solution was concentrated in vacuo to 5 mL and then poured into 50 mL of diethyl ether to give an oily product. It was dried in vacuo. The polymer thus isolated was about 0.10 g (28%).

Catalytic Hydrogenolysis of Copolymer 3a. To 0.37 g of copolymer (sample No. 1, Table I) dissolved in 25 mL of acetic acid 100 mg of PtO_2 was added. Hydrogenolysis was carried out at atmospheric pressure with vigorous shaking of a reaction flask. In 5 h, 150 mL of hydrogen gas was absorbed. Then, the catalyst was removed by filtration, and acetic acid was distilled out in vacuo. The distillation residue of polymer was washed thoroughly with diethyl ether and finally dried in vacuo to give 0.12 g of polymer. Anal. Found: C, 29.97; H, 4.73; P, 13.20.

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Copolymerization of Methyl α-*n*-Alkylacrylates (Alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) with Methyl Methacrylate[1,2]

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ABSTRACT: Methyl α-*n*-alkylacrylates (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) were copolymerized with methyl methacrylate in bulk at 50 °C using a free-radical catalyst (AIBN) and anionically (sodium) in toluene at room temperature. Free-radical copolymerizations yielded polymers having $\overline{M}_n$ from 11 600 to 29 000 (22–83% yield). Homopolymerizations, with longer reaction periods, resulted in dimers and trimers (14–18% yield). Anionic copolymerizations of methyl α-*n*-hexadecylacrylate yielded $\overline{M}_n$ from 6 708 to 20 000 (17–43% yield). With twice the reaction time (2 weeks), homopolymerization yielded $\overline{M}_n = 1940$ (42% yield). The rates of anionic and free-radical copolymerizations and homopolymerizations were low and approximately equal when the mol % methyl α-*n*-alkylacrylate in the initial monomer mix was >75. At <75 mol %, the rate of free-radical copolymerization increases rapidly with decreasing mol % methyl α-*n*-alkylacrylate in the initial monomer mix. The rate of anionic copolymerization increases slowly from 75 to 38 mol %. The long alkyl chain in the α position of the acrylic ester decreases markedly the polymerization rate. This is probably due to steric hindrance.

The behavior of methyl α-*n*-alkylacrylates (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) in copolymerization reactions with methyl methacrylate was investigated. This work is part of a study of polymers having long *n*-alkyl side chains attached directly to the polymer backbone.

In a previous paper,[3] the syntheses and homopolymerization reactions of methyl α-*n*-alkylacrylates (alkyl = $C_{12}H_{25}$, $C_{16}H_{33}$, and $C_{18}H_{37}$) were described. Monomers were prepared by a method which would yield an isomer free product. Anionic homopolymerizations were initiated with sodium metal or sodium naphthalene. The highest molecular weights and yields of polymer were obtained at 0 °C or above, using sodium metal as the catalyst. Yields and molecular weights, however, decreased with chain length (e.g., alkyl = $C_{12}H_{25}$, $\overline{M}_n = 15\,000$, 81% yield; alkyl = $C_{18}H_{37}$, $\overline{M}_n = 1380$, 12% yield). Free-radical polymerizations, in emulsion or bulk, yielded only small percentages of oligomers. Experimental evidence indicated that the steric effect of the long-chain α-*n*-alkyl group considerably decreased the rate of anionic homopolymerization and resulted in the formation of dimers and trimers in free-radical polymerization.

Prior to this work, the only homopolymers of α-*n*-alkylacrylic esters (alkyl > CH_3) reported were those of methyl α-*n*-alkylacrylates (alkyl $\lesssim C_4H_9$) prepared with anionic catalysts[4] or with diethylzinc–calcium complex[5] at −78 °C. The patent literature reports the polymerization of methyl α-*n*-alkylacrylates (alkyl = CH_3 to C_5H_{11}) initiated by heat (90–150 °C).[6]

It is well known,[7] however, that the copolymerization reactions of two olefinic monomers often show rate and mechanism characteristics considerably different from those of the homopolymerization reactions of either monomer alone. Copolymers, including monomers which would provide long alkyl side chains (in particular where the alkyl group is equal to or greater than $C_{16}H_{33}$), might, therefore, be accessible at higher polymerization rates and in yields sufficiently high for tech-

