Preparation and Homopolymerization of Methyl α-*n*-Alkylacrylates[1,2]

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Abstract: The homopolymerization of methyl α-*n*-alkylacrylates with long alkyl groups was studied. Methyl α-*n*-dodecyl-, methyl α-*n*-hexadecyl-, and methyl α-*n*-octadecylacrylate were prepared from the appropriate alkylmalonic monomethyl esters *via* a Mannich-type reaction which yielded a product free from isomeric impurities. Anionic homopolymerizations were carried out using sodium naphthalene (at −75°) and sodium metal (at 0° and room temperature) as initiators. The highest molecular weights and yields of polymer have thus far been obtained using sodium metal; *e.g.*, after 14 days at 0° a $\bar{M}_n$ of 15,000 (80% yield) was obtained for poly(methyl α-*n*-dodecylacrylate), and after 8 days at room temperature a $\bar{M}_n$ of 7083 (70% yield) was obtained for poly(methyl α-*n*-hexadecylacrylate). Emulsion polymerizations of the methyl α-*n*-dodecylacrylate and methyl α-*n*-octadecylacrylate with ammonium persulfate and sodium bisulfite yielded traces of oligomers. Poly(methyl α-*n*-dodecylacrylate) is a clear, colorless, sticky, rubbery polymer. Its X-ray diffraction pattern shows it to be amorphous at room temperature. The poly(methyl α-*n*-hexadecylacrylate) and poly(methyl α-*n*-octadecylacrylate) are white waxes which, when heated, resemble the poly(methyl α-*n*-dodecylacrylate). X-Ray diffraction studies at room temperature on a thin film of the polymers show crystallinity. All of the polymers are readily soluble in aromatic and aliphatic hydrocarbons and ethers and slightly soluble in alcohols and ketones.

As part of a study on polymers having long *n*-alkyl side chains, experiments were undertaken on the preparation and polymerization of methyl α-*n*-alkylacrylates (alkyl $\geq$ $C_{12}H_{25}$). Although a great deal of work has been reported on the polymerization of methacrylic esters, there is no information on the preparation and homopolymerization of methyl α-*n*-alkyl-substituted acrylic esters (alkyl $\geq$ C_6H_{13}).

Chikanishi and Tsuruta[3] prepared and successfully homopolymerized anionically at −78° a series of α-alkylacrylic esters (alkyl = C_2H_5 to C_4H_9). Attempts to initiate polymerization of these compounds with radical initiators resulted in either low molecular weight polymer or no polymer at all. Hasche and Utermohlen[4] reported that monohydric alcohol esters of α-ethylacrylic acid do not homopolymerize to solid high polymers under free-radical conditions. Polymers of methyl α-ethyl- and methyl α-*n*-butylacrylate using diethylzinc–calcium complex catalyst have been reported by Iwama *et al.*[5] The monomers were prepared by the same method as used by Chikanishi and Tsuruta.[3] The patent literature[6] reports the polymerization initiated by heat (90–150°) of methyl α-*n*-alkylacrylates (alkyl = CH_3 to C_5H_{11}).

Work on 1,1-disubstituted ethylenes, such as α-*n*-alkylstyrenes (alkyl = C_7H_{15} and C_9H_{19})[7] and α-*n*-alkylacrylonitriles (alkyl = C_7H_{15} to $C_{12}H_{25}$),[8] indicates that a monomer with fairly long α-alkyl groups will homopolymerize if prepared by a method yielding a pure, isomer-free product. Previously, Bailey *et al.*[9] prepared a series of α-alkylacrylonitriles (alkyl = C_2H_5 to C_6H_{13}) by a pyrolysis technique which minimized the formation of isomers. Polymerization of these monomers by peroxide resulted in the first report of moderately high molecular weight polymers for this series. They concluded that previous preparation of these monomers contained isomeric impurities which could act as chain-transfer agents and thus prevent polymer formation. They also concluded that steric effect of the α-alkyl group did not prevent polymerization but probably exaggerated the effect of isomeric impurities in polymerization.

