidentified end group (copolymer inhibitor-based end group?) or impurity, precludes an even lower photoinitiation rate. The UV absorption of the cumyloxy and phenoxy end group is similar to that of the phenyl group in polystyrene. Exceedingly low photoinitiation rates have been measured for anionically polymerized polystyrene.[5] The presence of styrene as a comonomer in acrylic–melamine coatings does not affect photoinitiation. Evidence exists to suggest that energy-transfer chemistry increases, however.[12] It is presently thought that these end groups should not contribute significantly to photoinitiation. The phenylcarboxy end group absorbs light above 280 nm and may contribute to photoinitiation either through primary photochemistry or, more likely, through energy transfer.

Among the end-groups observed to date, ketone end groups appear to be the most likely contributors to significant photoinitiation. The n to π^* transition of aliphatic ketones occurs at ~280 nm ($\epsilon \approx 15$) while that for an aromatic ketone occurs at ~320 nm ($\epsilon \approx 50$). Both transitions will be excited by light produced in the weathering chamber used. The total concentration of aliphatic and aromatic ketone end groups in the different acrylic–melamine coatings is given in Table II. The concentrations have been adjusted for the presence of 30% by weight melamine cross-linker. There is a clear trend of increasing photoinitiation rate with increasing ketone concentration. Aromatic ketone groups appear to contribute more strongly

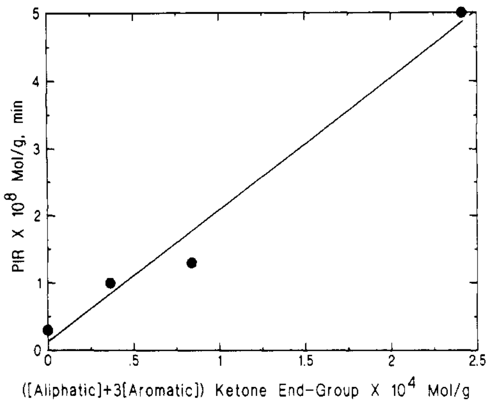


Figure 2. Coating photoinitiation rate (PIR) versus weighted sum (on the basis of relative extinction) of aliphatic and aromatic ketone concentration.

to photoinitiation than aliphatic groups in accord with their higher extinction coefficient. As shown in Figure 2, photoinitiation rates are proportional to a weighted average of the aromatic and aliphatic ketone concentrations where the weighting factor is taken as the ratio of aromatic to aliphatic ketone extinction coefficients—$\simeq 3/1$. This suggests that virtually all of the observed initial photoinitiation rate can be accounted for by ketone end groups incorporated as initiator or solvent fragments. Assuming that ketone end groups are solely responsible for photoinitiation, it is possible to calculate a quantum efficiency for free radical formation that takes into account the light intensity during exposure (0.07 mW/cm^2),[14] the observed photoinitiation rate, ketone end-group concentration, and average extinction coefficient. The calculation yields a quantum efficiency of roughly 0.05, a value qualitatively consistent with other quantum efficiencies measured in polymers.[15]

Although parallels are found between initial ketone end-group concentrations, initial photoinitiation rates, and the level at which photoinitiation is ultimately sustained, it is not clear how ketone end groups are involved, if at all, in this process. On the basis of the observed photoinitiation, ketone end groups should be completely consumed by primary photochemistry within the first 100 h of UV exposure. The measured photoinitiation rate does drop during this period, but the drop is to a sustained level in proportion to the initial photoinitiation rate measured prior to UV exposure. Experiments are under way to determine the nature of the chromophores responsible for the sustained photoinitiation rate, and to determine how they are related to the ketone groups responsible for the initial photoinitiation rate.

Conclusion

In this paper, rationales have been presented to associate the presence of specific copolymer end groups with synthesis conditions. Better than 75% of the total number of expected end groups are observed in the ^{13}C NMR spectra presented in part 1. A variety of initiator-based end groups are identified. Vinyl ester end groups thought to arise from the disproportionation termination of copolymer radicals are also observed. Their abundance suggests that disproportionation is the dominant mode of copolymer chain termination. The presence of aliphatic ketone end groups in copolymers synthesized in MAK demonstrates the active role that solvent can play in copolymer synthesis. Photoinitiation rate measurements on melamine cross-linked versions of the copolymers suggest that the weatherability performance of acrylic–melamine coatings is determined in part by copolymer synthesis conditions. Specifically, the level of ketone end groups incorporated from either synthesis solvent or initiator fragments in large part determines the measured photoinitiation rate and influences long-term weatherability.

Acknowledgment. We wish to thank Mr. J. Richert for his mass spectral determination of acetophenone.

Registry No. Cymel 325, 9003-08-1; AIBN, 78-67-1; MAK, 110-43-0; CHPO, 80-15-9; TBPB, 614-45-9; (HEA)(BMA)(AA) (copolymer), 72259-85-9.

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