Table I
Free-Radical Copolymerization of Methyl α-n-Alkylacrylates, $CH_2{=}C(R)CO_2CH_3$ (M_1), with Methyl Methacrylate (M_2)[a]

α-R group in M_1	$[M_1]_0$,[b] mol %	Polym time, h	Conversion, mol %	m_1,[c] mol %	$[M_1]$,[d] mol %	$\overline{X}_n$[e]	Anal.[f] % C	% H	% O	$\overline{M}_n$[g]
$C_{16}H_{33}$	20.0	24	61.2	12.0	26.4	184	65.15	9.45	25.62	23 000
$C_{16}H_{33}$	25.0	48	75.1	19.8	39.0	141	67.45	9.79	22.87	20 000
$C_{16}H_{33}$	33.3	48	64.2	22.8	53.7	196	68.33	10.06	21.72	29 000
$C_{16}H_{33}$	50.0	48	39.5	26.5	65.3	96	69.14	10.26	20.66	15 000
$C_{16}H_{33}$	66.7	168	41.6	47.5	80.2	144	72.82	11.19	16.19	29 000
$C_{16}H_{33}$	75.0	168	21.5	66.5	77.3	65	74.94	11.83	13.43	15 600
$C_{16}H_{33}$[h]	100.0	336	17.6	100		2	77.53	12.80	10.01	634
$C_{18}H_{37}$	20.0	24	65.5	13.5	26.2	175	66.12	9.44	24.54	23 100
$C_{18}H_{37}$	25.0	48	72.1	18.2	42.6	128	67.66	9.91	22.79	18 400
$C_{18}H_{37}$	33.3	48	53.8	21.7	46.9	110	68.67	10.11	21.33	16 700
$C_{18}H_{37}$	50.0	48	42.8	37.3	54.8	86	72.03	11.09	16.90	16 170
$C_{18}H_{37}$	66.7	168	44.9	52.7	72.4	74	74.25	11.71	14.30	16 600
$C_{18}H_{37}$[h]	100.0	336	13.9	100			78.27	12.14	9.59	1 216
CH_3[i]	0.0	18	92.7	0			60.46	31.25	8.30	>30 000[j]

[a] Monomer mixture, 5.5 mM; catalyst (AIBN), 0.002 mM; polymerization temperature 50–55 °C. [b] Mol % M_1 in initial monomer mixture. [c] Mol % M_1 in copolymer. [d] Mol % M_1 in unchanged monomer mixture when polymerization was stopped. [e] Number-average degree of polymerization; where $\overline{M}_n$ = 20 000–30 000 ± 10%. [f] Microanalyses done by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. [g] Determined by vapor pressure osmometry; where $\overline{M}_n$ = 20 000–30 000 ± 10%. [h] Monomer, 3 mM; catalyst (AIBN), 0.001 mM. Where R = n-$C_{16}H_{33}$, Calcd for monomer $C_{20}H_{38}O_2$: C, 77.36; H, 12.33; O, 10.31; mol wt 310. Where R = n-$C_{18}H_{37}$, Calcd for monomer $C_{22}H_{43}O_2$: C, 78.04; H, 12.51; O, 9.45; mol wt 339. [i] Monomer (100% M_2), 6 mM; catalyst (AIBN), 0.002 mM. Calcd for monomer $C_5H_8O_2$: C, 59.98; H, 8.05; O, 31.97; mol wt 100. [j] $\overline{M}_n$ well above the limit for the vapor pressure osmometer.

Table II
Anionic Copolymerization of Methyl α-n-Alkylacrylates, $CH_2{=}C(R)CO_2CH_3$ (M_1), with Methyl Methacrylate (M_2)[a]

α-R group in M_1	$[M_1]_0$,[b] mol %	Polym time, h	Conversion, mol %	m_1,[c] mol %	$[M_1]$,[d] mol %	$\overline{X}_n$[e]	Anal.[f] % C	% H	% O	$\overline{M}_n$[g]
$C_{16}H_{33}$	33.3	168	43.2	20.7	42.9	70	67.80	9.92	22.30	9 994
$C_{16}H_{33}$	50.0	168	31.8	33.8	57.6	117	70.59	10.66	18.67	20 000
$C_{16}H_{33}$	66.7	168	16.7	40.2	72.0	36	71.63	10.92	17.43	6 708
$C_{16}H_{33}$	75.0	168	0.34[h]							
$C_{16}H_{33}$[i]	100.0	336	42.5			6	77.53	12.32	10.17	1 940
CH_3[j]	0.0	24	91.7				60.32	31.35	8.54	>30 000[k]