In view of the above mentioned work on 1,1-disubstituted ethylenes, it was considered likely that methyl α-*n*-alkylacrylates (alkyl $\geq$ $C_{12}H_{25}$) would homopolymerize if prepared by a method that yielded a relatively pure isomer-free monomer. It was therefore decided to employ the series of reactions used by Chikanishi and Tsuruta[3] for the preparation of their monomers. This method combined the extension of the carbon skeleton with the feature of position specific introduction of the ethylenic group, and thereby yielding an unambiguous product. The reaction scheme is shown as follows

$$CH_2(COOCH_3)_2 + RBr \xrightarrow[\text{in } CH_3OH]{CH_3ONa} RCH(COOCH_3)_2 \xrightarrow[2.\ HCl]{1.\ KOH}$$

$$RCH(COOH)COOCH_3 \xrightarrow[2.\ HCHO]{1.\ NH(C_2H_5)_2} CH_2{=}C(R)CO_2CH_3$$

$$R = C_{12}H_{25}, C_{16}H_{33}, C_{18}H_{37}$$

The monomers chosen for study were methyl α-*n*-dodecyl-, methyl α-*n*-hexadecyl-, and methyl α-*n*-octadecylacrylate. It was decided to initially polymerize the monomers with anionic catalysts. As previously mentioned, the methyl α-alkylacrylates (alkyl = C_2H_5 to C_4H_9)[3] only polymerized using anionic catalysts but did not polymerize under radical conditions.

Results and Discussions

A. Monomers. The monomers were identified by elemental analysis and infrared spectroscopy. The intermediates prepared (dimethyl *n*-alkylmalonate and *n*-alkylmalonic monomethyl ester) were identified through elemental analysis. The yields of methyl α-*n*-alkylacrylates reported in the Experimental Section are those obtained from the reaction between the monomethyl ester and formaldehyde, and they ranged from 55 to 68%. The overall yields, however, starting with malonic ester, were 33.2, 34.7, and 29.0% for methyl α-*n*-dodecyl-, methyl α-*n*-hexadecyl-, and methyl α-*n*-octadecylacrylate, respectively.

In the preparation of the monomers, modifications were made in reaction time and temperature, proportions of solvent to reactants, and methods of purification from the procedure of Chikanishi and Tsuruta.[3] The long *n*-alkyl chain apparently decreases the reactivity as well as the solubility of the intermediates. Consequently, all the reactions leading to the monomers, in general, required longer reaction periods than those necessary for the short chain α-*n*-alkylacrylic esters.[3] In some instances, the application of heat was necessary.

B. Homopolymerization Studies. The results of anionic polymerizations of the methyl α-*n*-alkylacrylates are given in Table I. The polymers were purified by precipitation from a toluene (solvent)–methanol (nonsolvent) solu-

Table I
Anionic Polymerization of Methyl α-*n*-Alkylacrylates, $CH_2{=}C(R)CO_2CH_3$[a]

Reaction No.	R	Monomer Mol	Catalyst	Mol % of Catalyst to Monomer	Solvent	Vol. Solvent (ml)	Polym Time Days	Polym Temp (°C)	Conv %	*Anal.*[b–d] C (%)	H (%)	O (%)	$\bar{M}_n$[e]
1	*n*-$C_{12}H_{25}$	0.060	Sodium naphthalene	12	H_4furan	65[f]	21	−75	35	75.21	11.78	13.33	7,825
									12	75.56	12.11	13.26	4,756
									6	75.45	12.23	13.16	2,967
2	*n*-$C_{12}H_{25}$	0.013	Sodium naphthalene	8	H_4furan	34[g]	56	−75	52	75.87	11.84	12.02	9,040
3	*n*-$C_{12}H_{25}$	0.034	Sodium[h]	3[i]	None		7	RT	53	76.02	12.15	11.73	6,600
4	*n*-$C_{12}H_{25}$	0.032	Sodium[j]	9[k]	Toluene	7	14[l]	0	38	75.89	11.70	12.91	7,780
									31	76.24	12.04	12.30	2,178
5	*n*-$C_{12}H_{25}$	0.035	Sodium[j]	9[i]	Toluene	7	14	0	81	76.11	11.83	12.18	15,000
									2	76.02	12.02	12.42	2,600
6	*n*-$C_{12}H_{25}$	0.038	Sodium[j]	5[k]	Toluene	15	20	−5	16	75.55	11.87	12.83	8,760
									4	75.68	11.77	12.74	956
7	*n*-$C_{16}H_{33}$	0.011	Sodium naphthalene	4.5	H_4furan	40[m]	35	−75	14	77.64	12.00	10.36	621
8	*n*-$C_{16}H_{33}$	0.008	Sodium naphthalene	6.2	H_4furan	40	35	0	16	80.12	12.81	7.62	1,307[n]
9	*n*-$C_{16}H_{33}$	0.007	Sodium[j]	7.5[k]	Toluene	1.2	8	RT	70	77.22	12.33	10.42	7,083
									5	77.42	12.01	10.62	2,499
10	*n*-$C_{16}H_{33}$	0.017	Sodium[j]	3.6[k]	Toluene	15	28	0	10	77.39	12.27	10.48	2,360
11	*n*-$C_{18}H_{37}$	0.013	Sodium naphthalene	46	H_4furan	60[m]	20	−75	20	78.04	12.13	10.16	1,220
12	*n*-$C_{18}H_{37}$	0.002	Sodium naphthalene	35	H_4furan	34[m]	56	−75	20	77.97	12.20	9.70	1,321
13	*n*-$C_{18}H_{37}$	0.003	Sodium[j]	9[k]	Toluene	3	14	RT	27	77.81	12.25	10.10	1,380

[a] All polymers were soluble in aromatic and aliphatic hydrocarbons and ether and slightly soluble in alcohol and ketones. [b] Where R = *n*-$C_{12}H_{25}$, Calcd for monomer $C_{16}H_{30}O_2$: C, 75.59; H, 11.81; O, 12.60; mol wt 254. 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. [c] Polymers were fractionated from a toluene-methanol solution. Only fractions having $\bar{M}_n > 950$ are reported, with the exception of reaction 7. [d] Analyses done by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. [e] Determined by vapor pressure osmometry. [f] Almost 50% of monomer remained undissolved. [g] Some monomer remained undissolved in H_4furan. [h] Flakes of sodium. [i] Not all sodium consumed by end of reaction. [j] Sodium sand. [k] All sodium consumed by end of reaction. [l] Reaction was initiated at room temperature (RT), after 4 days the temperature was lowered to 0°. [m] Monomer only slightly soluble in H_4furan at −75°. [n] Elemental analyses indicates compound not poly(methyl α-*n*-hexadecylacrylate).

Table II
Emulsion Polymerization of Methyl α-*n*-Alkylacrylates, $CH_2{=}C(R)CO_2CH_3$

R	Monomer (g)	Ammonium Persulfate (g)	Sodium Bisulfite (g)	Duponol ME[a] (g)	Tween 20[b] (g)	Water (g)	Temp (°C)	Time (hr)	Conv (%)	$\bar{M}_n$
n-$C_{12}H_{25}$	10.0	0.006	0.01	0.40	0.80	37	50	3.5	Trace	875
n-$C_{18}H_{37}$	7.7	0.006	0.01	0.31	0.62	29	63	24.0	Trace	1005

[a] Sodium lauryl sulfate. [b] Polyoxyethylene (20) sorbitan monolaurate.

tion. In some cases, more than one fraction was isolated. All fractions having $\bar{M}_n > 950$ are reported in Table I. Elemental analyses (Table I) and infrared spectroscopy were employed to establish the identity of the poly(methyl α-*n*-alkylacrylates). The highest molecular weight polymer of methyl α-*n*-dodecyl- and methyl α-*n*-hexadecylacrylate and yields were obtained using sodium sand and toluene as the solvent (reactions 5 and 10). The molecular weights of poly(methyl α-*n*-octadecylacrylates) prepared using sodium naphthalene or sodium sand (reactions 12 and 13) were essentially the same. However, the yield of polymer isolated from the sodium sand catalyzed reaction was slightly higher, and the reaction time was significantly lower (14 days compared to 56 days).

Sodium metal produced polymers at 0° and room temperature. The monomers dissolved readily in toluene. The highest yields and molecular weights were obtained when the dilution with toluene was the least; 81%, $\bar{M}_n = 15{,}000$ for poly(methyl α-*n*-dodecylacrylate) (reaction 5) and 70%, $\bar{M}_n = 7083$ for poly(methyl α-*n*-hexadecylacrylate) (reaction 9). Since methyl α-*n*-dodecylacrylate (unlike hexadecyl and octadecyl) is a liquid at room temperature, an attempt was made to polymerize it without solvent (reaction 3). The reaction mixture became too viscous to stir after 7 days, and the reaction was terminated. Almost 50% of monomer remained unreacted.