[a] Monomer mixture, 6 mM; catalyst (sodium), 0.2 mM, not all consumed when reaction was terminated; polymerization temperature is room temperature; solvent (toluene), 0.7 mL (where $[M_1]$ = 75.0, 1 mL). [b] Mol % of M_1 in initial monomer mixture. [c] Mol % of M_1 in copolymer. [d] Mol % of M_1 in the unchanged monomer mixture when polymerization was stopped. [e] Number-average degree of polymerization. [f] Microanalyses done by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. [g] Determined by vapor pressure osmometry; where $\overline{M}_n$ = 20 000 ± 10%. [h] Wt %. [i] Monomer, 3 mM; catalyst (sodium), 0.2 mm, all consumed at end of reaction; solvent (toluene), 0.7 mL. Calcd for monomer $C_{20}H_{38}O_2$: C, 77.36; H, 12.33; O, 10.31; mol wt 310. [j] Monomer (100% M_2), 6 mM; catalyst (sodium), 0.2 mM, not all consumed at end of reaction; solvent (toluene), 0.9 mL. Calcd for monomer $C_5H_6O_2$: C, 59.98; H, 8.05; O, 31.97; mol wt 100. [k] $\overline{M}_n$ well above the limit for the vapor pressure osmometer.

nological significance. A copolymer of methyl methacrylate with a methyl α-n-alkylacrylate (alkyl = $C_{16}H_{33}$) would have a similar structure to the latter in that it would contain both ester and long alkyl side chain groups.

Very little work has been reported on the copolymerization of α,β-unsaturated compounds having an n-alkyl group in the α position. Chikanishi and Tsuruta[8] prepared copolymers of methyl α-n-alkylacrylates (alkyl $\lesssim$ C_4H_9) with styrene, in bulk, using azobis(isobutyronitrile) (AIBN) as the catalyst. No studies, however, have been made on copolymerization reactions of the α,β-unsaturated compounds where the alkyl group in the α position is > C_4H_9.

Since homopolymerization rates of the methyl α-n-alkylacrylates were low (particularly where alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$), work was undertaken to determine the effect of an α-n-alkyl group, such as hexadecyl and octadecyl, on copolymerization reactions of methyl α-n-alkylacrylates. Methyl methacrylate was chosen as the comonomer. Both anionic and free-radical initiated copolymerizations were investigated. Sodium metal (anionic) and AIBN (free-radical) were the initiators.

Results and Discussion

The free-radical copolymerizations of methyl α-n-alkylacrylates (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) with methyl methacrylate (MMA) are summarized in Table I and the anionic copolymerization of methyl α-n-hexadecylacrylate in Table II. Tables I and II also include elemental analyses, number average molecular weights ($\overline{M}_n$), and degrees of polymerization ($\overline{X}_n$) of the copolymers. Free-radical and anionic homopolymerizations are shown for comparative purposes.

Rates of copolymerization (free-radical and anionic) were plotted against the average mol % $[M_1]_{av}$ of the methyl α-n-alkylacrylate (M_1) in the monomer mix. The results are shown in Figure 1. Since the copolymerizations were allowed to

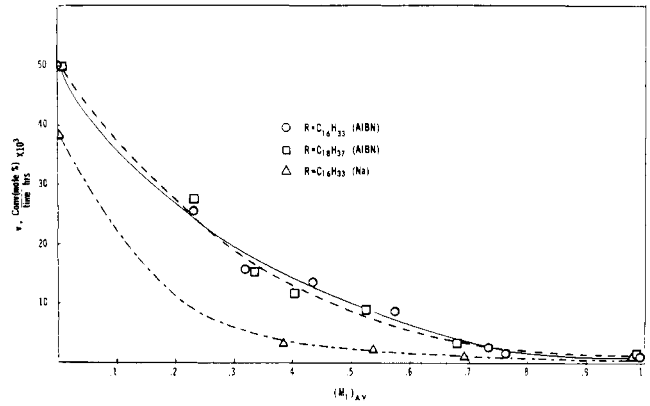

Figure 1. Relation between copolymerization rate (υ) and average monomer composition for the copolymerization system methyl α-R-substituted acrylates (M_1)–MMA (M_2).