Chikanishi and Tsuruta,[3] using anionic initiators, found that the highest yield of poly(α-alkylacrylate) (alkyl = C_2H_5 to C_4H_9) was obtained with sodium naphthalene at −78°. Their data indicated that as chain length of the α-alkyl group increases, the reaction time should be increased (*e.g.*, α-alkyl = C_2H_5, 3 days, *n*-C_4H_9, 7 days). It was therefore expected that by increasing the reaction time considerably, the long α-*n*-alkyl-chain acrylic esters would produce higher molecular weight polymers with sodium naphthalene than those actually obtained (Table I). The lower molecular weights were attributed to the fact that the solubility of the monomers in H_4furan at −75° decreased considerably with α-alkyl chain length. (In fact none of the monomers were completely soluble at −75° in the amount of H_4furan employed; see Table I.)

Methyl α-*n*-dodecylacrylate was the most soluble of the monomers, and the highest $\bar{M}_n$ polymers and yields were obtained with this monomer (reactions 1 and 2). In reaction 2 where the ratio of solvent to monomer and reaction time were increased, the $\bar{M}_n$ and yield of polymer increased. However, methyl α-*n*-hexadecyl- and methyl α-*n*-octadecylacrylate were only slightly soluble in H_4furan at −75° (reactions 7, 11, and 12), and a low yield of low $\bar{M}_n$ polymer was isolated.

Attempts to polymerize methyl α-*n*-hexadecylacrylate at 0° (all the monomer was soluble) resulted in a low molecular weight polymer. The elemental analysis of the product indicated that it was not poly(methyl α-*n*-hexadecylacrylate). Chikanishi and Tsuruta[3] found that with the shorter α-alkyl-chain α-alkylacrylic esters almost no polymer could be formed at 0° or higher with anionic catalysts. They suggested that some side reaction of catalyst and monomer may have taken place. (They did not report the use of sodium metal as a initiator.)

Polymerization carried out in emulsion with ammonium persulfate (initiator) and sodium bisulfite (activator) resulted in traces of low molecular weight polymer (Table II). Since emulsion polymerizations of the methyl α-*n*-dodecyl- and methyl α-*n*-octadecylacrylates were unsuccessful, attempts to polymerize methyl α-*n*-hexadecylacrylate were not made. Furthermore, attempts to polymerize methyl α-*n*-octadecylacrylate in bulk with azobisisobutyronitrile at 50° resulted, after 14 days, in a low molecular weight polymeric product ($\bar{M}_n = 1216$; 14% yield). These results indicate that the α-*n*-alkyl group exerts a strong effect in interfering with free radical polymerization. (Similar results were obtained with methyl α-*n*-alkylacrylates (alkyl = C_2H_5 to C_4H_9).)[3]

Poly(methyl α-*n*-dodecylacrylate) is a clear, colorless, sticky, rubbery polymer with a $\bar{M}_n > 9000$. The polymers having a $\bar{M}_n < 9000$ are not rubbery but more like a taffy which can be pulled into threads. Poly(methyl α-*n*-hexadecylacrylate) and poly(methyl α-*n*-octadecylacrylate) are white wax-like materials which when heated resemble the poly(α-*n*-dodecylacrylic ester) having the lower $\bar{M}_n$. X-Ray diffraction patterns made at room temperature on thin films of the poly(methyl α-*n*-hexadecylacrylate) and the poly(methyl α-*n*-octadecylacrylate) show crystallinity. The poly(methyl α-*n*-dodecylacrylate) is amorphous at room temperature. All the poly(methyl α-*n*-alkylacrylates) prepared were soluble in aromatic and aliphatic hydrocarbons, ethers, and chloroform. They were slightly soluble in alcohols and ketones.

This is the first report of homopolymers from methyl α-*n*-alkylacrylates (or α-*n*-alkylacrylic esters, in general) having an alkyl group larger than amyl. The experimental evidence indicates that these monomers will homopolymerize anionically, but the steric effect of the long-chain α-*n*-alkyl group may considerably decrease the rate of polymerization. Polymerizations at 0° or above, where there are no solubility problems (*e.g.*, with sodium metal), have thus far produced the highest molecular weight polymers.

Experimental Section

A. Monomers. Methyl *n*-dodecylmalonate (I) was prepared from dimethylmalonate (1.1 mol) and sodium methoxide (1.0 mol) in 600 ml of methanol and dodecyl bromide (1.0 mol) by the method reported for ethyl *n*-butylmalonate[10] except that the reaction mixture was warmed to 40° during the addition of the halide and then refluxed for 16 hr. The product was fractionated (Vigreux column) *in vacuo* and collected at 135–140° at 0.7–0.9 mm. A 67% yield was obtained. *Anal.* Calcd for $C_{17}H_{32}O_4$: C, 67.96; H, 10.74; O, 21.30; mol wt 300. Found: C, 67.97; H, 10.73; O, 21.20; mol wt 318.

***n*-Dodecylmalonic Monomethyl Ester (II).** To a solution of 43.1 g of potassium hydroxide (86.1%) in 270 ml of methanol was added 0.66 mol of I in 146 ml of methanol, and the solution was stirred for about 2 days (until approximately neutral). The resulting solution was evaporated almost to dryness *in vacuo* yielding a white salt, 1 l. of water was added, and the mix was stirred until the salt dissolved (3 hr). The resulting solution was acidified with 6 *N* HCl while stirring, and the half-ester precipitated. The product was filtered, washed with water until the washings were neutral, dissolved in ether, occluded water separated, the ether layer washed free from acid, and dried over anhydrous sodium sulfate. After filtering, the ether was evaporated off. The residue was recrystallized from methanol, dried in a vacuum oven, dissolved in anhydrous benzene, and percolated through a column of activated silica gel to separate it from any unreacted diester. The half-ester, which remained on the column, was eluted with ethyl ether, the ether evaporated, and the product dried in a vacuum oven. (The percolation through silica gel was repeated several times until the acid number corresponded approximately to the theoretical value of 286.) A 90% yield was obtained, mp 45–50°. *Anal.* Calcd for $C_{16}H_{30}O_4$: C, 67.09; H, 10.56; O, 22.35; mol wt 286. Found: C, 67.04; H, 10.52; O, 22.24; mol wt 285.

Methyl α-*n*-Dodecylacrylate (III). Diethylamine (0.22 mol) was added to II (0.22 mol), and the pasty mixture warmed on a steam bath and stirred until clear. To this was slowly added 0.22 mol of formaldehyde (37% in methanol-water solution). Stirring was continued, the solution was warmed until it began to cloud, and CO_2 was evolved (approximately 3 hr). The solution was cooled to room temperature, 10 ml of methanol was added, and stirring was continued for 1.5 hr. After standing overnight, two distinct layers had separated. The lower aqueous layer was saturated with potassium carbonate and any separated organic material was added to the upper organic layer. The organic layer was acidified with 3 *N* HCl, and the undissolved portion was washed free of acid and dried over anhydrous potassium carbonate. The product was filtered off and dissolved in the minimum amount of anhydrous benzene, and percolated through a column of activated silica gel to remove any unreacted II. The benzene was evaporated *in vacuo,* the product fractionated (Vigreux column) *in vacuo,* and collected at 120–127° at 1.0–1.8 mm. A zero acid number indicated the absence of any unreacted II. A 55% yield was obtained. *Anal.* Calcd for $C_{16}H_{30}O_2$: C, 75.53; H, 11.89; O, 12.58; O, 12.58; mol wt 254. Found: C, 75.20; H, 11.91; O, 12.37; mol wt 252.

Methyl *n*-hexadecylmalonate (IV) was prepared by a method similar to that used for I from hexadecyl bromide (1.0 mol), dimethyl malonate (1.1 mol), and sodium methoxide (1.0 mol) in 800 ml of methanol. After distilling off most of the methyl alcohol, the residue was stirred with water (1 l.) to dissolve the sodium bromide, and the remaining white solid product was filtered off, dissolved in ethyl ether, washed to remove salts and alkali, and dried over anhydrous sodium sulfate. After filtering, the ether and low boiling materials were distilled off *in vacuo,* and the product was fractionated (Vigreux column) *in vacuo* and collected at 182–184° (0.50–0.59 mm). A 68% yield of a white solid product was obtained. *Anal.* Calcd for $C_{21}H_{40}O_4$: C, 70.74, H, 11.31; O, 17.95; mol wt 356. Found: C, 70.36; H, 11.38; O, 18.15; mol wt 392.

***n*-Hexadecylmalonic Monomethyl Ester (V).** Compound IV (0.66 mol), dissolved in 1600 ml of hot methanol, was added to 43 g of potassium hydroxide (86.1%) in 270 ml of methanol, and the solution was stirred while warm for 4 days. Water (4 l.) was added to dissolve the potassium salt, and the solution was acidified with 6 *N* HCl to precipitate the half-ester. The remainder of the procedure follows that given for II. A 75% yield of monomethyl ester was obtained, mp 65–66°. *Anal.* Calcd for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18; O, 18.69; mol wt 342. Found: C, 69.92; H, 10.98; O, 18.98; mol wt 348.