proceed to high conversions, $[M_1]_{av}$ was used according to the following equation:

$$[M_1]_{av} = ([M_1]_0 + [M_1])/2$$

where $[M_1]_0$ and $[M_1]$ are the initial mole fraction of M_1 and the mole fraction of M_1 in the unchanged monomer mixture, respectively, when polymerization is terminated. This equation was adopted by Chikanishi and Tsuruta[8] in their work on the copolymerization of methyl α-n-alkylacrylates (alkyl $\lesssim C_4H_9$) with styrene.

The data in Figure 1 indicate that the rate of free-radical copolymerization decreases markedly as the mol % methyl α-n-alkylacrylate (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) increases in the comonomer mixture up to $[M_1]_{av} \sim 0.75$, which corresponds to 67 mol % methyl α-n-alkylacrylate (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) in the initial monomer mixture (Table I). At this point, the copolymerization rate approximates the homopolymerization rate of the corresponding methyl α-n-alkylacrylate (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$). Figure 1 indicates that the copolymerization rate of methyl α-n-hexadecylacrylate approximates that of methyl α-n-octadecylacrylate. The rates of anionic copolymerization of styrene with methyl α-ethylacrylate and methyl α-n-butylacrylate, where there is also an increase of two methylene groups in the α-alkyl chain, were reported to be similar.[8] The rate of anionic copolymerization is less than that of free-radical copolymerization up to approximately $[M_1]_{av} = 0.75$ where the anionic copolymerization rate approximates that of the free-radical rates as well as the anionic and free-radical homopolymerization rates. It should be noted that anionic polymerizations are very sensitive to such variables as dilution and temperature. Therefore, under another set of reaction conditions than those described in the Experimental Section, the rates might be quite different.

Although methyl α-n-alkylacrylate (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) in both the free-radical and anionic polymerizations of MMA decreases considerably the rate of the polymerization reaction, the MMA has the opposite effect on the rate of the free-radical polymerization of methyl α-n-alkylacrylate. This is most evident in the free-radical copolymerization where more than 25 mol % MMA is present in the initial monomer mixture (Figure 1, Table I). In the anionic polymerization of methyl α-n-hexadecylacrylate (Figure 1, Table II), with the addition of MMA, there is only a gradual increase in the polymerization rate up to 38 mol % MMA ($[M_2]_0$). At this point, it may be seen that the rate increases up to 100 mol % MMA.

Figure 1 also illustrates clearly how much the anionic and free-radical polymerization of an α-n-alkylacrylic ester is suppressed by the existence of a long α-n-alkyl group in place of a methyl. Chikanishi and Tsuruta[8] found this to be the case for the shorter α-n-alkyl groups (alkyl = C_2H_5 to C_4H_9) in their copolymerization studies of methyl α-n-alkylacrylates (alkyl $\lesssim C_4H_9$) with styrene. Furthermore, Gisser and Mertwoy[3] found that the anionic homopolymerizations of methyl α-n-alkylacrylates (alkyl $\gtrsim C_{12}H_{25}$) were more sterically hindered than those of the α-n-alkylacrylic esters (alkyl = C_2H_5 to n-C_4H_9). (Methyl α-n-alkylacrylates (alkyl = C_2H_5 to $C_{18}H_{37}$) will form oligomers slowly with free-radical catalysts.)

As can be seen in Tables I and II, the molecular weights ($\overline{M}_n$) and degrees of polymerization ($\overline{X}_n$) were significantly higher for the polymers obtained from the anionic and free-radical copolymerization reactions than those isolated from the homopolymerization reactions. In the free-radical initiated reactions, the yield of copolymer (mol % conversion) was greater than that of the homopolymer and increased significantly with increasing mol % of MMA in the initial monomer mix. The fact that the lower yields of copolymer were obtained in anionic catalyzed copolymerizations is attributed to low reaction rates.

All the polymers, which range from clear tacky (mol % MMA ~25) to hard solids (as mol % MMA increases beyond 25), are soluble in aromatic hydrocarbons and chloroform. Their solubility in aliphatic hydrocarbons increases with increasing mol % methyl α-n-alkylacrylate (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) in the copolymer. At 50 mol %, the polymers are completely soluble in cold hexane and hexadecane.

This is the first report of copolymers from methyl α-n-alkylacrylates (or α-n-alkylacrylic esters) having an alkyl group greater than butyl. The experimental evidence indicates that relatively high molecular weight copolymers of methyl α-n-alkylacrylates (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) with methyl methacrylate can be prepared in fairly high yields, in contrast to the homopolymerization reactions where both yields and molecular weights were low.

Experimental Section

(A) Monomers. Methyl α-n-hexadecyl- and methyl α-n-octadecylacrylate were prepared as described by Gisser and Mertwoy.[3] Before use, they were recrystallized from methanol and dried in a vacuum oven (40°, 1 mm) to constant weight. Methyl methacrylate was a commercial product and purified by the usual methods. It was distilled under nitrogen immediately before use.

(B) Radical Copolymerization. About 5–6 mM of monomer mixture of methyl α-n-alkylacrylate and methyl methacrylate were accurately weighed into a glass tube and 0.001 mM of azobis(isobutyonitrile) (AIBN) was added. After being evacuated and filled with nitrogen several times, the tube was sealed and placed in an oven at 50 °C. The reactions were allowed to proceed to relatively high conversions until there was no visible change noted in the viscosity of the contents in the tubes. At this point the tubes were opened, chloroform was added to dissolve the contents, and the resulting solution was filtered to remove any fragments of glass. The solution was then concentrated, and methanol was added to precipitate the polymer. The supernatant liquid was decanted, and the remaining polymer was washed several times with methanol and then dried at 40–50 °C (1 mm). Details of the polymerization are in Table I.

(C) Anionic Copolymerization. About 5.5 mM of monomer mixture of methyl α-n-hexadecylacrylate and methyl methacrylate were accurately weighed into a glass tube which had been flushed with dry nitrogen. The solvent (0.7 mL of toluene), dried by distilling over sodium under nitrogen, was added followed by 0.2–0.3 mM sodium (anionic initiator). Where the monomer mixture contained 75 mol % methyl α-n-hexadecylacrylate, it was necessary to add 1 mL of toluene. The tubes were sealed under nitrogen, as described in radical copolymerizations, and shaken at room temperature for 7 days. At this point the tubes were opened, and a small amount of methanol was added to terminate the reaction. The remaining procedure follows that for the radical copolymerization. Details of the anionic polymerization are in Table II.

(D) Purification of the Polymers. The copolymers were purified by repeated precipitation using either a toluene–methanol system or a chloroform–methanol system where the polymers were found to be less soluble. After each precipitation, the polymer was dried at 40 °C (1 mm) in a vacuum oven. Any unreacted methyl methacrylate would be removed in the drying process. The copolymer was considered pure when the absorption bands for olefinic linkages found in the methyl α-n-alkylacrylate had disappeared from its infrared spectrum.

(E) Identification of the Copolymers. Copolymers were identified through infrared spectroscopy[9] and elemental analyses (Tables I and II). Infrared spectra showed that the absorption bands for olefinic linkages at 1631 (vinyl CO) and 937 cm^{-1} (R—C[C(=O)—]=CH$_2$) found in the spectra of the methyl α-n-alkylacrylates (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) had disappeared in each of the copolymers. There was a slight shift of the absorption band at 1730 cm^{-1} (characteristic of α,β-unsaturated esters) to 1739 cm^{-1} (characteristic of saturated esters). There was a band at 720 cm^{-1} ($(CH_2)_n^-$, $n \gtrless 4$) indicating the presence of a long alkyl chain, which would also be present in the monomer. Copolymer composition was calculated on the basis of the average carbon content in the copolymer in duplicate analyses.