Methyl α-*n*-hexadecylacrylate (VI) was prepared from V (0.1 mol) in a manner similar to III with some modifications. The methanol (10 ml) was added to the reaction mixture after 1 hr stirring and warming. The reaction mixture was stirred for 2 additional hr and cooled to room temperature, and benzene was added to dissolve the white pasty mass. The aqueous layer, which separated, was saturated with potassium carbonate and washed with benzene, and the benzene washings were added to the organic layer. The organic layer was acidified with 3 *N* HCl. The upper organic layer was decanted off, washed free of acid, and dried over anhydrous potassium carbonate. If an emulsion formed on acidification, it was broken either by the addition of anhydrous sodium sulfate or by centrifuging. The benzene was evaporated *in vacuo,* the product (white solid) was dissolved in the minimum amount of benzene and purified in the same manner as III. The product was collected at 148° at 0.42 mm. A 68% yield was obtained, mp 30–31°. *Anal.* Calcd for $C_{20}H_{38}O_2$: C, 77.36; H, 12.33; O, 10.31; mol wt 310. Found: C, 77.59; H, 12.46; O, 9.87; mol wt 331.

Methyl *n*-octadecylmalonate (VII) was prepared from octadecyl bromide (0.45 mol), dimethyl malonate (0.50 mol), and sodium methoxide (0.50 mol) in 400 ml of methanol by the same method as IV, the reaction mixture being refluxed for 15 hr. After most of the methanol had been distilled off, 500 ml of water was added and the resulting mixture was stirred. The product was filtered off and dissolved in 350 ml of ether. After distilling off the low-boiling materials *in vacuo,* the product was recrystallized from methanol. A 69% yield was obtained, mp 46–47°. *Anal.* Calcd for $C_{23}H_{43}O_4$: C, 72.02; H, 11.30; O, 16.68; mol wt 384. Found: C, 71.89; H, 11.41; O, 16.78; mol wt 404.

***n*-Octadecylmalonic Monomethyl Ester (VIII).** Compound VII (0.17 mol) dissolved in a mixture of 600 ml of methanol and 300 ml of benzene was added to 11.3 g of potassium hydroxide (86.1%) in 67 ml of methanol, and the solution was stirred while warm for 3 days. Water (4 l.) was added to dissolve the potassium salt, and the solution was acidified with 6 *N* HCl to precipitate the half-ester. The remainer of the procedure follows that given for II. A 70% yield was obtained, mp 68.5–70.0°. *Anal.* Calcd for $C_{22}H_{42}O_4$: C, 71.30; H, 11.43; O, 17.27; mol wt 371. Found: C, 71.05; H, 11.52; O, 17.45; mol wt 375.

Methyl α-*n*-Octadecylacrylate (IX). Compound VIII (0.16 mol), diethylamine (0.16 mol), and formaldehyde (0.16 mol; 37% in methanol-water solution) were stirred with heating to initiate the reaction in the same manner as described in the procedure for preparing VI. After acidifying with dilute hydrochloric acid, the resulting mixture was washed with water until neutral. The remaining procedure follows that given for VI. The product was recrystallized from methanol. A 60% yield was obtained, mp 37–38°. *Anal.* Calcd for $C_{22}H_{42}O_2$: C, 78.04; H, 12.51; O, 9.45; mol wt 339. Found: C, 78.34; H, 12.12; O, 9.66; mol wt 355.

Infrared Spectra of the Methyl α-*n*-Alkylacrylates. The infrared spectrum of α-*n*-dodecylacrylate was obtained neat, those of methyl α-*n*-hexadecyl- and methyl α-*n*-octadecylacrylate were obtained from Nujol mulls. All the methyl α-*n*-alkylacrylates showed absorption bands in the regions characteristic for compounds having the structure $RR'C{=}CH_2$ where R is an *n*-alkyl group and R′ is an ester group.[11] The bands are as follows: 937 ($R{-}C[C({=}O){-}]{=}CH_2$), 1730 (vinyl COOR), 1631 (vinyl CO), 1195 and 1155 (C—O stretching of acrylates), 720 cm^{-1} ($-(CH_2)_n-$, $n \geq 4$).

B. Anionic Homopolymerization Studies. All reactions and distillations were carried out in an atmosphere of nitrogen (8 ppm of oxygen) which was further purified by passing it through copper gauze at 500° and then through a molecular seive. Tetrahydrofuran was purified by distilling over sodium and then redistilling from a solution of sodium naphthalene. Toluene was distilled twice over sodium.