(F) Homopolymerizations. Methyl α-n-alkylacrylates and methyl methacrylate were homopolymerized using free-radical (AIBN) and anionic (sodium) catalysts. In the free-radical catalyzed polymerizations, the reaction mixtures were as follows: 3 mM methyl α-n-alkylacrylate, 0.001 mM AIBN; 6 mM methyl methacrylate, 0.002 mM AIBN. The anionic polymerization reaction mixtures were as follows: 3 mM methyl α-n-alkylacrylate, 0.16 mM sodium, 1 mL of toluene; 6 mM methyl methacrylate, 0.23 mM sodium, 0.9 mL of toluene. The polymers were isolated, purified, and identified in the same manner as the copolymers.

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ESR Studies of Copolymerization of Crotonic Compounds with Acrylonitrile

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ABSTRACT: Copolymerization of 1,2-disubstituted vinylmonomers with acrylonitrile (AN) was studied by electron spin resonance. Using a rapid-flow mixing system the initial stages in the copolymerization of crotonic acid (CAC), crotonitrile (CNI), crotonaldehyde (CAD), and the ethyl ester of crotonic acid (CAEt) with acrylonitrile were studied in aqueous solution. The head-to-tail ratio of the formed monomer radicals follows the order CAEt ≈ CAC > CNI > CAD. The relative reactivities of the head and tail radicals toward AN correlate well with resonance and inductive effects in the monomers. The overall reactivity of the monomer radicals toward AN follows the order CAD > CAC > CAEt > CNI.

In previous studies of radical polymerization in our laboratory, using the ESR technique, the homopolymerization of monomers like vinyl esters, butadiene, trimethylolpropane monoallyl ether has been investigated.[1-3] Copolymerization of vinyl esters with various monomers[4,5] and copolymerization of water-soluble monomers like vinyl sulfonate and allyl sulfonate with acrylonitrile[7] have also been investigated. Reactions of 1,2-substituted vinyl monomers, i.e., crotonic compounds, when attacked by free-radical initiators were investigated by Izumi and Rånby.[6]

Electron spin resonance combined with a rapid flow mixing system is a powerful method for investigating the reactions in free-radical polymerizations. Particularly for copolymerizations this method has given good results. Conventionally, reactivity ratios in copolymerization are derived from the overall composition of the copolymers formed. This gives only a statistical picture of the system. With ESR studies it is possible to measure directly radical reactivities toward monomers.

In this study we present results obtained for copolymerization of four 1,2-substituted vinyl monomers (crotonic compounds) with acrylonitrile. The monomers studied are crotonic acid, crotonitrile, croton aldehyde, and ethyl crotonate (the ethyl ester of crotonic acid).

From ESR data the relative reactivities of the different monomer radicals to acrylonitrile monomer were derived and compared with reactivity ratios calculated from Q,e values from the literature. Furthermore, information about the conformation of the radicals was obtained from the ESR spectra.

Experimental Section

The ESR spectra were observed using a flow system[8-10] with a rapid-flow mixing cell[11] inserted into a TE 011 mode cylindrical cavity of a JES-ME-1X spectrometer from JEOL Ltd., Tokyo.

The flow rate used was 7.5 mL/s unless otherwise stated. This flow rate corresponds to a time lag from mixing to the center of the cavity of 0.018 s. The polymerization was initiated by hydroxyl radicals formed in a redox reaction between aqueous hydrogen peroxide (0.22 mol/L) in one of the solutions and aqueous titanium trichloride (0.016 mol/L) in the other. The pH was adjusted to 1.4 by adding sulfuric acid. The monomer concentrations used were in the range 0.005–0.07 mol/L. All measurements were made at room temperature (22 ± 2 °C).

The ESR signal was recorded as the first derivative of the microwave absorption vs. the magnetic field. Radical concentration was taken as proportional to signal amplitude times the square of the signal width. The magnetic field was calibrated with an Mn^{2+} sample. The following reagents were used: 15% titanium trichloride in water (Riedel-de Haen, Hannover), 30% hydrogen peroxide in water, concentrated sulfuric acid, acrylonitrile (AN), crotonic acid (CAC), croton aldehyde (CAD), ethyl crotonate (CAEt) (all from E. Merck AG, Darmstadt), and crotonitrile (CNI) (Merck-Schuchardt).