Polymerization with Sodium Naphthalene. The reaction tube was evacuated, flame dried, and filled with nitrogen. Freshly purified monomer (percolated through activated silica gel and distilled or recrystallized) and tetrahydrofuran were added through a septum with a hypodermic syringe. (The monomer, under nitrogen, was added neat if liquid or in tetrahydrofuran solution.) The reaction mixture was cooled to −75° and sodium naphthalene solution (prepared by Sorenson and Campbell's method[12]) was injected through the septum into the reaction tube. When the solution turned red-yellow, the reaction tube was sealed and stirring was continued. The polymerization was terminated with methanol. The reaction mixture was added to an excess of methanol, and the polymer settled out. Polymers were purified by the precipitation method using a toluene–methanol system. It was found in some cases that, by concentrating the supernatant liquid, additional fractions of polymer could be isolated. Details of the polymerizations are in Table I.

Polymerizations with Sodium. The appropriate amount of sodium was placed in the reation tube which had previously been evacuated, flame dried, and filled with nitrogen, a positive pressure of nitrogen being maintained. Toluene (0.5 ml) was injected through a septum, and the contents of the flask were heated and rapidly stirred to form fine sodium particles. Stirring was stopped and the contents were cooled to the reaction temperature for the polymerization. Monomer and solvent were added in the manner described for the sodium naphthalene polymerizations. The reaction tubes were sealed, and stirring was continued throughout the polymerization. (Initiation, indicated by a slight yellow color forming around the sodium, was not noted until the following morning. As polymerization progressed, the solution became a deeper yellow.) The contents of the polymerization tube were poured into methanol to terminate the reaction. (Where the sodium had not been entirely consumed during the reaction, the polymer solution was filtered through glass wool before addition to methanol.) Purification and fractionation of the polymers follow the procedure described in the polymerization with sodium naphthalene. Details of the polymerizations are given in Table I.

Infrared spectra and X-ray diffraction patterns of polymers were obtained by conventional methods. Infrared spectra showed that the absorption bands for olefinic linkages at 1631 and 935 cm^{-1} found in the spectra of the monomers had disappeared in each of the polymers, and 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} ($-(CH_2)_n-$, $n \geq 4$).

C. Homopolymerization in Emulsion. The distilled water (see Table II) was placed in a reaction flask. The water was boiled and then cooled to the reaction temperature. While positive nitrogen pressure was maintained, Duponol ME, Tween 20, sodium bisulfite, ammonium persulfate, and methyl α-*n*-alkylacrylate were added. (Methyl α-*n*-octadecylacrylate was added in the molten form.) The mixture was stirred vigorously during the reaction period after which the emulsion was added to acetone to precipitate any polymeric material which was then reprecipitated from a chloroform–methanol system. The details of these polymerizations are given in Table II.

References and Notes

(1) A patent has been granted covering most of the work discussed in this paper. H. Gisser and H. E. Mertwoy, U. S. Patent 3,687,922 (1972).

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Spontaneous Cohabitory Anionic Polymerization of Vinylidene Cyanide and Cationic Polymerization of Cyclic Ethers on Mixing the Two Monomers at 25°

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ABSTRACT: Mixing vinylidene cyanide with any one of the cyclic ethers tetrahydrofuran, oxetane, 2,2-dimethyloxirane, 2-chloromethyloxirane, and 2-phenyloxirane, either in bulk or in toluene, resulted in the polymerization of both the vinylidene cyanide and cyclic ether to afford homopolymers of both. The cyclic ethers trioxane, 3,3-bis(chloromethyl)oxetane, and oxirane initiated the polymerization of vinylidene cyanide but did not undergo ring-opening polymerization themselves. Other ethers such as 1,3-dioxolane, tetrahydropyran, and diethyl ether did not initiate the polymerization of vinylidene cyanide. In these polymerizations, vinylidene cyanide and the cyclic ethers polymerize *via* anionic and cationic propagation reactions, respectively. The rate of polymerization of vinylidene cyanide is rapid; polymerization of the cyclic ethers, when observed, takes place much more slowly. An initiation mechanism involving polar interaction between the vinylidene cyanide and the cyclic ether is proposed.

The polymerization of vinylidene cyanide takes place with anionic initiation, even with weak bases such as water and dimethylformamide at −78°. Vinyl ethers readily polymerize by cationic initiation, yet the mixing of these two kinds of monomers in solution (benzene) at 25° yields essentially homopolymers of the vinyl ethers and polymer containing high contents of vinylidene cyanide,[1] regardless of molar ratio of the vinyl ether to the vinylidene cyanide charged (5:1 to 1:5).[2] These results and the information[1] that the addition of trihydroxyethylamine inhibits the polymerization of the vinyl ethers and the addition of phosphorous pentoxide inhibits the polymerization of vinylidene cyanide in this system suggest simultaneous cationic and anionic polymerizations, respectively. These extraordinary results prompted us to explore the possibility that other monomers such as cyclic ethers, which are both electron donors and are susceptible to polymerization *via* cationic mechanisms, would also lead to the formation of homopolymers of each type of monomers (vinylidene cyanide and cyclic ether) when the two are mixed.[3]

Experimental Section

Materials. Vinylidene cyanide was prepared by the thermal decomposition of 1,1,3,3-tetracyanopropane,[1] bp 51° (10 mm) [lit.[1] bp 50.5° (10 mm)]. Tetrahydrofuran was heated to reflux over potassium hydroxide for 10 hr, distilled, and redistilled from a metallic sodium mirror. Purified material was stored over a metallic sodium mirror after the removal of air from the H_4furan by several freeze–thaw cycles under reduced pressure. Oxiranes and oxetanes were heated to reflux over potassium hydroxide, distilled, and then redistilled from calcium hydride. Trioxane was melted over calcium hydride and sublimed under reduced pressure. Toluene and dichloromethane were purified by the usual methods.

Polymerization Procedures for Vinylidene Cyanide and Cyclic Ethers (Table I). Polymerizations were carried out in the absence of light in Pyrex glass ampoules under reduced pressure. The dried monomers and solvents were transfered in a vacuum system by trap-to-trap distillation into ampoules, and then the ampoules were sealed and allowed to stand for definite periods of time at 25°. The ampoule was opened and the polymer produced was isolated by evaporating the volatile materials. The raw polymer was fractionated into the insoluble and soluble part in toluene at room temperature. Ir spectra and elemental analyses of these fractions showed that the insoluble fraction was a polymer predominantly consisting of poly(vinylidene cyanide), while the soluble fraction was essentially a homopolymer of cyclic ether.

The solution viscosities of the polymers were determined at 30° in benzene for the polymers of cyclic ethers, and in dimethylformamide containing 1% of acetic anhydride for the polymers of vinylidene cyanide.

A typical polymerization was carried out as follows. Vinylidene cyanide (1.0 g, 12.8 mmol) which had been dried over phosphorous pentoxide was distilled under reduced pressure (0.1 mm) into an ampoule cooled to −78° and then toluene (2.0 ml) was distilled into the same ampoule. The ampoule was warmed to room temperature, shaken, and then cooled to −78°. Oxetane (0.62 g, 12.8 mmol) which had been dried over sodium mirror was distilled into the ampoule under reduced pressure. The ampoule was sealed and shaken until the mixture was a clear solution and then was allowed to stand for 24 hr at 25°. The ampoule was opened and the volatile materials were distilled under reduced pressure (0.1 mm). The residue was extracted with toluene (20 ml). The insoluble fraction, dried *in vacuo*, was essentially a homopolymer of vinylidene cyanide as determined by its ir spectrum and elemental analysis. *Anal.* Calcd for $(C_4H_2N_2)_n$: C, 61.53; H, 2.58; N, 35.89. Found: C, 59.34; H, 2.61; N, 33.15.

The soluble fraction recovered by evaporation of toluene was a copolymer composed of poly(vinylidene cyanide) (~5%) and polyoxetane (~95%) as determined by elemental analysis. *Anal.* Found: C, 62.02; H, 9.82; N, 2.37.

Cyclic Dimers. In the spontaneous homopolymerization of vinylidene cyanide and either ethylene oxide or styrene oxide, cyclic dimers (dioxane or its derivatives) were found in the polymerization mixtures. In the case of ethylene oxide, 1,4-dioxane was isolated by glc of the distillate in yields of 42, 37, and 35% where the initial mol ratios of vinylidene cyanide to ethylene oxide were 1:5, 1:1.5, and 2.5:1, respectively. In the case of styrene oxide, *cis*- and *trans*-2,5-diphenyl-1,4-dioxanes were sepa-